

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Geometric Factors in f.c.c. and b.c.c. Metal-on-Metal Epitaxy. IV. Deposits of Rh, Ir, Pd and Pt on (001)W and (001)Mo

I. A. BRUCE and H. JAEGER, *Philos. Mag.*, 1979, **40A**, (1), 97-109

Deposits of Rh, Ir, Pd and Pt were formed by condensing the metal vapour in ultra high vacuum onto (001)W and (001)Mo substrates held at 300-1200K. As the deposition temperature was increased the deposit grain orientation changed. Above 700K deposits consisted entirely of (110) epitaxed grains. The structure of (001) epitaxed grain is always f.c.c. whereas that of (110) epitaxed grains is f.c.c. below 700K, f.c.c. + h.c.p. at 700K and entirely h.c.p. above 1000K. It was found that the geometric effect is sufficient to induce the deposit to adapt a structure not otherwise stable or even known for that metal.

The Interface Structure of Pd/(III)Au Epitaxial Films

J. G. ERLINGS and F. W. SCHAPINK, *Thin Solid Films*, 1979, **61**, (1), 33-39

Vacuum-deposited Pd grows in different modes on (111)Au single-crystal platelets obtained by chemical reduction in a gel. The final interfacial structure depends on the vacuum conditions during deposition and on the condition of the substrate surface. Under certain conditions dislocation-free interfaces are formed in the Pd/(111)Au bicrystals; these interfaces remain dislocation-free after annealing. The phenomenon of alloying Pd/Au thin film couples during ageing at room temperature is also reported.

Elastic Properties and Temperature Coefficient of Delay Time in Amorphous Pd-Si Alloys

K. FUKAMICHI, M. KIKUCHI and T. MASUMOTO, *Sci. Rep. Res. Inst. Tohoku Univ., Ser. A*, 1979, **27**, (2), 202-209

Pd₈₀Si₂₀ amorphous alloy and its amorphous alloys containing Ag or Cu were prepared from melts by a roller quenching method. The temperature coefficient of Young's modulus at room temperature was measured under various conditions, and together with the thermal expansion was used to calculate the temperature coefficient of delay time. A material with a small enough coefficient for use as delay lines was obtained by selecting the number of revolutions of the roller, heat-treatments, the degree of cold rolling, etc. This material would have a very small attenuation coefficient. Thus it was concluded that Pd-Si amorphous alloys would be applicable to ultrasonic delay lines.

Serrated Plastic Flow in Metallic Glasses

S. TAKAYAMA, *Scr. Metall.*, 1979, **13**, (7), 463-467

Plastic flow in Pd_{77.5}Cu₆Si_{16.5} metallic glass was studied by bonding and tensile deformation after drawing the wire. Deformation bands appeared on the lateral surfaces of the wires. The Pd-Cu-Si samples always showed serrations on their stress-strain curve after cold-drawing. The deformation bands revealed a correlation between serrations on the stress-strain curves and bursts of slip lines. Striations were observed on the large slip steps of samples that were drawn and subsequently bent.

Ion-Beam-Induced Formation of the PdSi Silicide

B. Y. TSAUR, S. S. LAU and J. W. MAYER, *Appl. Phys. Lett.*, 1979, **35**, (3), 225-227

PdSi was formed by implanting energetic Xe ions through a thin Pd or Pd₂Si film on a Si substrate. The PdSi phase formed near the Pd₂Si-Si interface. Phase formation was confirmed by glancing-angle X-ray diffraction analysis. Subsequent thermal annealing at 300-400°C resulted in successive growth of the phase. A uniform PdSi layer was obtained with sheet resistivity of 18μΩcm. Usually PdSi formation, for possible use in integrated circuit technology, has required high temperatures of >700°C.

Solar Energy Storage Reactions Involving Polynuclear Rhodium Isocyanide Complexes, Flash Photolysis Studies in Aqueous Sulfuric Acid Solutions

V. M. MISKOWSKI, I. S. SIGAL, K. R. MANN, H. B. GRAY, S. J. MILDNER, G. S. HAMMOND and P. R. RYASON, *J. Am. Chem. Soc.*, 1979, **101**, (15), 4383-4385

Thermal reaction between Rh₂(bridge)₄²⁺ and HCl generates a blue photoactive species [Rh₂(bridge)₄Cl²⁺]_n and H₂. Flash photolysis studies are interpreted by assuming n = 2 for [Rh₂(bridge)₄³⁺]_n which is prepared. It is suggested that EXAFS measurements on samples containing both polynuclear Rh species will contribute to the solution of the structural problem.

Photoproduction of Hydrogen from Water Using Rhodium(III) Bipyridyls

K. KALYANASUNDARAM, *Nouv. J. Chim.*, 1979, **3**, (8/9), 511-515

Ultraviolet irradiation of aqueous solutions of Rh(III) bipyridyls, such as (Rh'''bpy₂Cl₂)Cl in the presence of, for example, triethanolamine leads to evolution of H₂ gas. The reaction is catalytic with respect to the Rh and also the H₂ is pH dependent. Involvement of Rh(I) complexes as intermediates and possible mechanism for H₂ evolution is discussed.

Grain Growth in Ir-0.3Pct W Alloys

D. E. HARASYN and A. C. SCHAFFHAUSER, *Metall. Trans.*, 1979, **10A**, (7), 823-830

The grain size in Ir-0.3wt.%W alloy was studied as a function of time (up to 2000 h) and temperature (1310, 1415 and 1535°C). Growth rates were measured both perpendicular and parallel to the sheet surface in longitudinal cross section. In samples with Th, Al, Fe, Ni and Rh dopant additions the grain structure was elongated and grain growth was retarded. The undoped alloy had nearly the same grain size at any time, while the doped alloy was finer in grain size. The doping retarded grain growth in the alloy and increased the elongation of recrystallised grains in the rolling direction. The dopant/s responsible for this are not known.

Formation of Iridium Silicides from Ir Thin Films on Si Substrates

S. PETERSSON, J. BAGLIN, W. HAMMER, F. D'HEURLE, T. S. KUAN, I. OHDOMARI, J. DE SOUSA PIRES and P. TOVE, *J. Appl. Phys.*, 1979, **50**, (5), 3357-3365

The formation of Ir silicides from the interaction of Ir films with single-crystal Si surfaces were studied at 350-1000°C. Three distinct phases were identified. IrSi was formed at 400-600°C, another phase with a composition close to IrSi_{1.75} was formed at 500-950°C, while at ~1000°C growth of IrSi₃ from nuclei that spread laterally occurred. A marker experiment implied that in the formation of both IrSi and IrSi_{1.75} the dominating diffusion species is Si.

Behaviour of Osmium during Electrolytic Purification of Nickel

O. Z. BALAD'YAN, A. I. ZHURIN and E. K. BESPALENKOVA, *Zh. Prikl. Khim. (Leningrad)*, 1979, **52**, (9), 2002-2005

The behaviour of Os during purification of Ni in sulphate, sulphate-chloride and chloride electrolytes was studied by a kinetic method. Os was found to transfer in greater quantities than Pt or Pd, into the solution. The degree of Os extraction into the residue decreases with the increase in current density and with the concentration of chlorine ions in the electrolyte.

Kinetic Properties of Ruthenium under Magnetic Breakdown Conditions, Galvanomagnetic Effects

V. E. STARTSEV, A. N. CHEREPANOV, V. P. DYAKINA, N. V. VOLKENSHEIN, G. P. KOVTUN, V. A. VELENSKY and V. M. AZHAZHA, *Zh. Eksp. Teor. Fiz.*, 1979, **77**, (1), 193-207

The magnetoresistance and Hall effect of a pure Ru single crystal with $\rho_{273.2K}/\rho_{4.2K}$ up to 3000 were studied at 4.2K and magnetic field strengths of up to 100 kOe. Magnetic breakdown in Ru leads to the formation of three types of magneto-breakdown electron trajectories: open, closed and space-net type. In all three cases, the formation of magnetic breakdown trajectories is accompanied by quantum oscillations of the magnetoresistance.

Photoemission Studies of H₂S, H₂ and S Adsorbed on Ru(110): Evidence for an Adsorbed SH Species

G. B. FISHER, *Surf. Sci.*, 1979, **87**, (1), 215-227

H₂S, H₂ and S adsorbed on Ru(110) were studied by UPS. For low exposures of H₂S at 80K the work function rises to a value 0.16eV above that of clean Ru(110) while the associated UPS spectra have features similar to those of H(ads) and S(ads) and different from those of molecular H₂S. It is concluded that H₂S dissociates completely at low coverages on Ru(110) at 80K. At intermediate exposures the work function drops and the UPS spectra shows new features attributable to the presence of an adsorbed SH species. This appears to be the first observation of this surface complex. At higher exposures the work function saturates 0.36eV below the clean value, the UPS spectra changes and indicates the adsorption of molecular H₂S. Heating adsorbed H₂S leaves a stable layer of S(ads) Ru(110).

Photoinduced Electron Transfer across a Water-Oil Boundary as a Model for Redox Reaction Separation

I. WILLNER, W. E. FORD, J. W. OTVOS and M. CALVIN, *Nature*, 1979, **280**, (5725), 823-824

A photochemical electron transfer is reported across the interface of a water-in-toluene microemulsion in which EDTA is the donor and Ru(bipy)₃²⁺ is the photosensitiser. This system is proposed as a model for the separation of oxidised and reduced species, which are the active components in the decomposition of water. The electron transfer process is divided into two distinct parts, from the water to the interphase and then from the interphase into the continuous organic solution. Benzylmiconinamide (BNA), which concentrates at the interface was used as the electron acceptor. Thus electron transfer from photoexcited Ru(bipy)₃²⁺ to BNA was followed by the reduction of the dye dissolved in the continuous organic phase. The photosensitiser was then regenerated by the oxidation of EDTA. The process represents a net storage of energy.

Intramolecular Energy-Transfer Reactions in Mixed Metal Dimers. (NH₃)₅Ru^{II}LRh^{III}(NH₃)₅

J. A. GELROTH, J. E. FIGARD and J. D. PETERSEN, *J. Am. Chem. Soc.*, 1979, **101**, (13), 3649-3651

Evidence via metal-to-ligand charge transfer bands is presented for the first intramolecular energy transfer reaction in dilute aqueous solution using a Ru(II)-Rh(III) mixed metal dimer as a model compound. The pyrazine and 4-cyanopyridine Ru(II)-Rh(III) bridged dimers were studied and for the latter there appears to be an internal conversion from Ru(II) localised excited states to the LF excited state associated mainly with the Rh(III) metal. Thus Ru(II) is acting as an antenna for absorbing irradiation while the Rh(III) in communication with it undergoes a chemical reaction. The primary photolysis product may be a mononuclear complex.

CHEMICAL COMPOUNDS

Preparation of Highly Reactive Metal Powders. Preparation and Reactions of Highly Reactive Palladium and Platinum Metal Slurries

R. D. RIEKE and A. V. KAVALIUNAS, *J. Org. Chem.*, 1979, **44**, (17), 3069-3072

Highly reactive slurries of Pd and Pt have been prepared by alkali metal reduction of compounds $[P(C_2H_5)_3]_2MX_2$, (M = Pd, Pt, X = I, Br, Cl, CN) in ethers using simple apparatus and procedures. These slurries undergo oxidative insertion into carbon-halogen bonds of aryl halides, yielding organometallic compounds of the type *trans*- $[P(C_2H_5)_3]_2M(R)X$ where R = C₆H₅, C₆F₅. Such a Pd slurry reacts with allyl bromide yielding $P(C_2H_5)_3Pd(C_3H_5)Br$. Reducing PdI₂ with Li and naphthalene in the absence of phosphine gives a Pd powder which reacts with C₆F₅I to give C₆F₅PdI. The ability to prepare metal powders which undergo oxidative insertions and reactions with neutral ligands is of importance to organic, organometallic and inorganic chemistry, catalysis and surface chemistry.

Activation of Molecular Hydrogen by Transition Metal Complexes. 2. Formation of (0) and (+1) Palladium Complexes with Metal-Metal Bond in Hydrogenolysis of $[Ph_3PPd(OAc)_2]_2$

A. S. BERENBLYUM, A. G. KNIZHNIK, S. L. MUND and I. I. MOISEEV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, (8), 1687-1690

Studies of the stoichiometry and kinetics of interaction of $[Ph_3PPd(OAc)_2]_2$ with H₂ were carried out. The complexes of Pd(0)(Ph₃P)₂Pd₂ and Pd(+1)(Ph₃PPdOAc)₂ were formed with a metal-metal bond during hydrogenolysis. The products of hydrogenolysis are studied and analysed.

ELECTROCHEMISTRY

Corrosion of Platinum in Alkaline Solutions

E. I. KHRUSCHEVA, M. R. TARASEVICH, N. A. SHUMILOVA and N. I. CRISSON, *Zashch. Met.*, 1979, **15**, (5), 560-561

Corrosion behaviour of a Pt black electrode in 1N KOH solution was studied for 4 h, at 20-70°C in He. The dependence of the corrosion rate on the electrode potential was measured at 0.85-1.37V and 70°C. Corrosion rate increased sharply at 0.85-0.95V with a sharp fall after the peak at 0.95V. The rate changed only slightly between 1.05-1.25V but fell sharply after reaching 1.37V. The dependence was similar even after 4 h, but the maxima were less defined. The experiments were also performed in O₂. In alkaline solution saturated with O₂, the dependence was greater in O₂ than that in an inert atmosphere.

Some Aspects of the Reduction of Oxygen at a Platinum-Oxide Alloy Diaphragm

J. P. HOARE, *J. Electrochem. Soc.*, 1979, **126**, (9), 1502-1504

A steady-state galvanostatic polarisation curve was obtained on the front side of a Pt diaphragm in contact with O₂-stirred 2N H₂SO₄ solution, while the other side was in contact with concentrated HNO₃. The rest potential was the reversible O₂ potential. The rate of O₂ reduction on the Pt-O alloy diaphragm is lower at high current densities than on a bright Pt cathode. At very high current densities the system is driven into the H₂-evolution region where the H₂-η value is close to the literature values. When the system was back on open circuit, the rest potential returned to the normal O₂ potential after 24h.

The Purification of Sulphuric Acid Electrolyte Solutions

N. A. HAMPSON and M. J. WILLIAMS, *Surf. Technol.*, 1979, **9**, (2), 91-95

A method for purifying low level impurities from H₂SO₄ solutions using pre-electrolysis with a Pt-aqueous H₂SO₄ system was compared to that of charcoal purification. Cyclic voltammograms for smooth Pt with and without charcoal present were drawn in 1M H₂SO₄ between 0.05 and 1.5V at various sweep rates. The voltammograms indicate contamination when charcoal is present and spurious peaks occur in the double layer region as the organic material is adsorbed and oxidised at high anode potentials. The Pt-H₂SO₄ is of considerable commercial importance as a possible electrocatalytic system for oxidation of oxy-hydrocarbon fuels such as methanol.

Hydrogen Evolution from Water Induced by Visible Light Mediated by Redox Catalysis

J. KIWI and M. SPATZEL, *Nature*, 1979, **281**, (5733), 657-658

A dramatic improvement in the H₂ production rate has been observed during the catalytic light-induced reaction of water with methyl viologen. The improvement occurred by using very finely dispersed Pt stabilised by polyvinyl alcohol. As the particle size was decreased from 530-110Å the H₂ production rate increased to as high as 12l/day per litre of solution for the smallest particle size.

"Third Body" Effect in the Auto-Inhibition of Formic Acid Oxidation at Electrodes. Electrocatalysis of Formic Acid and Methanol Oxidation at Au-Pt Alloy Electrodes

B. E. CONWAY, H. ANGERSTEIN-KOZLOWSKA and G. CZARTORYSKA, *Z. Phys. Chem. (Frankfurt am Main)*, 1979, **112**, (2), 195-214

Studies of the electrochemical oxidation of formic acid at Au-Pt alloy electrodes are reported where the exact surface Au/Pt composition can be evaluated by cyclic voltammetry and related to the oxidation

current maxima for formic acid. The appreciable activation effects observed are due to the presence of Au atoms amongst Pt atoms in the alloy electrode surfaces, acting as "third body" centres and preventing formation of the auto-inhibitor in the reaction. The formic acid current can be calculated per Pt atom in the alloy electrode surfaces and increases as the Pt atoms become more isolated. Results for methanol oxidation on the same alloys are given.

Studies of Ethylene Adsorption on Ni, Pd and Pt Films and the Reactivity of the Selected Forms of the Adsorbate with Hydrogen

R. DUŠ and W. LISOWSKI, *Surf. Sci.*, 1979, **85**, (1), 183-199

A static capacitor method was used to study surface potential changes that occur during C₂H₄ adsorption on Pd, Pt and Ni films at 298K. The surface potential was related to the concentration of the various adsorbed species. C₂H₄ admolecules adsorbed in the second layer readily react with hydrogen, whereas those in the first layer do not. On Pt films, only the electropositively-polarised β⁺ hydrogen adatoms are reactive with C₂H₄, but with Pd and Ni films only the electronegatively-polarised β⁻ hydrogen adatoms are reactive. This is a mechanism for C₂H₄ self-hydrogenation.

Interaction of Palladium and Platinum with Sulphur Chloride

A. V. NECHEPURENKO and YA. I. IVASHENTSEV, *Zh. Prikl. Khim. (Leningrad)*, 1979, **52**, (7), 1620-1622

Interaction of S₂Cl₂ with Pd and Pt powders (particle sizes of 0.040-0.053 mm) were studied thermographically at 100-1100°C. The chlorination of Pt and Pd occurred in four Pt and three Pd kinetic phases, controlled by different mechanisms. The interaction of the chloro-agent with Pd and Pt, leads to the formation of both the chlorides and sulphides of Pt or Pd. Sulphides are however converted into chloride on further reaction with S₂Cl₂.

LABORATORY APPARATUS AND TECHNIQUE

Calcia-Doped Ceria Ceramic Tubes for Low Temperature Oxygen Sensors

R. T. DIRSINE, W. O. GENTRY, R. N. BLUMENTHAL and W. HAMMETTER, *Am. Ceram. Soc. Bull.*, 1979, **58**, (8), 778-783

Ce_{0.86}Ca_{0.12}O_{1.88} electrolyte tubes for use as O₂ sensors were manufactured and tested. These tubes were then assembled in cells of the type p_{O₂}, Pt|Ce_{0.88}Ca_{0.12}O_{1.88}|p'_{O₂}, Pt, where p_{O₂} = 1 atm and p'_{O₂} = air (0.21 atm) or CO + CO₂ mixtures. Measurements were made between 400 and 1000°C. When cells with Pt paste electrodes, fired in situ (≈400°C) were used to measure e.m.f. at around 430°C, good agreement between theoretical and experimental observations occurred. In cells with Pt

paste electrodes applied by pre-firing at 1000°C the e.m.f. deviated from the theoretical e.m.f. below 800°C. The observed difference is due to the irreversibility of the Pt electrodes. Overcoating the electrodes with, for example, a porous protective spiral may maintain their lives and reversibilities.

The Melting Point of Palladium and Its Dependence on Oxygen

T. P. JONES and K. G. HALL, *Metrologia*, 1979, **15**, (3), 161-163

The melting point of Pd in Ar was measured in Ar as 1555.0 ± 0.4°C, since it is an important reference temperature widely used for calibrating thermocouples above 1100°C. The effect of adding O₂ to the Ar on the melting point was examined. As the partial pressure of O₂ was increased from 0 to 10 (kPa)¹ the melting point dropped linearly from 1555°C to just over 1551°C. The melting point of 1555 ± 0.4°C is significantly different from the value of 1554°C quoted in the secondary reference temperatures in the IPTS 68. This indicates a need for further determining this temperature via a crucible blackbody and photoelectric pyrometer.

HETEROGENEOUS CATALYSIS

The Effect of Preparation Conditions of a Platinum Hydrogenation Catalyst on Its Activity and on the Dispersity of Platinum Crystallites

J. HANIKA, K. SPORKA, V. RŮŽIČKA and J. BAUER, *Collect. Czech. Chem. Commun.*, 1979, **44**, (9), 2619-2623

A hydrogenation catalyst containing 5% Pt/active C was prepared by saturation with H₂PtCl₆ or PtCl₄ followed by calcination in a stream of N₂ and by the reduction of the catalyst with H₂. The effects of the calcination and reduction temperatures on the dispersity of metallic Pt, on the formation of HCl during calcination and reduction, and on the catalytic activity during hydrogenation of 2-methyl-3-butene-2-ol and nitrobenzene in the liquid phase were studied. The catalytic activity was proportional to the dispersity of Pt.

Catalytic Converters: Current Trends, Based on SAE Paper 790306, Catalyst Systems with an Emphasis on Three-Way Conversion and Novel Concepts

P. ÖSER, *Automot. Eng.*, 1979, **87**, (8), 57-59

A 5:1 Pt/Rh oxidation catalyst system was found to be more suitable than the Pt/Pd oxidation system for open loop usage, for NO_x reduction and HC and CO conversion. With a metal supported catalyst the catalyst volume could be reduced by 55%. Pt/Rh catalysts for open loop systems and three-way catalysts with various Pt/Rh ratios are examined. Novel systems, such as a main supported catalyst with the inside of the exhaust pipe being catalytically coated, have given conversion efficiencies of 62% CO and 70% HC with 1g total noble metal coating.

Catalytic Transformations of Alkenyl- and Alkylidenecyclobutanes over Pt, Pd and Rh

O. V. BRAGIN, E. G. KELKOVSKAYA-SERGEEVA and A. L. LIBERMAN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, (5), 1037-1043

Catalytic transformations of alkenyl- and alkylidenecyclobutanes over Pt/C, Pd/C and Rh/C were carried out in H₂ and He. The reactions were predominantly hydrogenation and hydrogenolysis in H₂, while in He, isomerisation took place in the form of ring expansion and migration of the double bonds. Both the deposited metals and carriers were catalytically active, with the C carrier being active in the expansion of the four-part into five-part rings.

Investigations on Metal Catalysts. XXI. Physico-Chemical Characterisation of Pt-Ru and Pt-Ru/ η -Al₂O₃ Catalysts

S. ENGELS, N. P. KHUE and M. WILDE, *Z. Anorg. Allg. Chem.*, 1979, 452, 27-36

Pt-Ru samples prepared by reduction of a (NH₄)₂[PtCl₆] and [Ru₃O₂(NH₃)₁₄]Cl₆ compound mixture by H₂ were characterised by DTA, X-ray measurements, N₂ adsorption and CO chemisorption. The supported η -Al₂O₃ catalysts were prepared by impregnation with H₂[PtCl₆] and H₂[RuCl₆] or (NH₄)₂[PtCl₆] and "Ru-red". The effect of the composition of the bimetallic crystallites on the dispersion and adsorption behaviour with respect to CO is discussed.

Development of a Catalytic Gas Turbine Combustor

P. FLANAGAN, E. R. NORSTER and R. V. CARRUBBA, *J. Energy*, 1979, 3, (2), 75-81

A Pd catalyst coated on a 5-channel per inch zircon composite monolith was used in thermal combustion in a low-pressure-ratio gas turbine type system. Excellent emissions performance was obtained using gaseous propane fuel. A combustor design concept, applicable to gaseous fuelled gas turbine engines was developed. Straight-through flow and reverse-flow combustors were developed for use in conjunction with this catalyst system and fuel turndown ranges of about 10:1 were achieved with both. Exhaust emissions indices of NO_x(0.61), CO(0.95) and unburned hydrocarbons (<0.1) were achieved for the first generation engine.

Supported Palladium Catalysts for Methanation

M. A. VANNICE and R. L. GARTEN, *Ind. Eng. Chem., Prod. Res. Dev.*, 1979, 18, (3), 186-191

Pd/Al₂O₃ catalysts have specific activities (molecule/site) in the methanation reaction 70 fold greater than those for unsupported Pd and 35 fold greater than Pd/SiO₂ catalyst. Activity maintenance studies indicate that at high conversions and temperatures of 623-673K, these Pd/Al₂O₃ catalysts deactivate rapidly. Pd catalysts are preferred during methanation to Ni catalysts.

Ethylene Carbonylation on Deposited Pd/SiO₂ Catalysts

A. L. LAPIDUS, S. D. PIROZHKOVA, A. R. SHARIPOVA and A. N. DETYUK, *Neftekhimiya*, 1979, 19, (3), 433-437

Contact properties of 1%Pd/SiO₂ and 0.5%Pd/SiO₂ catalysts prepared by saturation of SiO₂ with aqueous solution of H₂PdCl₄ followed by drying in air and by reduction in H₂ were studied during C₂H₄ carbonylation in an autoclave. The 0.5%Pd/SiO₂ catalyst was shown to be highly active and selective during the reaction forming propionic acid, with a C₂H₄ conversion of 95% and 92% for C₂H₅COOH.

"Combined" Hydrogenolysis of Furan Compounds on Rhodium Catalysts

B. B. BLINOV, S. A. FIGENSON, O. C. KORNEVA, A. A. NAZARYAN, M. V. VAGADOV, R. A. KARAKHANOV and K. G. DANELYAN, *Zh. Prikl. Khim. (Leningrad)*, 1979, 52, (9), 2071-2075

"Combined" hydrogenolysis of furan on Rh/C catalysts at 350°C and 1 atm were studied and compared with data obtained theoretically. The reaction yielded methylpropylketone, methylethylketone and acetone in parallel, each of them being of first order. The reaction of combined hydrogenolysis occurred at a planar orientation on the surface of the catalyst.

Behaviour of Ruthenium and Osmium during Carbonylation of Copper-Nickel Sulphidised Alloys

V. I. BADER, A. S. MNUKHIN and A. F. SIDOROV, *Izv. Akad. Nauk SSSR, Met.*, 1979, (5), 54-59

X-ray studies of Ru and Os behaviour in Cu-Ni-S-Ru(Os) alloys containing various amounts of Ru and Os were performed during carbonylation at 200°C and 250 atm of CO. During the treatment, both the Ru and Os entered into the Cu-Ni solid solution. Ru distributed uniformly throughout whereas Os concentrated in the localised area isomorphically replacing Cu. Ru and Os were retained in the solid residue of the carbonylation synthesis when the initial materials also contained Pt or Pd which dissolve completely in the non-carbonyl metallic solid Cu based solutions and so replace Ru or Os.

HOMOGENEOUS CATALYSIS

Molecular and Crystal Structure of Bis(μ -acetato)-bis(norbornadiene)dirhodium(I): A Catalyst for the Isomerization of Quadricyclane to Norbornadiene

A. H. REIS, C. WILLI, S. SIEGEL and B. TANI, *Inorg. Chem.*, 1979, 18, (7), 1859-1863

The isomerisation of quadricyclane to norbornadiene is catalysed by [Rh(NBD)(AcO)]₂, the structure of which was characterised. A rhodocyclobutane intermediate is formed which is consistent with a stepwise mechanism involving insertion of Rh(I) into a cyclopropyl ring. The reverse reaction, the photoisomerisation of norbornadiene to quadricyclane may act as a solar energy storage system.

Alkyrhodium Tetracarbonyl Derivatives as Catalytic Intermediates in Homogeneous Hydroformylation Reactions. An Infrared Spectroscopic Study

R. B. KING, A. D. KING and M. Z. IQBAL, *J. Am. Chem. Soc.*, 1979, **101**, (17), 4893-4896

The Rh-catalysed hydroformylation of C_2H_4 in n-tetradecane solution was monitored by i.r. spectroscopy of the $\nu(CO)$ region. Various Rh(I) carbonyl derivatives generate systems that catalyse the hydroformylation of C_2H_4 at 35°C and 20-100 atm pressure. In each system absorption bands due to an unstable metal carbonyl derivative develop as the hydroformylation proceeds. These bands occur at $\nu(CO)$ frequencies and are attributable to unstable Rh allyl, $C_2H_5Rh(CO)_4$. This is the first time evidence for a $RRh(CO)_4$ derivative has been obtained.

The Activity of Homogeneous and Heterogeneous Rh(I) Complexes in Hydrogenation of Alkenes

Z. KOZAK and M. ČAPKA, *Collect. Czech. Chem. Commun.*, 1979, **44**, (9), 2624-2632

Kinetics of liquid phase hydrogenation of alkenes catalysed by homogeneous Rh(I) complexes prepared in situ from $[RhCl(C_6H_{14})_2]_2$ and (3-triethoxysilyl)propyldiphenylphosphine in toluene and by heterogeneous analogue catalyst on SiO_2 was studied. The reaction was first order in H_2 , alkene and catalyst. The activity of 0.3-0.6% Rh/ SiO_2 was not affected by pore size within the 4-10 mm region. The supported catalysts prepared by the saturation of the support followed by drying were more active and stable than their homogeneous counterparts.

NEW PATENTS

METALS AND ALLOYS

Current Carrying Alloys of Titanium

JOHNSON MATTHEY & CO. LTD. *British Patent* 1,552,427

Ti alloys containing 6-40% Ir, Rh and/or Ru possess improved corrosion resistance compared with Ti metal, particularly when subjected to a.c. current at high densities, such as when used as water heater electrodes. Preferred alloys contain 94% Ti, 6% Ir and 88% Ti, 6% Pt, 6% Ir.

ELECTROCHEMISTRY

Composite Electrode

INTERNATIONAL NICKEL CO. INC.

U.S. Patent 4,157,943

A composite electro-winning electrode has a barrier layer of platinum group metal or Au on the substrate, a RuO_2 -containing non-electrodeposited surface layer and an intermediate layer of electroplated Ru-Ir in a partially oxidised state.

ELECTRICAL AND ELECTRONIC ENGINEERING

TiN as a Diffusion Barrier in the Ti-Pt-Au BEAM-Lead Metal System

W. J. GARCEAU, P. R. FOURNIER and G. K. HERB, *Thin Solid Films*, 1979, **60**, (2), 237-247

The Ti-Pt-Au beam-lead metallisation system has good reliability for connections on integrated circuits. Interdiffusion of the metal films (Ti and Pt) can sometimes result in the formation of unetchable intermetallic compounds that may impair device performance. This can be eliminated by the incorporation of a thin ($\sim 150\text{Å}$) TiN layer between the Ti and Pt films. Electron microprobe and secondary ion mass spectrometry analyses measured the effectiveness of TiN as a diffusion barrier.

Anodic Iridium Oxide Films: A New Electrochromic

J. L. SHAY and G. BENI, *IEEE Trans. Electron Devices*, 1979, **ED-26**, (8), 1138-1143

The preparation and properties of electrochromic anodically grown Ir oxide film (AIROF) are reviewed. A heat process which improves the response time and improves stability of AIROF is discussed. Maximum coloration and speed of response were found to be independent of pH and a transmission device is described whereby the AIROF is grown on a semi-transparent conducting substrate. There are two distinct electrochromic processes with different isotherms which colour AIROFs. Both processes are dominated by internal entropy changes of non-interacting particles.

ELECTRODEPOSITION AND SURFACE COATINGS

Brush Electroplating

WELDEX A.G.

European Appl. 3,680

An improved electrode for brush electroplating is a stylus fabricated for instance from Pt, adapted to hold plating solution, and having its tip surrounded by an absorbent abrasive material made from synthetic fibres, such as a polypropylene/nylon felt bonded with acrylic resin.

Electroless Plating on Non-Conductive Surfaces

HONEYWELL INC.

U.S. Patent 4,154,869

Pinhole-free and crack-free electroless coatings can be obtained on Pd-Sn activated non-conductive surfaces by using a two-stage plating process. The plated surface is removed from the bath when a visible plating has been formed and is reactivated before being returned to the electroless plating bath.