

# ABSTRACTS

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

### PROPERTIES

#### The Reduction of Nitric Oxide with Hydrogen on the Pt(III) Surface

J. L. GLAND and E. B. KOLLIN, *J. Catal.*, 1981, **68**, (2), 349-354

The reduction of NO with H<sub>2</sub> was studied in the pressure range 10<sup>-9</sup> to 10<sup>-8</sup> Torr on the Pt(III) surface from 100-800K. Reaction products were N<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>O. Reduction of NO occurs rapidly above 400K; in excess NO the main product is N<sub>2</sub>. Below 550K, in excess NO, N<sub>2</sub> inhibits the NO reduction. Above 550K, the dissociation of NO limits NH<sub>3</sub> and N<sub>2</sub> formation. In excess H<sub>2</sub>, NH<sub>3</sub> is the main product from 300-500K, above 500K, N<sub>2</sub> formation dominates. The formation of an NH<sub>3</sub>-NO surface complex appears to inhibit NH<sub>3</sub> formation between 300-400K.

#### Graded-Index Pt-Al<sub>2</sub>O<sub>3</sub> Composite Solar Absorbers

H. G. CRAIGHEAD, R. E. HOWARD, J. E. SWEENEY and R. A. BUHRMAN, *Appl. Phys. Lett.*, 1981, **39**, (1), 29-31

The solar absorption properties of thin composite films of co-evaporated Pt and Al<sub>2</sub>O<sub>3</sub>, formed with a graded composition-depth profile, are compared to those of an identical film overcoated with a microscopically textured layer of SiO<sub>x</sub>. The films have refractive indices slowly varying to unity at the front surface. This gives low reflectance film. The solar absorptivity is as high as 0.98.

#### Kinetics of Hydrogen Absorption of Tantalum Coated with Thin Films of Palladium, Iron, Nickel, Copper and Silver

K. NAKAMURA, H. UCHIDA and E. FROMM, *J. Less-Common Met.*, 1981, **80**, (1), P19-P30

The effects of Pd, Ag, Ni, Cu and Fe coatings on the kinetics of H atom absorption of Ta wire were measured at 300-700K. Thin Pd coatings were the most effective and yielded absorption rates near the theoretical value for a diffusion-controlled reaction mechanism. This corresponds to an enhancement factor of  $\geq 10^4$  at room temperature.

#### Analysis of Selected Alloys in the Systems Cr-Pd, Cr-Ru, V-Pd and Ta-Pt

R. M. WATERS-STRAT, *J. Less-Common Met.*, 1981, **80**, (1), P31-P36

Electron microprobe studies were performed on selected and appropriately annealed Cr-Pd, Cr-Ru, V-Pd and Ta-Pt alloys. The data give a basis for the establishment of a more accurate location of phase boundaries which have not been accurately defined in previous studies. (12 Refs.)

#### Structure and Growth of the Interface of Pd on a-Si : H

R. J. NEMANICH, C. C. TSAI and T. W. SIGMON, *Phys. Rev. B*, 1981, **23**, (12), 6828-6831

The structure of the Pd-a-Si : H interface is probed using interference-enhanced Raman scattering. It was found that  $\sim 2$  nm of Pd was initially consumed to form a crystalline silicide at the Pd : a-Si : H interface. Annealing to 300°C caused a spectroscopic change, which is associated with a structural change, and additional annealing at 500°C caused the formation of crystalline Si.

#### Effect of Thorium Addition on Metallurgical and Mechanical Properties of Ir-0.3pct W Alloys

C. T. LIU, H. INOUE and A. C. SCHAFFHAUSER, *Metall. Trans.*, 1981, **12A**, (6), 993-1002

Metallurgical and mechanical properties of Ir-0.3%W alloys were studied as a function of Th concentration in the range 0-1000 ppm by weight. The solubility limit of Th in Ir-0.3%W is  $< 30$  ppm. Above this excess Th reacts with Ir to form second-phase particles. Th additions retard grain growth at high temperatures. Tensile tests at 650°C showed grain-boundary (GB) separation for undoped alloys, and transgranular fracture for alloys with  $< 500$  ppm Th. Intergranular fracture in doped alloys is suppressed by GB separation of Th. For a given grain size, especially in the fine-grain size range, Th doped alloys are much more ductile and GB fracture resistant.

#### Corrosion Resistant Alloys Mo-Ru-X (X = Fe, Co, and Ni)

R. L. MENG, S. Z. HUANG and C. W. CHU, *Appl. Phys. Lett.*, 1981, **38**, (5), 339-341

Some Mo-Ru-X (X = Fe, Co and Ni) were produced with exceptional corrosion resistance and variable magnetic and mechanical strengths both in bulk and thin-film forms.

### CHEMICAL COMPOUNDS

#### Synthesis of Hexahydroxy Palladium (IV) of Some Alkali Metals

N. U. VENSKOVSII, B. N. IVANOV-EMIN and I. V. LIN'KO, *Khim. Khim. Tekhnol.*, 1981, **24**, (5), 531-534

The first synthesis of hexahydroxy Pd compounds M<sub>2</sub>[Pd(OH)<sub>6</sub>] where M = K, Rb is reported. X-ray diffraction crystal studies confirmed proposed coordination formula and amorphism of K salts with hexahydroxy Pd. Thermographic studies of the synthesised salt showed increased stability in the degree of oxidation of Pd(IV) to hydroxy- or oxypalladates.

## Synthesis and X-Ray Crystal and Molecular Structure of the Mixed-Metal Cluster Anion $[\text{Os}_6\text{Au}(\text{CO})_{20}\text{H}_2]^-$

B. F. G. JOHNSON, D. A. KANER, J. LEWIS and P. R. RAITHBY, *J. Chem. Soc., Chem. Commun.*, 1981, (15), 753-755

The unsaturated mixed-metal cluster anion  $[\text{Os}_6\text{Au}(\text{CO})_{20}\text{H}_2]^-$  has been prepared as its  $[\text{N}(\text{PPh}_3)_2]^+$  salt by the reaction of  $[\text{Os}_3\text{Au}(\text{CO})_{10}(\text{PR}_3)\text{H}]$  (R = Ph, Et) with  $[\text{N}(\text{PPh}_3)_2]^+\text{Cl}^-$ . The X-ray crystal structure shows that the Au<sup>I</sup> atom links two  $\text{Os}_3(\text{CO})_{10}\text{H}$  units by co-ordination to two short Os-Os bonds.

## ELECTROCHEMISTRY

### Studies on the Durability of Platinum and Ruthenium Oxide Coated Titanium Anodes in the D-Ribono- $\gamma$ -Lactone Electro-Reduction Process

A. KORCZYŃSKI, A. DONIEC and J. SWIDERSKI, *Corros. Sci.*, 1981, 21, (5), 329-332

Studies of Pt and Ru oxide coated Ti anodes in D-ribono- $\gamma$ -lactone during electroreduction are described. When the anodes were in 10%  $\text{H}_2\text{SO}_4$  contaminated with lactone, the reduction and hydrolysis products and  $\text{Cl}^-$  and  $\text{NH}_4^+$  ions all diffused through a ceramic diaphragm. In 10%  $\text{H}_2\text{SO}_4$  alone or contaminated only with  $\text{NH}_4^+$ , the Pt coated Ti was more durable than Ru oxide coated Ti by over an order of magnitude.

### Permeation of Electrolytic Hydrogen through Palladium. Consideration of the Cathodic Process Mechanism

V. I. CHERNENKO and T. G. YAKUNINA, *Dopov. Akad. Nauk Ukr. RSR, Ser. B, Geol. Geofiz. Khim. Biol. Nauki*, 1981, (6), 80-84

Electrolytic H permeation through a Pd membrane was studied and the rate of formation of cathodic H ions was considered. The velocity of H permeation through the membrane depends on the metal properties and also on the cathodic process kinetics. These include the transport of ions to the reaction zone which is due to molecular diffusion and migration into the diffusion layer.

### Tritium Separation from Light and Heavy Water by Bipolar Electrolysis

M. PETEK, D. W. RAMEY and R. D. TAYLOR, *J. Appl. Electrochem.*, 1981, 11, (4), 477-488

Using multiple bipolar electrolytic separation of H isotopes with Pd-2%Ag electrodes, the mathematical feasibility of this method of tritium separation was shown and experimentally verified. Factors measured for multiple H-D separation were closer to the values measured in single-stage cell measurements. A separation of sufficient magnitude was achieved to show the feasibility for application to the extraction of tritium from large-volume systems at high current density. (29 Refs.)

## Effect of Ruthenium on Anodic Behaviour of Ductile Chromium in Sulphuric Acid

N. D. TOMASHOV, G. P. CHERNOVA and E. N. USTINSKI, *Zashch. Met.*, 1981, 17, (4), 401-407

Studies of corrosion and electrochemical behaviour of 0.1-0.4wt.% Ru-Cr alloys were made in 40%  $\text{H}_2\text{SO}_4$  at 65°C. It is shown that Ru inhibits the active dissolving of the alloys in two ways; by blocking (Ru in solid solution) and by a screening effect (Ru aggregates on the surface of the alloy).

## PHOTOCONVERSION

### Photoassisted Isomerisation of Olefins by Platinum Complexes

P. COURTOT, R. PICHON and J.-Y. SALAÜN, *J. Chem. Soc., Chem. Commun.*, 1981, (11), 542-543

Photoassisted isomerisation of C = C was performed for the first time in the presence of Pt complexes such as *trans*- $[\text{PtCl}_2(\text{tmpy})(\text{C}_2\text{H}_4)]$ , where tmpy = 2,4,6-trimethylpyridine; pent-2-ene, hex-2-ene, and 1,2-dichloroethane can be *cis-trans* interconverted with high efficiency (typically 80 : 20 for *trans* and *cis* hex-2-ene).

### Platinum Hydrosols in the Sensitized Photoreduction of Water

A. J. FRANK and K. L. STEVENSON, *J. Chem. Soc., Chem. Commun.*, 1981, (12), 593-594

Pt hydrosols (22Å diameter) catalyse  $\text{H}_2$  evolution from water with nearly 100% efficiency in the light-induced redox reaction which involves the  $\text{Ru}(2,2'-\text{bipyridine})^{2+}$ -methyl viologen-EDTA model system. The catalytic step is not rate determining.

### Photocatalytic Water Decomposition and Water-Gas Shift Reactions over NaOH-Coated, Platinized $\text{TiO}_2$

S. SATO and J. M. WHITE, *J. Catal.*, 1981, 69, (1), 128-139

The photocatalytic decomposition of gaseous water took place over platinized  $\text{TiO}_2$  coated with NaOH (>7wt.%). The quantum efficiency for  $\text{H}_2$  and  $\text{O}_2$  production reaches 7% (20  $\mu\text{mole H}_2/\text{h}$ ) at the beginning of the reaction but declines with product build-up due to the thermal back reaction over Pt. The back reaction effect can be reduced by increasing the NaOH loading. The photocatalytic activity of platinized  $\text{TiO}_2$  for the water-gas shift reaction increases with increasing NaOH coating.

### Photochemical Hydrogen Production: Development of Efficient Heterogeneous Redox Catalysts

J.-M. LEHN, J.-P. SAUVAGE and R. ZIESSEL, *Nouv. J. Chim.*, 1981, 5, (5/6), 291-295

A number of heterogeneous Pt, Pt compounds and Rh catalysts were prepared and tested for the photoproduction of  $\text{H}_2$  using two different systems. They comprised colloidal metals, polymer supported

metals and metals deposited on solid supports (such as zeolite, and semiconductor powders). A large range of efficiencies was observed, and the catalyst sequences were different for the two systems. Pt- or Rh/semiconducting powders and colloidal species were the most efficient of the materials investigated. (28 Refs.)

### Photoanodic Properties of Thin Film Electrodes Composed of Titanium Dioxide and Ruthenium Dioxide

H. YONEYAMA, H. SASAKI and H. TAMURA, *Denki Kagaku*, 1981, **49**, (4), 222-226

Thin film electrodes made of RuO<sub>2</sub> and TiO<sub>2</sub> were prepared by thermal decomposition of mixed aqueous solutions of RuCl<sub>3</sub> and TiO<sub>3</sub> on Ti substrates at 450°C followed by heat-treatment at 700°C in a stream of Ar. Their photoelectrochemical properties were studied as a function of the Ru content of the film. Maximum photosensitivity was observed at an electrode containing 20mol.%RuO<sub>2</sub>.

### Kinetic Studies of Photoinduced Methyl Viologen Reduction with Ruthenium Complexes and Hydrogen Evolution from Water by Hydrogenase

I. OKURA and N. KIM-THUAN, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, (6), 1411-1415

Highly active photoinduced systems for methyl viologen reduction were developed with the use of Ru complexes with long lifetimes in the photoexcited state. The order of activities was as follows: Ru(dimephen)<sub>3</sub><sup>2+</sup> > Ru(Cl-phen)<sub>3</sub><sup>2+</sup> > Ru(phen)<sub>3</sub><sup>2+</sup> > Ru(bpy)<sub>3</sub><sup>2+</sup>. When hydrogenase was added to the systems containing Ru complex, methyl viologen and reducing agent, H<sub>2</sub> evolution was observed in every system. A higher activity of H<sub>2</sub> evolution was observed for the system with a higher activity for methyl viologen reduction.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Recent Advances in Pt Coating of Microspheres by a Batch Magnetron Sputtering Process

E. J. HSIEH and S. F. MEYER, *J. Vac. Sci. Technol.*, 1981, **18**, (3), 1205-1208

Progress in Pt coating microspheres is outlined. Better yields by batch magnetron sputtering are achieved without a confining screen over the bouncer pan because of the higher sputtering rate and better visibility. There is a linear increase in oxygen content with doping flow rate, in agreement with the observed increasing coating brittleness. Resistivity measurements on very thin flat films indicate the H<sub>2</sub> gas can remove the O in the Pt, and that subsequent O gas will only adsorb on the surface. A direct result of O<sub>2</sub> absorption is an increase in Pt sheet resistance.

### Electroplating of Gold and Rhodium Directly on Molybdenum

D. J. LEVY, C. R. ARNOLD and D. H. MA, *Plat. Surf. Finish.*, 1981, **68**, (5), 104-107

Rhodium was plated directly on TZM Mo alloy (0.5%Ti-0.08Zr-Mo) followed by vacuum heat treatment at 1000°C to vaporise the oxide and achieve diffusion bonding. The plating bath was a commercial low-stress Rh sulphate solution containing 4-6g/l Rh, 50-70g/l H<sub>2</sub>SO<sub>4</sub>, 15-60g/l stress reducer and a specific gravity of 1.04-1.16. The thickness of the Rh plate was determined by gravimetric measurements.

## LABORATORY APPARATUS AND TECHNIQUE

### Hydrogen Sensitive MOS-Structures. Part I: Principles and Applications

I. LUNDSTRÖM, *Sens. Actuators*, 1981, **1**, (4), 403-426

The physical mechanisms of H<sub>2</sub> sensitive structures, such as Pd(or Pt)-SiO<sub>2</sub>-Si and ways of monitoring a dipole layer at a metal-insulator interface in Ar and air, respectively, are examined. Chemical reactions at the catalyst surface, and surface and interfacial adsorptions are considered. The responses of the devices to H<sub>2</sub> in Ar, ethanol, various types of smoke, H<sub>2</sub>S and NH<sub>3</sub> is discussed. Lastly their long-term stability is commented on.

## HETEROGENEOUS CATALYSIS

### Heating of a Testing Room by Use of a Hydrogen-Fueled Catalytic Heater

J. MERCEA, E. GRECU and T. FODOR, *Int. J. Hydrogen Energy*, 1981, **6**, (4), 389-395

Space heating experiments were performed using catalytic (flameless) combustion of H<sub>2</sub> with atmospheric O<sub>2</sub> on Pt and oxide catalyst pads. Heating rates and oxygen depletion and steam production were derived. The results indicate that catalytic heating has significant potential for space heating, regardless of size, and this type of heating can assure a temperature level comparable to any conventional system. Oxygen depletion did not pass a comfort level. The water vapour levels indicate the device is not suitable for heating homes or closed working places, since a continuous or periodical forced air flow is necessary, but it is suitable for greenhouses.

### Catalytic Waste Water Treatment by Electrochemical Catalysts

W. FAUL and B. KASTENINGS, *Galvanotechnik*, 1981, **72**, (8), 808-812

A 0.5-1.0%Pt/C catalyst was used for treating waste electroplating water together with H<sub>2</sub> and O<sub>2</sub> as oxidation and reduction media. The catalyst is graphite with specially treated activated C and the Pt is in the active layer.

## Transformation of Normal Heptane in the Presence of Catalysts with a Large Pore Mordenite Base Exchanged with Silver and Impregnated with Platinum

J.-P. FRANCK, M.E.L. MALKI and R. MONTARNAL, *Rev. Inst. Fr. Pet.*, 1981, **36**, (2), 211-227

The results of transformations under  $H_2$  atmospheres of normal heptane, using a Ag-exchanged Pt-impregnated large-pore mordenite as catalyst, are interpreted by a bifunctional mechanism. However, in taking into consideration the effect of  $H_2$  partial pressure on the isomerisation and cracking rates, a twin-site mechanism must be used to explain the cracking by  $\beta$  cleavage of the carbonium ions. This implies the participation of a proton in the vicinity of the carbonium ion with both sites being linked to the acid support.

## Comparative Study of "Structure Sensitive" Reactions on Pt- $Al_2O_3$ and Ir- $Al_2O_3$ Catalysts

J. BARBIER and P. MARECOT, *Nouv. J. Chim.*, 1981, **5**, (7), 393-396

The hydrogenolysis of ethane (1) and cyclopentane (2), and the exchange (3) or hydrogenation (4) of benzene were performed on Pt/ $Al_2O_3$  and Ir/ $Al_2O_3$  with various metal dispersions. On Pt and Ir the hydrogenolyses of (1) seem to occur by the same mechanism and exhibit the same structure sensitivity. Therefore for (1), geometric factors may be involved in catalytic activity. For reactions (2), (3) and (4) the behaviour of both metals with respect to their dispersions is different and electronic factors are better than geometric ones in describing their discrepancies.

## Immobilized Transition-Metal Carbonyls and Related Catalysts

D. C. BAILEY and S. H. LANGER, *Chem. Rev.*, 1981, (2), 109-143

Amongst carbonyls considered are Ru, Rh, Ir, Pt and bimetallic clusters. Their surface bonding with organic and inorganic supports is reviewed and anchoring metal carbonyls on functionalised inorganic oxides, and synthesising metal carbonyls within the porous structure of the support are considered. (308 Refs.)

## The Sintering of Supported Metal Catalysts. III. The Thermal Stability of Bimetallic Pt-Ir Catalysts Supported on Alumina

A. G. GRAHAM and S. E. WANKE, *J. Catal.*, 1981, **68**, (1), 1-8

The effects of thermal treatment in  $O_2$  (300-600°C) and  $H_2$  (500-800°C) on the metal dispersions of 1% Pt, 1% Ir and 1% Pt-1% Ir catalysts were studied. Treatment in  $O_2$  at 400-600°C increased the dispersion for the Pt catalysts. Small increases in dispersion for the Ir catalysts were observed after  $O_2$  treatment

at 300°C, at higher temperatures the Ir dispersion decreased. Metal segregation occurred in Pt-Ir during  $O_2$  treatment. The largest decreases in dispersion due to  $H_2$  treatment were observed for Pt.

## Some Features of the Hydrocarbon Reactions on Supported Catalysts Prepared by Decomposition of Surface Complexes. II. Reaction of n-Hexane on the (Mo + Pt)/ $SiO_2$ , (W + Pt)/ $SiO_2$ and (Re + Pt)/ $SiO_2$ Catalysts

ZH. LORAN, A. IU. RYDNIIN, B. N. KUZNETSOV, A. N. STARTSEV, A. PENIENERO and IU. I. ERMAKOV, *Kinet. Katal.*, 1981, **22**, (3), 680-683

The effect of modifiers Mo, W and Re on catalytic properties of surface dispersed Pt prepared by decomposition of Pt complex metals fixed on the surface of  $SiO_2$  was studied during conversion of n-hexane. The addition of the modifiers resulted in the increase in rates of all the n-hexane conversion reactions; selectivity of the conversion depending on the modifier. The increase of the temperature resulted in the production of dehydrocyclisation and hydrogenation n-hexane products.

## Catalysts Prepared by Interaction of Organometallic Compounds with a Support Surface. A Study of the State of Supported Components in the (Sn + Pt)/ $SiO_2$ Catalysts

A. P. SHEPELIN, A. P. CHERNYSHEV, V. I. KOVAL'CHUK, P. A. ZHDAN, E. N. IURCHENKO, B. N. KUZNETSOV and IU. I. ERMAKOV, *Kinet. Katal.*, 1981, **22**, (3), 716-721

X-ray diffraction and spectroscopic studies of a reduced (Sn + Pt)/ $SiO_2$  catalyst prepared by interaction of  $Sn(CH_3COO)_2$  and  $Pt(C_4H_9)_2$  with  $SiO_2$  showed that Sn ions fixed on the  $SiO_2$  surface are localisation centres for atoms of deposited Pt. This results in an increase of thermal stability of the catalyst and in changes in electronic properties of the deposited Pt. Electron microscopy studies of Pt particle sizes in (Sn + Pt)/ $SiO_2$  catalysts reduced at 600°C showed them to be, on average, 6-9Å.

## Oxidative Dehydrogenation of Ethylbenzene over Modified Palladium Catalysts

K. FUJIMOTO and T. KUNUGI, *Ind. Eng. Chem., Prod. Res. Dev.*, 1981, **20**, (2), 319-323

Ethylbenzene was oxidatively dehydrogenated selectively to styrene in the vapour phase on supported 1wt.% PdNaBr/ $\gamma$ - $Al_2O_3$  (Pd : Br = 1:1 atom ratio) and Pd-KBr/ $\gamma$ - $Al_2O_3$  catalysts. Bromide ions selectively suppressed the  $CO_2$  formation to produce the styrene selectively at about 99 mol.% at 230-280°C. It was suggested that bromide additives act as modifiers after they are converted to HBr and then react with Pd metal to form surface bromides. The activity and the selectivity of a Pd-KBr/ $\gamma$ - $Al_2O_3$  catalyst was shown to be stable for more than 50 h in the presence of 64 ppm HBr.

## Oxidative Acetoxylation of Propylene in the Presence of Palladium Catalysts. 1. Catalytic Composition. 2. Nature of Active Centres

S. F. POLITANSKII, A. M. SHKITOV, V. V. KHARLAMOV, E. S. SHPIRO, G. V. ANTOSHIN, KH. M. MINACHEV, I. I. MOISEEV and O. M. NEFEDOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, (7), 1479-1484, 1485-1489

Catalytic composition of Pd-AcOK/amorphous aluminosilicate was highly active and selective during oxidative acetoxylation of propylene in the gaseous phase. Spectroscopic studies of the Pd composition of the surface layer showed a formation of active sites in the AcOK with Pd oxidation states of between 0 and +2. The active centres of oxidative acetoxylation contained AcO-Pd-Pd-OAc fragments.

## Decomposition of Copper (II) Formate on Palladium Catalysts

L. ČERVENÝ, A. MARHOUL and V. RŮŽIČKA, *Chem. Prum.*, 1981, 31, (4), 179-182

Activity of Pd catalysts containing 3% Pd on a substrate was characterised by the decomposition rate of Cu(II) formate in an aqueous solution. The distribution of Pd on the cross-section of the grain was studied by electron microscopy both before and after the decomposition; the distribution of Cu was also determined.

## Active Metals from Potassium-Graphite. Palladium-Graphite as Catalyst in the Hydrogenation of Nitro-Compounds, Alkenes, and Alkynes. Palladium-Graphite-Catalysed Vinyllic Substitution Reactions

D. SAVOIA, C. TROMBINI, A. UMANI-RONCHI and G. V. ERARDO, *J. Chem. Soc., Chem. Commun.*, 1981, (11), 540-541, 541-542

Pd/graphite was an effective catalyst for the hydrogenation of aromatic nitro-compounds, alkenes, and alkynes to aniline, alkanes, and (Z)-alkenes, respectively. It is also a convenient catalyst for the arylation or alkenylation of activated C=C with aryl or vinyl iodides.

## Liquid Phase Hydrogenation of the Aromatic Hydrocarbons on Catalyst Ru/Al<sub>2</sub>O<sub>3</sub>

E. L. TSISUN, E. F. LITVIN, B. K. NEFEDOV and K. I. STOIAKINA, *Neftekhimiya*, 1981, 21, (3), 342-345

Studies were made of the mechanism of hydrogenation of alkylbenzene on 0.5-5% Ru/Al<sub>2</sub>O<sub>3</sub> and 2% Pd/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by saturation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by aqueous solutions of Ru(OH)Cl<sub>3</sub> or PdCl<sub>2</sub> followed by drying and reduction in H<sub>2</sub> at 300°C for 3 h. The activity of Ru/Al<sub>2</sub>O<sub>3</sub> catalysts during hydrogenation of monocyclic aromatic hydrocarbons was higher than that of Pd/Al<sub>2</sub>O<sub>3</sub> catalysts. Hydrogenation of xylene on Ru/Al<sub>2</sub>O<sub>3</sub> catalysts yielded predominantly *cis*-isomers.

## The Use of Membrane Catalysts for Extraction of Hydrogen from CO and CO<sub>2</sub> Mixture

IU. M. SEROV, C. G. GUL'ANOVA and V. M. GRIAZNOV, *Khim. Khim. Tekhnol.*, 1981, 24, (3), 321-323

The use of a membrane catalyst made of 6% Ru-Pd alloy coated with a Ru or Ni layer for extraction of H<sub>2</sub> from a CO and CO<sub>2</sub> mixture is suggested. Catalytic activity of these layers in relation to hydrogenation of C oxides to methane allows an increase in H penetration of the membrane catalyst, and the heat formed during hydrogenation of C oxides is used for sustaining the required temperature.

## HOMOGENEOUS CATALYSIS

### The Hydroformylation Reaction: Catalysis by Platinum(II)-Tin(II) Systems

II. C. CLARK and J. A. DAVIES, *J. Organomet. Chem.*, 1981, 213, (2), 503-512

Complexes [Pt(ER<sub>3</sub>)(CO)Cl<sub>2</sub>] (E = P, As; R = aryl, alkyl) are active precursors for the catalytic hydroformylation of olefins in the presence of added Sn(II)Cl<sub>2</sub>. The yield of aldehyde may be maximised and is limited by steric crowding at the metal centre. Terminal aliphatic monoenes are hydroformylated readily with a high n:iso ratio; hindered internal olefins, cyclic and conjugated aromatic olefins are less easily hydroformylated, but with no competing hydrogenation. The catalyst system is active under mild conditions of temperature and pressure.

### Transition-Metal Photocatalysis: Rhodium(I)-Promoter Hydrosilation Reactions

R. A. FALTYNEK, *Inorg. Chem.*, 1981, 20, (5), 1357-1362

Rh(I) complexes, ClRh(PPh<sub>3</sub>)<sub>3</sub> in the presence of O<sub>2</sub> or soluble oxidising agents were found to be active photocatalyst precursors for the hydrosilation reaction. Substrates studied include Si-H, Si-vinyl functionalised siloxanes and simple terminal alkenes. Near-u.v. irradiation enhanced dissociation of catalyst precursors and the intermediate, ClRh(PPh<sub>3</sub>)<sub>2</sub>, is paramount for catalytic success. The positive oxygen dependence and photocatalytic nature of the hydrosilation are unprecedented in Si-H addition catalysis.

### The Direct Conversion of $\alpha$ -Olefins into Vinyl- and Allyl-Silanes Catalysed by Rhodium Complex

A. MILLAN, E. TOWNS and P. M. MATTLIS, *J. Chem. Soc., Chem. Commun.*, 1981, (14), 673-674

An efficient direct conversion of  $\alpha$ -olefins into unsaturated silanes and the reaction conditions are reported. At high  $\alpha$ -olefin:Et<sub>3</sub>SiH ratios and at temperatures  $\leq 40^\circ\text{C}$  [(RhC<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Cl<sub>4</sub>] catalyse the formation of vinyl- and allyl-silanes.

## Ethylene Glycol from Synthesis Gas via Ruthenium Melt Catalysis

J. F. KNIFFTON, *J. Am. Chem. Soc.*, 1981, **103**, (13), 3959-3961

A unique, highly active catalyst system for direct synthesis of ethylene glycol from CO and H<sub>2</sub> (synthesis gas) involving melt catalysis where the Ru source, Ru(IV) oxide or Ru(III) acetylacetonate, is dispersed in a molten quaternary phosphonium or ammonium salt is disclosed. Turnover frequencies may surpass  $7.8 \times 10^{-3}$  at 220°C.

## CHEMICAL TECHNOLOGY

### Experience with Titanium Heat Exchanges in Oil Refineries

K. SUZUKI and Y. NAKAMOTO, *Mater. Perform.*, 1981, **20**, (6), 23-26

A review of Ti and Ti alloys in oil refineries is presented. The Pd thin film (thickness <0.2 μm) coating technique for Ti tube surfaces was developed for tubes in overhead condensers to halt corrosion. Very little corrosion occurred and life expectancy is high.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Interaction of Evaporated Palladium Thin Films with Gallium Arsenide

A. OUSTRY, M. CAUMONT, A. ESCAUT, A. MARTINEZ and B. TOPRASERTPONG, *Thin Solid Films*, 1981, **79**, (3), 251-256

The development of semiconductor devices based on GaAs substrates are dependent on the control of the

GaAs-metal contacts. A number of ohmic contacts were developed using Pd-based alloys. Pd becomes associated with GaAs during annealing to form PdAs<sub>2</sub> alloys at low temperature (T = 300°C) and PdGa alloys at T ≥ 400°C. The compounds are closely connected with the thickness of the coated layer. The elements concerned had undergone interdiffusion prior to the formation of the alloy.

### A Stable Hydrogen-Sensitive Pd Gate Metal-Oxide Semiconductor Capacitor

M. ARMGARTH and C. NYLANDER, *Appl. Phys. Lett.*, 1981, **39**, (1), 91-92

A Pd gate metal-oxide semiconductor device has serious drift problems which can be eliminated by the introduction of a thin Al<sub>2</sub>O<sub>3</sub> layer between the metal and the SiO<sub>2</sub>. This makes it possible to use Pd metal-oxide semiconductor devices as stable and accurate H<sub>2</sub> sensors.

## TEMPERATURE MEASUREMENT

### Interpolation Methods for Platinum Resistance Thermometers between 13.81K and 273.15K

R. C. KEMP, W. R. G. KEMP and L. M. BESLEY, *Metrologia*, 1981, **17**, (2), 43-48

The interpolation process used to determine the values of temperature other than the defining fixed points, measured by a Pt resistance thermometer on IPTS-68 is unsatisfactory. This paper summarises previous attempts to overcome the problems, discusses their advantages and disadvantages and proposes improved schemes.

## NEW PATENTS

### METALS AND ALLOYS

#### Thorium-Doped Iridium Alloy for Radioisotope Heat Sources

U.S. DEPARTMENT OF ENERGY U.S. Patent 4,253,872

The impact resistance of Ir and Ir-W alloys containing 0.2-2%W used to encapsulate radioisotope fuels in both terrestrial and space applications, is enhanced by the addition of 100-500 ppm of Th. The Th addition assists grain-growth resistance during long term exposure to high temperatures.

#### Y-Containing Platinum Group Metal-Doped Superalloys

JOHNSON MATTHEY & CO. LTD.

East German Patent 146,305

Superalloys are claimed containing 5-25% Cr, 2-7% Al, 0.5-5% Ti, 0.01-3% Y and/or Sc, 3-15% platinum group metal(s), remainder Ni. These Ni-based alloys are suitable for glass fibre production.

### ELECTROCHEMISTRY

#### Metal-Hydrogen Electric Cells

UNITED KINGDOM ATOMIC ENERGY AUTHORITY

British Patent 1,589,765

In a Ni-H<sub>2</sub> or Ag-H<sub>2</sub> battery a carrier layer between the positive and negative electrodes is vacuum impregnated with an alkaline electrolyte and polyvinyl alcohol to prevent the electrolyte being drawn into the electrode layer by capillary action. Pt-coated negative electrodes are used in the cell.

#### Method of Raising Steam for Desalination

H. P. A. NELSON

British Appl. 2,066,293 A

Steam is raised by decomposing distilled H<sub>2</sub>O in an electrolyser having Pt, Ag or base metal plated electrodes, recombining H<sub>2</sub> and O<sub>2</sub> in a burner to form superheated steam, which is then converted to a greater tonnage by mixing in a desuperheater with further distilled water.