

# ABSTRACTS

*of current literature on the platinum metals and their alloys*

## PROPERTIES

### Drastic Reduction of Adsorption of CO and H<sub>2</sub> on (111)-Type Pd Layers

H. POPPA and F. SORIA, *Phys. Rev. B.*, 1983, **27**, (8), 5166-5168

Clean surfaces of (111)-type Pd layers, grown from the vapour phase on Mo(110) at room temperature were used to study the adsorption of CO and H<sub>2</sub> by various techniques. Mild annealing of the as-grown layers during a single desorption cycle (to ~600K) drastically reduces the adsorptions. Low-dose Ar<sup>+</sup> bombardment restores high adsorption probability.

### Photographic Properties of Palladium-Containing TiO<sub>2</sub> Layer under Nickel Physical Development

V. V. SVIRIDOV, N. I. KUNTSEVICH, G. A. SOKOLIK and I. N. EVTUKHOVICH, *Vestn. Akad. Nauk BSSR, Ser. Khim. Nauk*, 1983, (1), 30-35

The photographic properties of Pd-containing TiO<sub>2</sub> layers under Ni development depends on the Pd concentration in the layer, TiO<sub>2</sub> preparation conditions and on the development conditions. Both negative and positive images can be obtained depending on the Pd<sup>2+</sup> content.

### A Study of the Palladium-Platinum-Hydrogen System over a Wide Range of Hydrogen Pressures

B. BARANOWSKI, F. A. LEWIS, W. D. MCFALL, S. FILIPEK and T. C. WITHERSPOON, *Proc. R. Soc. London*, 1983, **386A**, 309-332

Measurements of changes in electrical resistivity in Pd-Pt alloys caused by absorption of H<sub>2</sub> at 30 kbar pressures, were made at 25-70°C. Substantial resistivity changes due to H<sub>2</sub> absorption occur over increasingly higher ranges of pressure with increasing Pt contents. There is a gradually accelerating increase of resistivity with increasing H<sub>2</sub> pressure up to maximum values, followed by a decrease back to close to initial H<sub>2</sub>-free values. An extrapolation of results suggests it may be possible to attain a solid solution of H<sub>2</sub> in pure Pt up to a composition of ~PtH<sub>0.25</sub> at H<sub>2</sub> pressures of ~100 kbar at 25°C.

### Properties and Electron Transfer Reactivity of Coordination Compounds for the Photochemical Splitting of Water

L. MOGGI, *NTIS, Chemistry*, 3 May 1983, 426

Photochemical, photophysical and electrochemical properties have been determined for the excited states of many polypyridine complexes of Rh(III), Ir(III), Ru(II), Os(II) and Cr(III) for use in cyclic photochemical systems for the splitting of water.

### Blue Sputtered Iridium Oxide Films (Blue SIROF's)

K. S. KANG and J. L. SHAY, *J. Electrochem. Soc.*, 1983, **130**, (4), 766-769

"Blue" sputtered Ir oxide films (blue SIROF) were prepared and compared with "black" SIROF's and anodically grown Ir oxide films (AIROF's). Blue SIROF's are prepared by reactive d.c. sputtering of Ir in an Ar:O<sub>2</sub> 80:20 mixture, at deposition rates of ~200 Å/min on substrates held at 238K. Blue SIROF's have similar physical properties to AIROF's. In contrast to SIROF's previously deposited in pure O<sub>2</sub> onto substrates held at 289K the new films have an optical absorption spectrum which peaks at 610nm. The blue SIROF's have an improved open-circuit bleached state and memory.

### Oxidation of Ruthenium

S. P. SHARMA and L. L. HINES, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1983, **CHMT-6**, (1), 89-92

Ru has been heated in air at 100-400°C to find its usefulness as an electrical contact. At up to 200°C Ru oxidises to produce a film which causes high contact resistance. Above 300°C Ru forms an oxide film RuO<sub>2</sub> which has low contact resistance. The film <200°C is a lower Ru oxide (probably RuO).

### Preparation, Electrical Resistivity and Its Temperature Dependence of RuO<sub>2</sub>-Polystyrene Composite Powder

T. NISHIZAWA, M. SENNA and H. KUNO, *J. Mater. Sci.*, 1983, **18**, (5), 1346-1352

RuO<sub>2</sub>-polystyrene composite powder was prepared by mixing fine powdered RuO<sub>2</sub> and PS beads thoroughly in ethanol. RuO<sub>2</sub>-coated PS beads were also prepared by direct suspension polymerisation of styrene in an aqueous phase in the presence of suspended RuO<sub>2</sub> powder. The apparent d.c. volume resistivity, ρ<sub>v</sub>, of the hot-pressed composite was measured from 20-80°C, pressure 3.5-35 MPa and volume fractions of RuO<sub>2</sub>. ρ<sub>v</sub> increased linearly with temperature on a double logarithmic scale. The composite prepared by direct polymerisation completed a network of the conductive phase at a smaller fraction of RuO<sub>2</sub>.

### Ion Mixing to Produce Amorphous Mo-Ru Superconducting Films

B. X. LIU, B. M. CLEMENS, R. GABORIAUD, N. L. JOHNSON and M.-A. NICOLET, *Appl. Phys. Lett.*, 1983, **42**, (7), 624-626

Amorphous Mo<sub>3</sub>Ru<sub>4</sub> alloy films were formed by ion mixing of multilayered samples. The ion mixed films, which contain no metalloid element, show excellent superconducting properties.

## CHEMICAL COMPOUNDS

### Chemistry of Triosmium Carbonyl Cluster Compounds and Its Implications for Catalysis

R. D. ADAMS, *Acc. Chem. Res.*, 1983, **16**, (2), 67-72

A study of a series of triosmium carbonyl cluster complexes formed by the addition of a variety of small heteronuclear unsaturated molecules to the cluster complex  $H_2Os_3(CO)_{10}(I)$  is presented. The reactions of (I) with isocyanides, nitriles, aryl isocyanates, carbodiimides, aryl isothiocyanates and  $CS_2$  are described. The evidence suggests that cluster compounds have unique chemical properties allowing development as a new class of reaction catalysts.

## ELECTROCHEMISTRY

### Transient Behaviour in Electroreductions of Ethylene and Acetylene on Pt in $H_2SO_4$ Solution

T. MASUI and H. KITA, *Denki Kagaku*, 1983, **52**, (2), 250-255

Studies were made of transient behaviour in electroreductions of  $C_2H_4$  and acetylene on a Pt electrode. Open circuit potential measurements under the contact of the electrode prepolarised at 0V with  $C_2H_4$  and acetylene showed that from the three kinds of adsorbed H atoms on Pt the second stable one takes part in the reactions, while the most stable one is inactive.

### Crystallographic Anisotropies in Electrochemical Etching of Pt

R. CARACCILO and L. D. SCHMIDT, *J. Electrochem. Soc.*, 1983, **130**, (3), 603-607

Single crystal microspheres of Pt are examined by SEM after electrochemical and chemical etching in chloride and cyanide solutions. In all cases, a single major crystal plane is formed which is not the close packed (111) plane. Electrochemical chloride etching with a.c. potentials produces large smooth planes near (100), and the (111) plane is attacked readily to form (100) facets.

### Electroreduction of Acetone on Pt-Ni Catalysts

A. D. SEMENOVA, A. I. BARKOVSKII and G. D. VOVCHEENKO, *Vestn. Mosk. Univ., Khim.*, 1983, **24**, (2), 159-162

Studies of adsorption and catalytic properties of metallic Pt-Ni alloys were made during electroreduction of acetone in 1N KOH at 25°C. Analysis of polarisation curves of the electroreduction on Pt, Ni and Pt-Ni alloys showed that alloys containing >60 at.% Pt have a form of curves similar to Pt and Ni, whereas alloys containing <50 at.% Pt have different forms of curves. It is concluded that ordered atoms in Pt-Ni system give higher catalytic activity. Alloys in equiatomic systems have 6 times higher activity than Pt in the studied reaction.

### Anodic Characteristics of Amorphous Palladium-Iridium-Phosphorus Alloys in a Hot Concentrated Sodium Chloride Solution

M. HARA, K. HASHIMOTO and T. MASUMOTO, *J. Non-Cryst. Solids*, 1983, **54**, (1, 2), 85-100

The corrosion resistance and electrocatalytic activity for  $Cl_2$  and  $O_2$  evolutions at amorphous Pd-ir-P alloys containing a small amount of Ti, Rh, Pt and/or Ru in hot concentrated NaCl solution were investigated. The electrocatalytic activity of several amorphous alloys for  $Cl_2$  evolution was much higher than that of dimensionally stable  $RuO_2/Ti$  anodes, while their catalytic activity for  $O_2$  evolution was lower than that of the  $RuO_2/Ti$  electrode, suggesting amorphous alloys can produce high purity  $Cl_2$  at high efficiencies.

### Interfacial Properties of Oxides Used as Anodes in the Electrochemical Technology

A. DAGHETTI, G. LODI and S. TRASATTI, *Mater. Chem. Phys.*, 1983, **8**, (1), 1-96

A review of surface chemistry of oxides and the behaviour of the relevant insoluble oxides is presented. The oxides are the components of electrodes used in chlor-alkali cells, water electrolysis, electro-organic oxidations, metal electrowinning and cathodic protection. Oxides discussed include  $RuO_2$  and  $IrO_2$ . (492 Refs.)

### Ruthenium Behaviour during Electrochemical Dissolution of Its Binary Alloys with Copper

V. F. BORBAT, O. V. ZAVEL'eva and M. A. ORLOV, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall*, 1983, (2), 54-57

Studies of Ru behaviour during electrochemical dissolution of Cu-Ru binary alloys containing 0.004% and 0.01-0.03% Ru were made in solutions of  $H_2SO_4$  and  $CuSO_4$  of various acidities by anodic polarisation measurements. Anodic polarisation curves rose in more electropositive areas with the increase of the Ru content in the alloy. An increase in acidity resulted in dissolution of Ru into the solution, and at 1.4V the dissolution of Ru in 4N  $H_2SO_4$  + 1.5N  $CuSO_4$  was nearly complete. The rate of dissolution of Ru in the electrolyte was found.

### XPS Studies of Oxygen Evolution on Ru and $RuO_2$ Anodes

R. KÖTZ, H. J. LEWERENZ and S. STUCKI, *J. Electrochem. Soc.*, 1983, **130**, (4), 825-829

Anodic oxidation of Ru and  $RuO_2$  electrodes in 1N  $H_2SO_4$  has been investigated using XPS. During  $O_2$  evolution of Ru, a highly defective hydrate oxide film is formed as a result of corrosion. At 310°C in vacuum this film decomposes to metallic Ru. The surface of  $RuO_2$ -anodes prepared by thermal decomposition of  $RuCl_3$  contains some  $RuO_3$  which is stable during anodic polarisation.

## PHOTOCONVERSION

### Photo-Induced Hydrogen Evolution Accelerated at Semiconductor/Liquid Interface

T. SHIMIDZU, T. IYODA, Y. KOIDE and N. KANDA, *Nouv. J. Chim.*, 1983, 7, (1), 21-27

A novel water photoreduction system is presented, where an appreciable quantity of  $H_2$  is catalytically produced by visible light illumination in neutral aqueous solution containing an appropriate electron donor, platinised semiconductor powder and a water soluble Zn porphyrin. The  $ZnTPPS_4-ZnO/Pt-TEA$  system showed the highest catalytic activity. A platinised semiconductor powder plays the role of an excellent electron relay and redox catalyst for  $H_2O$  reduction.

### Factors Influencing Product Distribution in Photocatalytic Decomposition of Aqueous Acetic Acid on Platinized $TiO_2$

H. YONEYAMA, Y. TAKAO, H. TAMURA and A. J. BARD, *J. Phys. Chem.*, 1983, 87, (8), 1417-1422

Reaction products of the photocatalytic decomposition of acetic acid/acetate mixtures at  $Pt/TiO_2$  were examined. The relative yield of  $C_2H_6:CH_4$  produced was high when the decomposition rate was high, and the amount of  $CO_2$  produced usually exceeded that of the methyl radical consumed in the formation of  $CH_4$  and  $C_2H_6$ . Ethanol and acetaldehyde were produced. The production occurred even under adverse conditions, and even when a very high acidic bias completely suppressed any cathodic reaction  $CH_4$  was produced in higher yields than  $C_2H_6$ .

### Photoassisted Water-Gas Shift Reaction over $Pt/TiO_2$ (100)

S.-C. TSAI, C.-C. KAO and Y.-W. CHUNG, *J. Catal.*, 1983, 79, (2), 451-461

Saturated  $H_2$  production was observed over platinised  $TiO_2$  (100) in the presence of  $H_2O$  vapour and CO with or without u.v. illumination. The thermal reaction is dominant at temperatures over 400K. Below 400K the photoreaction is dominant, and is independent of  $H_2O$  and CO partial pressures in the range 0.5 to 18 Torr and 0.1 to 10 Torr, respectively. Reaction rate increases monotonically with increasing u.v. intensity.

### Hydrogen Generation by Photocatalytic Oxidation of Gases by Platinized n- $TiO_2$ Powder

M. R. ST. JOHN, A. J. FURGALA and A. F. SAMMELLS, *J. Phys. Chem.*, 1983, 87, (5), 801-805

The photocatalytic reaction of glucose in aqueous solution containing platinised n- $TiO_2$  powder occurred at  $pH = 4.5$ . Under an inert atmosphere  $H_2$  and  $CO_2$  were produced, but under an  $O_2$  atmosphere, only  $CO_2$  was produced. For a 2.8M glucose solution and at 60°C, the initial  $H_2:CO_2$  ratio was near 10, but decreased to near 3 at times >100 hours. Gas evolution rates were determined.

### Semiconductor Electrodes. 48. Photooxidation of Halides and Water on n-Silicon Protected with Silicide Layers

F.-R. F. FAN, R. G. KEIL and A. J. BARD, *J. Am. Chem. Soc.*, 1983, 105, (2), 220-224

The electrochemical and photoelectrochemical behaviour of n-type Si electrode coated with noble metal silicides and  $RuO_2$  in aqueous solutions containing various redox couples was studied. Ir silicide coated n-Si electrodes, n-Si(Ir), and  $RuO_2$ -modified n-Si(Ir) electrodes can photogenerate  $I_2$ ,  $Br_2$  and  $Cl_2$  with high stability and efficiencies (75%). The photo-oxidation of  $H_2O$  on these electrodes is also feasible.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Changing Concepts in the Electroplating of Platinum Group Metals - Part I

H. M. SMITH, *Met. Finish.*, 1983, 81, (3), 55-58

Electrodeposits of Pt, Pd, Rh and Ru, are discussed. Properties, electroplating applications and an analysis of platinum group metals in industry are examined. Physical properties reviewed include internal stresses, reflectance, corrosion and solubility, wear resistance, contact and arc resistances, electrical resistivity, solderability and thermal expansion.

### The Electrolytic Deposition of Pd-Ni-Coatings from an Ammoniacal Electrolyte

M. BUTZ, F. FRIEDRICH and CH. J. RAUB, *Metalloberflaeche*, 1983, 37, (3), 89-93

Factors connected with the electrolytic deposition of Pd-Ni coatings from an ammoniacal electrolyte are examined. These include the plating bath conditions, the composition of the deposit, temperature and pH, the H content in the deposit, internal voltages and deposit thicknesses. The use of a high deposition rate is also considered. The H content of the deposits is a strong indicator of the working conditions.

## LABORATORY APPARATUS AND TECHNIQUE

### Urea Sensor Based on Iridium Dioxide Electrodes with Immobilized Urease

R. M. IANNIELLO and A. M. YACNYNCH, *Anal. Chim. Acta*, 1983, 146, 249-253

An  $IrO_2$  electrode with immobilised urease was found to be useful as a potentiometric detector for pH changes resulting from hydrolysis of urea at the electrode surface. Electrodes constructed by urease entrapment in a PVC film are superior to electrodes with urease covalently immobilised to the oxide layer via a cyanuric chloride linkage. Logarithmic response is obtained for the range  $5 \times 10^{-5}$ - $5 \times 10^{-3}$ M urea, with a slope of  $-51$  mV/decade. The slope is constant for  $\sim 12$  days. Recoating a stripped electrode with PVC-urease has essentially no effect on the slope.

### Effects of Impurities on Hydrogen Permeability through Palladium Alloy Membranes at Comparatively High Pressures and Temperatures

H. YOSHIDA, S. KONISHI and Y. NARUSE, *J. Less-Common Met.*, 1983, **89**, (2), 429-436

The Pd alloy membrane method was studied as a means for purifying fusion reactor fuel by investigating the effects of impurities on the permeation characteristics, at high pressures and temperatures, of Pd alloys. The H<sub>2</sub> permeability of Pd-25wt.%(Ag-Au-Ru) was not affected by impurities such as NH<sub>3</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub> and N<sub>2</sub> which are present at concentrations 10-10,000ppm in H<sub>2</sub>. However, permeability deteriorates on contamination with oil vapour, but is easily recovered.

### A Proposed Method of Hydrogen Isotope Separation Using Palladium Alloy Membranes

J. EVANS, I. R. HARRIS and D. K. ROSS, *J. Less-Common Met.*, 1983, **89**, (2), 407-414

The viability of using Pd alloy membranes in cascade to separate the H, D and T produced in a fusion reactor is discussed. Values of the permeation separation factor are estimated for Pd-20%Ag, and estimates for the number of stages and membrane area are given for the required isotope purification. Using Pd-8%Y will probably even further improve the performance.

## HETEROGENEOUS CATALYSIS

### Palladium-Catalyzed and Sonically Accelerated Hydrogenations of Olefins Using Formic Acid as a Hydrogen Transfer Agent

P. BOUDJOUK and B.-H. HAN, *J. Catal.*, 1983, **79**, (2), 489-492

In the presence of Pd/C, formic acid is a very efficient H donor at room temperature. Ten olefins, including terminal and internal alkenes, a diene, a vinyl ether and an  $\alpha$ ,  $\beta$ -unsaturated ketone were hydrogenated in high yields at room temperature and atmospheric pressure. In the presence of sonic waves, the rate of hydrogenation was significantly increased.

### Oxidation of Polyunsaturated Ethers and Esters with Molecular Oxygen Catalysed by Palladium Salts

G. A. DZHEMILEVA, V. N. ODINOKOV, U. M. DZHEMILEV and G. A. TOLSTIKOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, (2), 343-348

Studies of oxidation of polyunsaturated ethers and esters with O<sub>2</sub> over PdCl<sub>2</sub>-CuCl catalysts showed the formation of a series of new mono-, di- and triketoesters. A synergetic effect in quaternary ammonium salts was observed during O<sub>2</sub> oxidation and was followed by an increase in the yield of carbonyl compounds.

### On the Properties of Monodispersed Pd/MgO Catalysts

G. D. ZAKUMBAEVA, N. A. ZAKARINA, V. A. NAIDIN, A. M. DOSTIAROV, N. F. TOKTABAIEVA and E. N. LITVIAKOVA, *Kinet. Katal.*, 1983, **24**, (2), 449-453

Microcalorimetric studies of adsorption of H<sub>2</sub> and O<sub>2</sub> on mono-(25-75Å) and polydispersed Pd/MgO catalysts showed an increase in adsorption temperature of H<sub>2</sub> and O<sub>2</sub> with the decrease of Pd particle diameter. Selectivity and activity of Pd catalysts was found to depend on its dispersity and level of Pd reduction.

### An Active Methanation Catalyst Prepared from an Amorphous Pd<sub>35</sub>Zr<sub>65</sub> Alloy

A. YOKOYAMA, H. KOMIYAMA, H. INOUE, T. MASUMOTO and H. KIMURA, *Chem. Lett.*, 1983, (2), 195-198

A highly active methanation catalyst was prepared in situ from an amorphous Pd<sub>35</sub>Zr<sub>65</sub> alloy. In the reaction at 260°C and 1 atm the catalytic activity had a 100-fold increase with time and after 60 hours had a steady value, compared to the initial value.

### Palladium Alloys as Hydrogen Permeable Catalysts in Hydrogenation and Dehydrogenation Reactions

V. M. GRYAZNOV, M. M. ERMILOVA, L. S. MOROZOVA, N. V. OREKHOVA, V. P. POLYAKOVA, N. R. ROSHAM, E. M. SAVITSKY and N. I. PARFENOVA, *J. Less-Common Met.*, 1983, **89**, (2), 529-535

H<sub>2</sub> permeation across a binary Pd alloy catalyst (Pd alloyed with Al, Ti, Ni, Cu, Mo, Ru, Rh, Ag, In, W, Re, Pt) enhances the rate and selectivity of hydrogenation compared with what is observed when the compound being hydrogenated is mixed directly with H<sub>2</sub>. The principal product of diene hydrogenation when the H<sub>2</sub> permeates through a membrane catalyst is not a saturated hydrocarbon but the corresponding olefin from which polymers can be synthesised.

### Water Gas Shift Reaction Catalyzed by Iridium Complexes Supported on Zeolites

R. GANZERLA, F. PINNA, M. LENARDA and M. GRAZIANI, *J. Organomet. Chem.*, 1983, **244**, (2), 183-189

Ir compounds, supported on 13-X faujasite type zeolite catalyse the water gas shift reaction. During the reaction carbonyl complexes are formed and are detected by i.r. spectroscopy. Addition of ethylene diamine enhances the catalytic activity.

### Synthesis and Characterisation of an Alumina-Supported RuOs<sub>3</sub> Cluster Catalyst

J. R. BUDGE, J. P. SCOTT and B. C. GATES, *J. Chem. Soc., Chem. Commun.*, 1983, (7), 342-343

Al<sup>+</sup>[H<sub>3</sub>RuOs<sub>3</sub>(CO)<sub>12</sub>]<sup>-</sup>/Al<sub>2</sub>O<sub>3</sub> was formed upon heating [H<sub>2</sub>RuOs<sub>3</sub>(CO)<sub>13</sub>] adsorbed on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 373-473K under a H<sub>2</sub> + CO atmosphere. The material is catalytically active for ethylene hydrogenation at 340K and for but-1-ene isomerisation at 330K.

### Kinetics of the Fischer-Tropsch Synthesis

R. S. DIXIT and L. L. TAVIARIDES, *Ind. Eng. Chem., Process Des. Dev.*, 1983, **22**, (1), 1-9

The kinetics of the Fischer-Tropsch synthesis reactions were studied in an internally recycled reactor over a 0.5% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Steady-state turnover numbers were obtained for 3:1 and 2:1 H<sub>2</sub>:CO feed gas at 200-300°C. Intrinsic kinetic data were obtained on surface-impregnated catalysts. A mechanism for the Fischer-Tropsch synthesis was given and several kinetic models were developed. The product selectivity and CO conversion were strongly influenced by temperature.

### Physical Effects on Fischer-Tropsch Synthesis over Composite Ru Catalysts

C.-H. YANG and J. G. GOODWIN, *Can. J. Chem. Eng.*, 1983, **61**, (2), 213-217

Fischer-Tropsch synthesis was studied over composite catalysts formed by addition of SiO<sub>2</sub> to Ru/Al<sub>2</sub>O<sub>3</sub> and Ru/TiO<sub>2</sub>. The results showed that the presence of excess amounts of SiO<sub>2</sub> with the primary Ru catalysts produced significant changes in conversion and product selectivity.

### Ruthenium-Based Catalyst for the Gas-Phase Synthesis of Alcohols from CO and H<sub>2</sub>

M. INOUE, T. MIYAKE, T. INUI and Y. TAKEGAMI, *J. Chem. Soc., Chem. Commun.*, 1983, (2), 70-72

Hydrogenation of CO with H<sub>2</sub> at 86kg/cm<sup>2</sup> and 255°C over a Ru, Mo and Na<sub>2</sub>O catalyst gives a series of straight-chain primary alcohols as essentially the only liquid products. Since the liquid product was uncontaminated by hydrocarbons and other oxygenated products, the refining of the alcoholic products would be much simpler than with the conventional Fischer-Tropsch reaction.

### Metal-Support Effects in the Catalytic Hydrogenation of CO over Ruthenium Y-Zeolites: Influence of Zeolite Basicity on Olefin Selectivity

J. R. LEITH, *J. Chem. Soc., Chem. Commun.*, 1983, (2), 93-94

The electronic interaction between small metal crystallites and basic or electron-donor sites in zeolite Y enhances the olefin selectivity of Ru in the hydrogenation of CO to hydrocarbons.

## HOMOGENEOUS CATALYSIS

### Pd(I) Complexes in Co-ordination Chemistry and Catalysis

O. N. TEZHKIN and L. G. BRUK, *Usp. Khim.*, 1983, **52**, (2), 206-243

A review is given of Pd(I) complexes in co-ordination chemistry including formation and physical properties of Pd(I) complexes, their methods of synthesis and reactions, and the role of Pd(I) compounds in stoichiometric and catalytic reactions. (163 Refs.)

### Study of Glycolic Ester Formation in Olefin Catalytic Liquid Phase Oxidation. VII. State of the Components in CH<sub>3</sub>COOH-Dioxane-HNO<sub>3</sub>-Pd(II) Contact Solutions

M. G. KOLKHOVSKII, V. A. LIKHOLOBOV and IU. I. ERMAKOV, *Kinet. Katal.*, 1983, **24**, (2), 347-351

Studies were made of the state of components in contact solution CH<sub>3</sub>COOH-dioxane-HNO<sub>3</sub>-Pd(II) during oxidation of ethylene to saturated glycolic ester. Spectrophotometric studies showed that absorption of ethylene by contact solution at the beginning of the reaction resulted in formation of Pd nitrite complexes yielding saturated glycolic esters.

### Mechanism of the Reaction of Oxidative Conjunction of Unsaturated Hydrocarbons in the Presence of Palladium (II) Complexes

I. V. KOZHEVNIKOV, *Usp. Khim.*, 1983, **52**, (2), 244-267

A review is given of data on the mechanism of liquid phase reaction of oxidative conjunction of arenes to diaryls, arenes with olefins to aryl-olefins and olefins to diene-1,3 in the presence of Pd(II) complexes. (161 Refs.)

### New Catalysts for Hydrosilylation of Acetylenic Compounds

M. G. VORONKOV, V. B. PUKHNAREVICH, I. I. TSYKHANSKAYA, N. I. USHAKOVA, YU. L. GAFT and I. A. ZAKHAROVA, *Inorg. Chim. Acta, Artic.*, 1983, **68**, 103-105

The regio- and stereo-selectivity in the homogeneous hydrosilylation of acetylene and heptene-1 monosubstituents and carbonyl functional ethylene derivatives in the presence of Pd and Pt catalysts of a new type [Pd<sub>2</sub>(Ph<sub>3</sub>P)<sub>4</sub>Cl<sub>2</sub>]B<sub>10</sub>Cl<sub>10</sub>, [Pd<sub>2</sub>(Ph<sub>3</sub>P)<sub>4</sub>Cl<sub>2</sub>]B<sub>12</sub>Cl<sub>12</sub>, [Pt(Ph<sub>3</sub>P)<sub>3</sub>Cl<sub>2</sub>]B<sub>10</sub>Cl<sub>10</sub> etc., have been studied. Unlike H<sub>2</sub>PtCl<sub>6</sub> and other commonly used catalysts, their application for hydrosilylation of acetylenic compounds makes the process regio specific, forming the  $\beta$ -adduct.

### Heat Activated Silicone Foam

C. L. LEE, G. M. RONK and S. SPELLS, *J. Cell. Plast.*, 1983, **19**, (1), 29-33

The production and properties of a Rh catalysed flame resistant silicone foam are compared to those of a Pt catalysed one. RhCl<sub>3</sub>(Bu<sub>2</sub>S)<sub>3</sub> when used as catalyst produced a foam with a working time of at least 8 hours at room temperature and which foams rapidly upon heating at 100-150°C, - "heat activated foam". Its flame retardancy is comparable to that of Pt catalysed foams. The "heat activated foam" cures slowly at room temperature to give an elastomeric material after a few days. Foaming at higher temperature and higher catalyst concentration gives a lower density foam. The heat activated foam has a honeycomb-like structure which makes it useful as window coating for a solar heating panel.

## Two New Routes to Ethylene Glycol from Synthesis Gas

*Chem. Eng. News*, 1983, **61**, (15), 41-42

Industrial processes for ethylene glycol production using platinum group metal complex catalysts are described. One method, based on the catalytic hydroformylation of formaldehyde to glycolaldehyde and subsequent hydrogenation to ethylene glycol, uses stable Rh catalyst  $\text{HRh}(\text{CO})_2 [\text{P}(\text{C}_6\text{H}_5)_3]_2$  in the presence of excess phosphine ligands.

## Clay Intercalation Catalysts Interlayered with Rhodium Phosphine Complexes. Surface Effects on the Hydrogenation and Isomerization of 1-Hexene

R. RAYTHATHA and T. J. PINNAVAIA, *J. Catal.*, 1983, **80**, (1), 47-55

Clay intercalation catalysts formed by interlayering of  $\text{Na}^+$ -hectorite with Rh phosphine complexes of the type  $\text{Rh}(\text{NBD})(\text{Ph}_3\text{P})_2^+$  and  $\text{Rh}(\text{NBD})(\text{dppe})^+$ , where NBD = norbornadiene and dppe = 1,2-bis(diphenylphosphino)ethane, were examined as catalyst precursors for the hydrogenation-isomerisation of 1-hexene in methanol. The intercalated catalysts have a much lower tendency to isomerise the substrate to the less reactive internal olefin 2-hexene under homogeneous conditions. The results showed that surface chemical effects can dramatically alter the catalytic properties of metal complexes immobilised in clay interlayers.

## Alkane C-H Bond Activation: New Hope for Catalysis Research

J. HAGGIN, *Chem. Eng. News*, 1983, **61**, (7), 9-12

The history and recent advances in alkane C-H bond activation are examined. Catalysts discussed include the diacetone Ir complex with two hydride and two triphenylphosphine ligands used by Bergman. Bergman has also found that there is a preferential attack on primary C-H bonds. Graham's work using an Ir catalyst, a new hydridoneopentyliridium compound, is discussed. Work on  $[\text{C}_2(\text{CH}_3)_5]\text{Rh}[\text{P}(\text{CH}_3)_3]\text{H}_2$  which selectively activates alkane C-H bonds is examined. Work on heterogeneous catalysis and on arene C-H bond activation with Rh complexes is also considered.

## An Osmium Catalyst for the Selective Electrochemical Oxidation of Alcohols

F. C. ANSON, T. J. COLLINS, S. L. GIPSON and T. E. KRAFFT, Book of Abstracts, 185th ACS National Meeting, Seattle, Washington, March 20-25, 1983, Abstract No. 240

Addition of alcohols to bis(pyridine)  $[\text{N}, \text{N}^1\text{-bis}(3,5\text{-dichloro-2-hydroxybenzamido})_{1,2}\text{-ethane}]\text{Os}(\text{IV})$ , (I), in  $\text{CH}_2\text{Cl}_2$  was studied. Controlled oxidation of (I) in the presence of alcohols forms a new Os species which shows catalytic activity for alcohol oxidation. Controlled potential oxidation of 0.5M benzyl alcohol in the presence of 40  $\mu\text{M}$  catalyst produced >40 catalyst turnovers with the selective production of benzaldehyde.

## The $\text{OsO}_4$ -Catalysed Decomposition of Hydrogen Peroxide

L. J. CSÁNYI, Z. M. GALBÁCS and L. NAGY, *Magy. Kem. Foly.*, 1983, **89**, (3), 131-140

The rate of  $\text{H}_2\text{O}_2$  decomposition in the presence of  $\text{OsO}_4$  as catalyst was proportional to the first power of the  $\text{OsO}_4$  concentration, and to the power 1-1.2 of the  $\text{H}_2\text{O}_2$  concentration. Hydroxyl and superoxide radicals were formed during the decomposition.

## Standardised Tethering of $\text{Ru}_3\text{-Ru}_6$ Clusters to High Surface Area Oxides

J. EVANS and B. P. GRACEY, *J. Chem. Soc., Chem. Commun.*, 1983 (5), 247-249

Molecularly-specific routes to support Ru clusters have been developed to find the particle size effects on the catalytic activity of materials. Complexes  $\text{Ru}_3(\text{CO})_9\text{L}$ ,  $\text{H}_2\text{Ru}_4(\text{CO})_{11}\text{L}$ ,  $\text{Ru}_5(\text{CO})_{12}\text{L}$  and  $\text{Ru}_6(\text{CO})_{16}\text{L}$  [ $\text{L} = \text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OEt})_3$ ] have been isolated and used to tether  $\text{Ru}_{3-6}$  units to  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  supports in a standard manner.

## Ethanol from $\text{H}_2$ and CO via Homogeneous Ruthenium Catalysis

B. K. WARREN and B. D. DOMBEK, *J. Catal.*, 1983, **79**, (2), 334-347

Ru carbonyl complexes, obtained from  $\text{Ru}_2(\text{CO})_{12}$  in the presence of an iodide promoter, an acid and a phosphine oxide, provide an unusually selective system for the direct conversion of CO and  $\text{H}_2$  to ethanol. Reaction conditions were 30 to 87 MPa and 180 to 250°C. Other products include methanol, methane, acetaldehyde, ethylene glycol and n-propanol.

## FUEL CELLS

### Composite Catalysts for Carbon Monoxide Resistant Fuel Cell Anodes

A. J. COLEMAN, A. A. ADAMS, J. A. JOEBSTL and L. S. JOYCE, Extended Abstracts, 83-1, 163rd Spring Meeting of the Electrochem. Soc., San Francisco, May 8-13, 1983, 1262-1263

A comparison is made between a standard Pt-fuel cell anode and a 50/50 wt.% Pt-Ru alloy electrode, and a WC anode and a WC electrode with 0.1 wt.% Pt. The electrolyte was phosphoric acid and the reactants were pure  $\text{H}_2$  and a 3%  $\text{CO-H}_2$  mixture. A modest gain in activity occurred for the 0.1% Pt/WC electrode and a sizeable gain for the 1% Pt/WC sample when  $\text{H}_2$  was the reactant. With CO present the 1% sample lost 96% of its activity, while the 0.1% sample decrease by 26%. A Pt/WC electrode can be made where the WC supports the anode reaction at low temperatures, with the Pt becoming active as temperature and the reaction rate increase. Anode polarisation curves for Pt and Pt-Ru, in the presence of CO, show the advantage of using Pt-Ru especially below 160°C. Pt-Ru and Pt/WC may be alternative anode electrocatalysts for fuel cells, started from low temperatures on reformat fuel.

## CATHODIC PROTECTION

### Hydrogen Absorption and Embrittlement of Tantalum by Cathodic Loading

H. HEUBERGER, A. KNÖDLER and CH. J. RAUB, *Metall*, 1983, **37**, (3), 244-248

The takeup and embrittlement of Ta by electrolytically produced H<sub>2</sub> was investigated on various samples. The oxide surface layers affect the H<sub>2</sub> uptake. Surface coatings of varying thicknesses with platinum group metals as alloying constituents were tested as anodic protection for Ta.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Precious Metal Inlays for P.C. Connector Contacts

D. MADDICK, *New Electron.*, 1983, **16**, (2), 44, 46, 49

An evaluation of noble metal alloy inlays as replacements for Au electrodeposits is presented. Solderability, high temperature mechanical endurance, effects of rapid change of temperature, mechanical endurance, solvent resistance and costs were examined. Alloys considered were 6Pt-25Ag-69Au, 40Ag-60Pd and 6Ni-94Au of thicknesses 0.5  $\mu$ m and 0.75  $\mu$ m.

## NEW PATENTS

### METALS AND ALLOYS

#### Electrical Contact Material

DEGUSSA A.G. *European Appl.* 74,507

A lower priced material for contacts, especially low current contacts, consists of a noble metal (preferably Au, Ag and/or Pt) and 1-50% of a glass frit (softening range more than 100%, at 400-750°C).

#### Electric Contact Alloy

W.C. HERAEUS G.m.b.H. *German Offen.* 3,121,069

An improved dispersion-hardened contact material is a Ag alloy containing 10-30% Pd and 0.03-0.2% Mg as Mg oxide and 0.03-0.2% Ni, 0.1-0.5% Ce as Ce oxide or 0.1-0.5% Mn as Mn oxide.

## ELECTROCHEMISTRY

### Brine Electrolysis Cathode

DIAMOND SHAMROCK CORP. *U.S. Patent* 4,350,608

A power-efficient electrode, for use in a brine cell, is obtained by coating a substrate formed by compressing a prefused mixture of C black with PTFE with an electrocatalytic coating. A preferred coating contains chloroplatinic acid which may be reduced to Pt.

### An Integrated CO-Sensitive MOS Transistor

D. KREY, K. DOBOS and G. ZIMMER, *Sens. Actuators*, 1983, **3**, (2), 169-177

MOS transistors with hole-structure Pd gates are detectors for CO. The CO-sensitive transistors, studied at 180°C, showed reproducible sensitivities with measured threshold shifts of 75mV for 0.1 Torr CO pressure. By using a protective Al layer on the Pd gate, a considerable improvement in CO selectivity with respect to H<sub>2</sub> was obtained.

## TEMPERATURE MEASUREMENT

### The Use of Industrial-Grade Platinum Resistance Thermometers between 77K and 273K

L. M. BESLEY and R. C. KEMP, *Cryogenics*, 1983, **23**, (1), 26-28

Measurements made on the stability of seven industrial platinum resistance thermometers when exposed to thermal cycling between 77K and 373K are described. A two point calibration method giving an accuracy of  $\pm 35$ mK for thermometers of this type over the range 70-273K is also described, which is better than that obtainable with IPTS-68.

### Oxygen Generating Electrode

JAPAN CARLIT CO. LTD. *U.S. Patent* 4,353,790

An O<sub>2</sub> generating electrode, for use in electrowinning, electrodeposition and electrolysis cells, has improved durability when it is formed from Ti or a Ti substrate coated with a first layer of metallic Bi or Bi oxide and a top layer containing IrO<sub>2</sub> and 5-50 mole % metallic Ir, preferably applied via an Ir halide solution.

### Energy Efficient Electrolyser for Hydrogen Production

WESTINGHOUSE ELECTRIC CORP.

*U.S. Patent* 4,357,224

A high surface area anode for use in an electrolyser for H<sub>2</sub> production has packed porous C pellets, preferably containing 1-5% Pt, pressed tight against an inert current collector which assists easy access of bisulphite ions to the anode. The conducting plate of the electrode may be of Pt, Au or TiO<sub>2</sub>-coated Ti.

### Anode Catalyst for Brine Electrolysis

GENERAL ELECTRIC CO.

*U.S. Patent* 4,360,416

A catalytic coating containing Ru oxide and 5-25% Mn oxide has good stability when used on an anode for halogen gas generation.