

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Combined Reduction of Oxides by Carbon in the Presence of Metals of the Platinum Group. Parts 1 and 2

D. OTT and C. J. RAUB, *Metall.*, 1978, **32**, (1), 35-41; (2), 140-144

The reduction of Cr, Si, Al, Mg and Zr oxides by C in the presence of Pt metals, and the effects of Pt, Pd, Ru and Rh on the reduction of Cr_2O_3 and SiO_2 by C in vacuum are discussed. From 600-1000°C Pd and Pt strongly enhance reduction by the formation of solid solutions and/or Cr and Si carbides, but Ru and Rh have little influence. The influence of Pt, Pd, Rh and Ru on the reduction of Al_2O_3 , ZrO_2 and MgO by C in a vacuum is also discussed.

Competitive Hydrogenation of Benzene and Toluene Dehydrogenation of the Corresponding Naphthenes over Platinum Wire

J. F. AKYURILU and W. E. STEWART, *J. Catalysis*, 1978, **51**, (1), 101-107

The relative rates for benzene and toluene hydrogenation on a Pt wire catalyst were examined at 600-672K and 4.4-24.9 atm. The catalyst activity declined during processing but was restored by H_2 treatment. Kinetic and equilibrium constants and the common stoichiometric number for the reactions are given. The ratio of the rates during a catalytic deactivation implies that the two reactions use the same number and kinds of sites in their controlling steps.

Structure of the Rare-Earth-Platinum Compounds R_7Pt_3 , R_2Pt , R_5Pt and RPt

J. LE ROY, J. -M. MOREAU and D. PACCARD, *Acta Cryst. B*, 1978, **34**, (1), 9-13

Rare-earth-platinum compound structures are identified. R_7Pt_3 compounds (R = La, Ce, Pr, Nd, Sm, Gd) crystallise with Th_3Fe_3 type structure. PrPt and NdPt have a high temperature modification corresponding to the CrB type. R_2Pt and R_5Pt_3 crystallise with the Ni_2Si and Mn_5Si_8 structures, with R = Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y for both structures.

The Ordered Phase Fields of the Iron-Nickel-Platinum Equilibrium Diagram

G. T. STEVENS, M. HATHERLY and J. S. BOWLES, *J. Mater. Sci.*, 1978, **13**, (3), 499-504

The approximate limits of the ordered phases in the Fe-Ni-Pt system at 600°C were examined. Continuous solid solutions form between FePt and NiPt, and between Fe_3Pt and Ni_3Pt , at temperatures below the relevant critical temperatures,

but not between FeNi_3 and Ni_3Pt . Two tetragonal phases were found in alloys containing 60 at. % Pt. Since high magnetic hardness of ordered Co-Pt alloys is due to small ordered particles, the ability to produce similar structures in Fe-Ni-Pt alloys can be used to test this, and may lead to the discovery of alloys with similar properties.

A Low-Temperature X-ray Diffraction Study of Pd and Some Pd-H Alloys

H. W. KING and F. D. MANCHESTER, *J. Phys. F: Metal Phys.*, 1978, **8**, (1), 15-26

Measurements of the lattice parameter of Pd from room temperature down to 4K showed it to be a smooth function of temperature over this range. Studies of the X-ray diffraction patterns of some β -phase Pd-H alloys, and a mixed ($\alpha + \beta$) phase alloy, and of their dependence on cooling through the 50K region showed no visible effect on the state of the Pd lattice.

Hydrogen Sorption by Palladium-Gold Wires

D. D. ELEY and E. J. PEARSON, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, (2), 223-236

Hydrogen sorption was studied on Pd-Au wires prepared in ultra high vacuum, at a H_2 pressure of 6.25 μ Pa and wire temperatures of 100, 150, 200 and 304K. The initial sticking coefficient for Pd at 100K was 0.16, falling to 0.006 at a fractional monolayer coverage $\theta = 0.8$. The activation energies decreased sharply with coverage to a value of ~ 20 kJ/mol. H_2 sorption increased slightly from Pd to 90Pd-10Au, decreasing sharply towards zero at 40Pd-60Au.

Isothermal Section of a Phase Diagram of the System Ag-Pd-Dy at 600°C

A. G. SLAVEV, V. K. PORTNOI, M. V. RAEVSKAYA and E. M. SOKOLOVSKAYA, *Vest. Moskov. Univ., Ser. II Khim.*, 1977, **18**, (6), 695-698

The characteristics of phase equilibrium in the system Ag-Pd-Dy were studied at 600°C by microanalysis, by hardness and microhardness and by X-ray spectroscopy. The formation of a new ternary phase was observed. The growth of the Pd content was found to increase alloy hardness.

The Energy Loss Spectra and Auger Spectra of Palladium Hydride and Palladium Glasses

L. Y. L. SHEN, H. S. CHEN, R. C. DYNES and J. P. GARNO, *J. Phys. Chem. Solids*, 1978, **39**, (1), 33-38

The Auger and energy loss spectra of Pd hydrides and Pd glasses, Pd-Ni-P and Pd-Cu-Si, were measured. The energy loss spectra of these amorphous and crystalline state alloys are similar and the surface compositions of Pd glasses are in good agreement with their bulk compositions.

Strong Metal-Support Interactions. Group 8 Noble Metals Supported on TiO₂

S. J. TAUSTER, S. C. FUNG and R. L. GARTEN, *J. Am. Chem. Soc.*, 1978, **100**, (1), 170-175

The reduction of noble metals on TiO₂ at 200°C produces well dispersed metals which exhibit the capacity to sorb both H₂ and CO. Reduction of the same materials at 500°C, however, decreases H₂ and CO sorption to near zero. Loss of this sorption capacity is not due to metal agglomeration. The effect for well dispersed metals is evidence for a chemical interaction between the noble metal and its support. This interaction is examined in terms of metal-metal bonding between noble metal and Ti cations.

Adsorption of Nitrogen on Iridium

J. -M. DEROCHE, *Phys. Status Solidi A*, 1978, **45**, (1), 163-169

Adsorption of N₂ on perfect and stepped planes of Ir, carried out by a high sensitive probe hole technique at 77K, was studied. Positively charged N₂ is found on the (111), (100) and (311) faces, while a negative N₂ film is found on all the other surfaces examined. For the (110) plane the two films occur, first positive, then negative, and this is attributable to the face surface structure.

Adsorption and Desorption of Ammonia, Hydrogen, and Nitrogen on a Ruthenium (0001) Surface and Electron Beam Induced Effects

R. L. DANIELSON, Washington State University Ph.D. Thesis, 1977

The adsorption and desorption of NH₃, H₂ and N₂ on a Ru(0001) surface were investigated by AES, LEED and thermal flash desorption. NH₃ adsorbs at 100K into two weakly bonded molecular states, but not at room temperature. At 400K it adsorbs with activation energy of 0.52eV and forms a (2×2) LEED pattern. Evidence that dissociation of NH₃ and diffusion of N atoms into the bulk also occurs is presented. H₂ adsorbs at 100K and desorbs with 2nd order kinetics between 350-450K. N₂ does not adsorb on Ru(0001). Maximum N₂ coverage was <2% of a monolayer.

CHEMICAL COMPOUNDS

Reactions of Acetylene with Noble-Metal Carbonyl Halides. II. Insertions into the Chloro-Platinum Bond

F. CANZIANI, L. GARLASCHELLI and M. C. MALATESTA, *J. Organometal. Chem.*, 1978, **146**, (2), 179-196

The reaction of dichlorodicarbonylplatinum with ROCC=CCOOR (R = CH₃, C₂H₅) in benzene and toluene gives carbonyl chloro(1,2-*trans*-dicarbalkoxy-2-chloroethenyl)Pt compounds by insertion of the active acetylene molecule into the Pt-Cl bond. These chelated stable square-planar vinyl derivatives react with neutral donor ligands to give simple σ -alkenyl derivatives.

A Novel Ruthenium Bronze: KRu₄O₈

M. WILHELM and R. HOPPE, *Z. Anorg. Allgem. Chem.*, 1978, **438**, (1), 90-96

Crystal structure studies of a new compound KRu₄O₈ prepared as black rod-shaped crystals showed it to crystallise tetragonal in the space group C_{4h}^b-14/m, with a=9.88 and c=3.12Å, c/a=0.316 and Z=2.

ELECTROCHEMISTRY

The Electrocatalytic Reduction of Nitrogen Compounds. Part II: The Influence of the Electrode Material on the Electrochemical Reduction of Nitrite

J. F. VAN DER PLAS and E. BARENDRECHT, *Rec. Trav. Chim.*, 1978, **97**, (3), 65-69

The electrochemical reduction of nitrite was studied at Pt, Ir, Rh, Nb, Pb and Ta electrodes in 7.5M H₂SO₄ solutions. The results showed that the thin oxide films on the Pt, Ir and Rh did not interfere with the reduction process. However, a thick oxide layer, as on Nb and Ta, positively shifted the reducing potential by several hundreds of mV. It is concluded that poisoning of the active surface area of the electrodes by O₂ changes the reduction mechanism of nitrite.

The Platinum/Platinum Oxide/Carbonate/Carbon Dioxide Electrode at 350°C in Fused Potassium and Sodium Nitrates

A. G. KEENAN and T. R. WILLIAMSON, *J. Phys. Chem.*, 1978, **82**, (1), 46-49

A preoxidised Pt electrode responds reversibly to the electroactive species CO₂ and CO₃²⁻ in pure Na and K nitrate melts at 350°C. The electrode reaction was Pt + CO₃²⁻ = PtO + CO₂ + 2e⁻. Standard potentials for this system with respect to a Ag/Ag nitrate reference electrode in the pure solvents are given. For work involving the solute CO₃²⁻, the system may be exposed to the ambient atmosphere which provides the necessary equilibrium concentration of CO₂.

Study of Platinum Electrodes by Means of Electrochemistry and Low-Energy Electron Diffraction. Part II. Comparison of the Electrochemical Activity of Pt(100) and Pt(111) Surfaces

A. T. HUBBARD, R. M. ISHIKAWA and J. KATEKARU, *J. Electroanal. Chem. Interfacial Electrochem.*, 1978, **86**, (2), 271-288

LEED patterns were obtained for Pt(100), Pt(111) and polycrystalline electrodes before and after exposure to aqueous 1M H₂SO₄ and linear potential scan voltammograms were recorded. The maximum amount of chemisorbed H₂ corresponded to one H atom per surface Pt atom. The Pt(100) [1×1], Pt(111) and the polycrystalline electrode surfaces appeared to withstand prolonged voltammetric characteristics at -0.2 to 1.2 V vs. a calomel reference electrode.

Investigation of the Surface of Platinum Paste Electrodes

N. H. TURNER, *J. Electroanal. Chem. Interfacial Electrochem.*, 1978, **87**, (1), 67-72

AES and XPS studies of electrodes made from a Pt paste on stabilised zirconia showed the presence of C, O₂, Ag, S and chlorine in addition to Pt. The results showed the existence of Pt oxides together with metallic Pt.

The Effect of Electrolyte Concentration on the Catalytic Activity of Platinum for Electrochemical Oxygen Reduction in Phosphoric Acid

H. R. KUNZ and G. A. GRUVER, *Electrochim. Acta*, 1978, **23**, (3), 219-222

Catalytic activity of Pt supported on C for the electrochemical reduction of O₂ in H₃PO₄ was studied as a function of temperature (up to 191°C) and electrolyte concentration. The exchange current decreased with an increase in electrolyte concentration from 88-105 wt.%. The activation energy was ~22kcal/mole and independent of electrolyte concentration from 85 to 105 wt.%.

Use of the Coulometrically Measured Amount of Adsorbed Hydrogen to Determine the Active Surface Area of Platinum for the Electro-Oxidation of Iron(II)

T. C. FRANKLIN and R. GRAVES, *Surface Technol.*, 1978, **6**, (5), 347-359

The kinetics of the electron transfer between Fe(II) and bright Pt electrodes was studied in 2N H₂SO₄ and in H₂SO₄ containing azide, bromide, chloride, oxalate, thiocyanate and tetrafluoroborate ions. Chloride, bromide and azide ions functioned only as blocking agents for the electron transfer reaction. The oxalate increased the measure current by forming an Fe(III) complex which increased the desorption rate of the oxalate from the electrode, thus cleaning the electrode surface.

ELECTRODEPOSITION AND SURFACE COATINGS

The Behaviour of Electroplated Noble Metal Coatings in Different Atmospheres

U. MAYER, *Metalloberfläche*, 1978, **32**, (1), 3-7

Electroplated deposits of Ru, Rh and Pd and of 99.8% Au, Au alloys (75% Au, Cu, Cd and 67% Au, Cu) with and without a covering of 0.5µm hard gold (sandwiches) were exposed to several natural and artificial atmospheres. The corrosion resistance of the sandwiches is nearly comparable to the resistance of high purity hard Au deposits. The corrosion behaviour of electrodeposited Ru, Rh and Pd depends on the test atmosphere. Pd is highly stable in artificial atmospheres. No single laboratory atmosphere can predict the long term tarnishing of noble metal electrodeposits.

HETEROGENEOUS CATALYSIS

Effects of Platinum and Palladium Impregnation on the Performance and Durability of Automobile Exhaust Oxidising Catalysts

J. C. SUMMERS and L. L. HEGEDUS, *J. Catalysis*, 1978, **51**, (2), 185-192

The performance and durability of noble metal/Al₂O₃ oxidation catalysts are influenced by the relative location of the metals along the radius of the pore catalyst pellets. Five Pt and Pd containing catalysts were prepared by varying the metal distribution along the radius of the catalyst pellets. The catalysts were either poisoned or sintered. Improvements in steady-state and light-off performance occurred when the catalyst had an outer shell of Pt and an inner shell of Pd.

Activity of Platinum-Palladium Catalysts in the Dehydrogenation of Cyclohexane

N. S. KOZLOV, L. YA. MOSTOVAYA, M. V. ZARETSKII and I. P. STREMOK, *Neftekhimiya*, 1978, **18**, (2), 178-181

X-ray and spectroscopic studies of the catalytic activity of supported Pt-Pd catalysts prepared by the impregnation of γ-Al₂O₃ supports by aqueous solutions of H₂PtCl₆ or PdCl₂ (containing 0.6 wt.% metal in total) were carried out during dehydrogenation of cyclohexane in a flow reactor at 250°C. The rate of dehydrogenation over catalysts containing ≤50 wt.% Pd-Pt alloys was found to be the same as over 0.6 wt.% Pt/Al₂O₃ catalysts. The results showed the formation of Pt and Pd solid compounds on the surfaces of the catalysts.

Catalytic Dehydrogenation of Reducing Sugars in Alkaline Solution at Ambient Conditions. Transfer Hydrogenation of Fructose

G. DE WIT, J. J. DE VLEGER, A. C. KOCK VAN DALEN, A. P. G. KIEBOOM and H. VAN BEKKUM, *Tetrahedron Lett.*, 1978, (15), 1327-1330

In an alkaline medium under ambient conditions in the presence of transition metals, aldoses can be converted to their sugar acids with high selectivity and with production of H₂. Glucose gave excellent results when either 5% Pt/C or 5% Rh/C was used as the catalyst.

Effects of Mn Deposits from MMT on Automotive Catalysts in the Absence and Presence of Other Fuel Additives

K. OTTO and R. J. SULAK, *Environ. Sci. Technol.*, 1978, **12**, (2), 181-184

The chemical effects of deposits from methylcyclopentadienyl manganese tricarbonyl(MMT) on three-way catalysts containing Pt and Rh were investigated. Automotive exhaust emissions were simulated by burning isooctane and MMT and/or other fuel additives were introduced. Two formulations on monolithic supports did not show any

chemical poisoning beyond that caused by the same fuels without MMT. MMT had no effect on H₂SO₄ formation over these catalysts.

Hydrogenation of Acetylene in Excess Ethylene on an Alumina-Supported Palladium Catalyst at Atmospheric Pressure in a Spinning Basket Reactor

W. T. MCGOWN, C. KEMBALL and D. A. WHAN, *J. Catalysis*, 1978, **51**, (2), 173-184

The hydrogenation of acetylene in the presence of ethylene and CO was investigated in a spinning basket reactor on a supported Pd catalyst. The rate of acetylene disappearance was controlled by pore diffusion at low acetylene concentrations. In the non-diffusion controlled region the reaction of acetylene was first order in H₂, and the rate of ethane formation was independent of both ethylene and acetylene pressures.

Catalytic Cigarette Filter for Carbon Monoxide Reduction

D. R. ROWE and W. G. LLOYD, *J. Air Pollut. Contr. Ass.*, 1978, **28**, (3), 253-255

The efficiency of a Pd(II)/Cu(II) catalyst as a cigarette filter to reduce CO levels in cigarette smoke was studied. This works by effectively oxidising CO to CO₂ via Pd(II) chloride which is reduced by CO to Pd(O), then being reoxidised to Pd(II). The catalyst was supported on 14/28 mesh Al₂O₃. The catalyst removed over 90% of the CO present in the cigarette smoke, and such a catalytic filter could reduce CO lung exposure by from 15 to 20 ppm. CO removal is improved by increased catalyst and longer exposure times.

Dehydrogenation of Isopropyl Alcohol on Membrane Catalysts from Binary Alloys of Palladium with Ruthenium or Nickel

N. N. MIKHALENKO, E. V. KHRAPOVA and V. M. GRYAZNOV, *Neftekhimiya*, 1978, **18**, (2), 189-192

The effect of composition of membrane catalysts made from binary alloys of Pd with Ru or Ni, and their preliminary treatment, on their catalytic activity was studied in a flow reactor during the dehydrogenation of isopropyl alcohol. The membranes were made of Pd foils, containing 5.5 wt.% Ni or either 6.8, or 10 wt.% Ru, on which a Ru layer 1 μm thick was electrochemically deposited. Pd and 10 wt.% Ru-Pd alloy catalysts were found to be the most active.

Palladium Catalysed Amine Exchange Reaction of Tertiary Amines. Insertion of Palladium(0) into Carbon-Hydrogen Bonds

S.-I. MURAHASHI, T. HIRANO and T. YANO, *J. Am. Chem. Soc.*, 1978, **100**, (1), 348-350

A novel Pd catalysed exchange reaction of tertiary amines possibly involving an initial insertion of Pd into a C-H bond adjacent to the N₂, is described. This leads to a highly active intermediate iminium ion complex.

Selective Hydrogenation of Heptyne-1 and Its Mixture with Hexene-1 on Pd/BaSO₄

D. V. SOKOL'SKII, V. A. SHOSHENKOVA and N. P. TRUKHACHEVA, *Zh. Priklad. Khim.*, 1978, **51**, (2), 409-412

Hydrogenation of acetylene-heptyne-homologues and their mixture with ethylene-hydrocarbons-hexene was carried out over 5% mole Pd/BaSO₄ catalyst and 5% PdO/BaSO₄ in 96% mole ethanol, and the selectivity of the reaction after addition of CdSO₄ into the system was measured. The presence of CdSO₄ increases the selectivity of the hydrogenation of heptyne-1 to heptene-1 and the adsorption of Cd cations depresses the migration of double bonds on Pd/BaSO₄ catalysts. It is concluded that the addition of the optimal amount of CdSO₄ allows a strong selective release of hexene-1 (90%) from heptyne-1 (10%).

Hydrogenation of Acetylene over Supported Metal Catalysts. Part 2. [¹⁴C] Trace Study of Deactivation Phenomena

A. S. AL-AMMAR and G. WEBB, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, (3), 657-664

Deactivation of supported Pd/SiO₂, Rh/SiO₂, Ir/SiO₂ and Pd/Al₂O₃ catalysts was studied during C₂H₂ hydrogenation using [¹⁴C] trace. The results are interpreted in terms of the hydrogenation reaction occurring by a H transfer mechanism between a dissociatively adsorbed C₂H_x species and associatively adsorbed acetylene.

Hydrogenation of Unsaturated Compounds on Rhodium Skeletal Catalysts from Rh-Mg Alloys

T. K. KABIEN, D. V. SOKOL'SKII and G. SH. OSPANOVA, *Dokl. Akad. Nauk S.S.S.R.*, 1978, **239**, (1), 120-122

The hydrogenation of unsaturated compounds, isoprene, phenylacetylene and hexene-1, were carried out over skeletal Rh catalysts (prepared by the leaching of 5-60 wt.% Rh-Mg alloys in a 20% solution of CH₃COOH at 96°C for 1h) in the presence of 96% ethanol at 20°C. Catalysts containing 5-26 wt.% Rh were found to be most active, and the specific activity of the catalysts sharply decreased when increasing Rh content resulted in the appearance of the Rh₂Mg₃ phase.

Particle size Effect in the Carbon Monoxide Chemisorption on Supported Rhodium

N. KAUFHERR, M. PRIMET, M. DUFAX and C. NACCACHE, *Compt. Rend., Sér. C*, 1978, **286**, (4), 131-133

Spectroscopic studies of CO adsorption on Rh catalysts supported by zeolite and Al₂O₃ showed that particle sizes below 10 Å (Rh dispersed on zeolite) were suitable for the formation of gem dicarbonyl species detected in i. r. spectra around 2100 and 2040/cm. The chemisorption led to linear and multicentred species for particles > 20 Å (Rh/Al₂O₃).

Hydroformylation, Hydrogenation, and Isomerization of Olefins over Polymer-Immobilized Rhodium Complexes

H. ARAI, *J. Catalysis*, 1978, **51**, (2), 135-142

In order to make a catalyst with the selectivity and activity of a homogeneous catalyst but with the advantages of a heterogeneous catalyst, Rh complex ($\text{RhCl}(\text{CO})_2$) was co-ordinatively bonded to the phosphine group on polystyrene-coated silica gel. Its activity was tested for hydroformylation, hydrogenation and isomerisation of olefins in the vapour phase. The dependence of rates and product yields on the partial pressure of H_2 , CO and olefins was examined and compared with those of homogeneous catalysis. The reaction rate dependence for olefins on partial pressure was in the order olefin $> \text{H}_2 > \text{CO}$. Hydroformylation, hydrogenation and isomerisation are all inhibited by CO.

A Fischer-Tropsch Study of Supported Ruthenium Catalysts

D. L. KING, *J. Catalysis*, 1978, **51**, (3), 386-397

The effect of catalyst support on activity and selectivity of CO hydrogenation by Ru is discussed. The specific activity and selectivity depend on the support and the metal loading. Activity increases with metal particle size either by increasing metal loading or having a support which poorly disperses the metal. Product saturation increases with increasing CO conversion. Hydrocarbon chain length depends on temperature, pressure and support. Branched-chain hydrocarbons are produced on acid supports, SiO_2 - Al_2O_3 or zeolites, and isomerisation of straight-chain products. The support may alter the catalytic behaviour of Ru through electronic and dispersal effects.

HOMOGENEOUS CATALYSIS

Study of Hydrogenation of Olefins Catalysed by Polymer-Bound Palladium (II) Complexes

M. TERASAWA, K. KANEDA, T. IMANAKA and S. TERANISHI, *J. Catalysis*, 1978, **51**, (3), 406-421

A polymer-bound Pd(II) chloride complex catalyst was prepared by the reaction of PdCl_2 with a phosphinated polystyrene. Under mild conditions it catalyses the hydrogenation of alkenes and alkynes, particularly selective hydrogenation of conjugated dienes to monoenes. Catalytic activity decreases in the order: conjugated dienes $>$ non-conjugated dienes $>$ terminal olefins $>$ internal olefins. O_2 -containing solvents promote catalytic activity. Hydrogenation rates, dependent on substrate concentration, catalyst concentration, pressure and temperature, have been worked out. The reactivities of the polymer Pd complex catalysts and of an analogous catalyst system $\text{PdCl}_2(\text{PPh}_3)_2\text{SnCl}_2$ reflect the electronic state and co-ordination number of the complexes.

Transfer Hydrogenation and Transfer Hydrogenolysis: XII. Selective Hydrogenation of Fatty Acid Methyl Esters by Various Hydrogen Donors

T. TAGAWA, T. NISHIGUCHI and K. FUKUZUMI, *J. Am. Oil Chem. Soc.*, 1978, **55**, (3), 332-336

The selective hydrogenation of methyl linoleate was studied using various organic compounds as hydrogen sources in the presence of homogeneous Pd, Ru, Rh and metallic Pd catalysts. Complete selectivity to monoenes and little formation of isolated *trans* double bonds occurred by the hydrogen transfer from L-ascorbic acid at 47% conversion of the starting material to hydrogenation products. Hydrogenation by *trans*-1,2-cyclohexanediol catalysed by $\text{RuH}_2(\text{PPh}_3)_4$ showed high selectivity to *cis*-monoenes. In the reaction catalysed by $\text{RuH}_2(\text{PPh}_3)_4$ the presence of these hydroxy compounds increased the isomerisation of methyl elaidate to *cis*-monoenes.

Rhodium Catalysed Cyclopropenation of Acetylenes

N. PETINIOT, A. J. ANCIAUX, A. F. NOELS, A. J. HUBERT and PH. TEYSSIE, *Tetrahedron Lett.*, 1978, (14), 1239-1242

Rhodium carboxylates are reported to be very effective for the cyclopropenation of acetylenes. The catalyst influence on the competitive insertion-cyclopropenation reactions for acetylenic alcohols, that is control of the relative reactivities of a triple bond against an alcohol group in intramolecular competitions, is examined.

Homogeneous Catalytic Hydrogenation of Aldehydes by $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ by Chlorine up to Turnover Figure 95,000

W. STROHMEIER and L. WEIGELT, *J. Organometal. Chem.*, 1978, **145**, (2), 189-194

Linear and branched aliphatic and aromatic aldehydes are homogeneously hydrogenated with the catalyst $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$ at 160-200°C and H_2 pressure of 15 atm. Mean catalytic activities up to 243 and turnover numbers up to 95,000 were observed. With branched aliphatic aldehydes no side reactions were found and selectivity for alcohol formation was up to 99%.

CHEMICAL TECHNOLOGY

Determination of Precious Metals at PPB Levels in Rocks by a Combined Wet Chemical and Flameless Atomic Absorption Method

B. J. FRYER and R. KERRICH, *At. Absorp. Newsl.*, 1978, **17**, (1), 4-6

An easier method to determine the presence, at ppb levels, of Pt, Pd, Au and Ag in igneous rocks than previously involves using an aqua regia extraction followed by HF treatment to eliminate silica. Quantitative precipitation of precious metals is achieved by reduction of Te chloride to Te

metal by stannous chloride. A double Te precipitation is performed on samples. This method can handle quantities of rocks up to 30g in mass, and can therefore be used on rocks containing very little precious metals.

Interfacial Noble-Metal Corrosion in Metal to Ceramic Reaction Welding

H. J. DE BRUIN, *Nature*, 1978, 272, (5655), 712-713
Welding refractory ceramic oxides to transition metals to form Pd/MgO and Pd/Al₂O₃ couples involves two different bond types when annealed in air. Below 800°C a visible intermediate oxide layer forms, the thickness of which increases with time, and the bond strength depends on the corrosion of the metal and strength of the oxide layer. Above 800°C there is a sharp metal-ceramic interfacial discontinuity and the bond strengths reach their maximum after a few hours and do not deteriorate with time. These different bond types suggest a new corrosion phenomenon.

ELECTRICAL AND ELECTRONIC ENGINEERING

Investigation of the Ti-Pt Diffusion Barrier for Gold Beam Leads on Aluminium

S. P. MURARKA, H. J. LEVINSTEIN, I. BLECH, T. T. SHENG and M. H. READ, *J. Electrochem. Soc.*, 1978, 125, (1), 156-162

Ti-Pt diffusion barriers were inserted between Al and Au beam lead sealed structures (used in integrated circuit multichip assemblies) to stop interactions. The Al-Ti-Pt-Au structures were then aged and examined by electron microscopy, X-ray diffraction and sheet resistance measurements. Metallurgical interactions occurred at hillocks in Al, forming black spots which eventually covered the surface. This was inhibited by annealing Al before barrier metallisation and using at least 2000Å each of Ti and Pt in the barrier. Thicker Ti covers the Al hillocks and prevents Al-Pt interactions, and thicker Pt prevents Ti-Au interactions.

NEW PATENTS

ELECTROCHEMISTRY

Electrode

T.D.K. ELECTRONICS CO. LTD.

British Patent 1,508,091

Cl₂ is produced free from O₂ by the electrolysis of brine in the presence of an anode which is a conductive substrate (Ti, Ta or Zr) coated with a mixture of Pd oxide (5-40 mol.%), Ru oxide (2-10 mol.%), and Sn oxide (50-93 mol.%), of which up to 40 mol.% may be substituted by TiO₂.

The Semiconductivity and Stability of Palladium Oxide

E. REY, M. R. KAMAL, R. B. MILES and B. S. H. ROYCE, *J. Mater. Sci.*, 1978, 13, (4), 812-816

The use of Pd oxide in photoelectrolytic cells was investigated in an attempt to use it to convert sunlight to electricity. Pd oxide is a semiconductor with an estimated band gap at 820nm. The extrapolated bond gaps of Pd oxide films, prepared by oxidation of sputtered Pd films were examined by optical absorption spectroscopy and photoconductivity measurements. Band gaps occur at 2.13 ± 0.03 and 2.67 ± 0.03 eV, respectively. Photoconductivity occurs for energies smaller than the extrapolated band gap. The thermal stability of the films was reduced from 580K in a vacuum down to 350K by H₂.

TEMPERATURE MEASUREMENT

Temperature Detectors

Engng. Mater. Design, 1978, 22, (4), 284

A ceramic bodied Pt resistance thermometer covering the temperature range -220°C to +800°C has been developed, with a close physical tolerance (± 0.013 mm) for interchangeability. Thermal shocks do not alter its stability.

MEDICAL USES

Stainless Tubing Provides High-Reliability Connector

E. J. STEFANIDES, *Design News*, 1978, 34, (1), 82-83

A high-reliability connector for the leads of a cardiac pacing system is used for a lithium battery powered pulse generator. It provides a low-resistance electrical connection with high mechanical strength. One end of each conductor is attached to the flat-tipped platinum-iridium electrodes. The terminals and the electrodes are encased in moulded silicone rubber jackets.

Electrodes

SOLARIO LTD.

U.S. Patent 4,054,496

In the electrolysis of heavy water the electrodes may be of Ru, Rh, Pd, Os, Ir or Pt, or coatings of these metals on substrates of Ti, Nb or Ta.

Palladium Electrode

SEMICONDUCTOR SENSORS INC.

U.S. Patent 4,058,368

A device for the detection of hydrogen has a metal electrode made of Pd, Ni and/or Pt.