

# ABSTRACTS

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

## PROPERTIES

### Adsorption and Dehydrogenation of Alcohols and Ethers on Platinum(III)

K. D. RENDULIC and B. A. SEXTON, *J. Catal.*, 1982, **78**, (1), 126-135

The adsorption of 11 alcohols ( $C_1-C_4$ ) and ethers ( $C_1-C_2$ ) has been studied on Pt(III) by temperature programmed reaction spectroscopy. Each molecule adsorbed sequentially in two distinct states at 100K: a monolayer phase and a multilayer phase. Temperature programming the layers from 100 to 800K desorbed >90% of the parent molecule intact. The remaining monolayer fraction dehydrogenated to form adsorbed CO, H and  $CH_x$ .

### Decomposition of $NO_2$ to NO and O on Pt(III)

D. DAHLGREN and J. C. HEMMINGER, *Surf. Sci.*, 1982, **123**, (2/3), L739-L742

The adsorption and subsequent chemistry of  $NO_2$  on Pt(III) has been studied. At  $\sim 120K$   $NO_2$  adsorbs molecularly on the Pt surface. The decomposition of  $NO_2$  to NO and O becomes appreciable at temperatures >240K. The decomposition of  $NO_2$  on Pt(III) provides an efficient source of adsorbed O on this surface. The coverage of adsorbed O from this source can be significantly larger than the saturation coverage obtained from adsorption of  $O_2$ .

### Infrared Absorption of Thin Metal Films: Pt on Si

G. D. MAHAN and D. T. F. MARPLE, *Appl. Phys. Lett.*, 1983, **42**, (3), 219-221

The absorption of 3.39 $\mu m$  radiation for Pt films of thickness 0-250Å on Si has been measured. When the radiation approaches from the Si side the maximum absorbance occurs for a film of thickness 80Å. The peak absorbance at this thickness is  $0.5 \pm 0.1$ . Schottky i.r. photodetectors are concluded to be more efficient when the metal film is very thin.

### Surface Tension and Density of Alloys of Platinum with Iridium

T. A. APOLLOVA, E. L. DYBININ, M. M. MITIKO, A. I. CHELODAEV and L. L. BEZUKLADNIKOVA, *Izv. Akad. Nauk SSSR, Met.*, 1982, (6), 55-57

The density and surface tension of Pt-0-50at.%Ir alloys were measured from the alloying temperature to 2200°C. Extrapolation of the isomers of surface tension and density of the alloys from pure Pt to pure Ir at temperatures higher than the alloying temperature for pure Ir (2450°C) gives the temperature dependence of the density and surface tension of Ir.

### Thin Palladium Films on Silicon and Titanium

L. A. HARRIS, *J. Electrochem. Soc.*, 1982, **129**, (12), 2689-2694

Films on Pd from 20 to 160Å thick were deposited on sputter-etched Si and on Ti films on Si and then tested electrochemically in 0.5M  $H_2SO_4$ . The characteristic Pd metal behaviour was lost with prolonged storage or with extended electrochemical cycling. The thinner films had oxidation and reduction peaks in the voltammograms similar to those of Pt metal.  $H_2$  sorption measured from the voltammograms indicated a definite diffusion component which limits  $H_2$  sorption for Pd films >~80Å.

### Irradiation Damage in Proton Irradiated Palladium-Iron Solid Solutions

K. JANGHORBAN and A. J. ARDELL, *J. Nucl. Mater.*, 1983, **114**, (1), 66-74

TEM was used to investigate irradiation damage especially irradiation induced precipitation(IIP) by 400keV protons, over the temperature range 110 to 750°C, in Pd-Fe alloys containing 2, 8, 12 and 18at.%Fe. The irradiation microstructure was dislocation loops over temperatures 110 to 550°C, and voids up to 650°C. IIP of  $Pd_3Fe$  was observed only in Pd-18at.%Fe between 110 and 500°C. Absence of IIP in the more dilute alloys is attributed to the fast back diffusion of Fe atoms due to the high mobility of vacancies.

### Isothermal Heat-Treatment and Phase Transformation of Fe-Pd Permanent Magnet Alloys

K. WATANABE, *J. Jpn. Inst. Met.*, 1982, **46**, (9), 925-928

Fe-Pd alloys containing 20-45 at.%Pd were heat treated from 0-900°C to find the phase transformations and the transformation process. The alloys showed a high coercive force after prolonged heat treatment at relatively low temperatures.

### Diffusivity and Solubility of Hydrogen in Pd-Ag and Pd-Au Alloys

Y. SAKAMOTO, S. HIRATA and H. NISHIKAWA, *J. Less-Common Met.*, 1982, **88**, (2), 387-395

The temperature dependences of the diffusion coefficient and the solubility of  $H_2$  in Pd-Ag and Pd-Au alloys containing 0-50 at. % Ag and Au, respectively, were investigated by the electrochemical method. The composition dependence of the diffusion coefficients of  $H_2$  in both Pd-Ag and Pd-Au shows approximately opposite behaviour to the solubility of  $H_2$  and thus the  $H_2$  permeability is almost independent of composition.

## A Study of the Properties and NMR Spectra of Amorphous and Crystalline Zr-Pd Hydrides

R. C. BOWMAN, M. J. ROSKER and W. L. JOHNSON, *J. Non-Cryst. Solids*, 1982, **53**, (1, 2), 105-122

A study of the hydrides of  $Zr_{65}Pd_{35}$  and  $Zr_{67}Pd_{33}$  metallic glasses is presented. The alloys absorb  $H_2$  at temperatures ranging from 150 to 225°C, to a final H concentration of  $Zr_{67}Pd_{33}H_{.95}$ . Various measurements were taken and NMR studies of amorphous  $Zr_{67}Pd_{33}H_{.95}$  and single-phase crystalline hydrides  $Zr_2PdH_{1.94}$  and  $Zr_2PdH_{2.90}$  are reported. The amorphous hydrides exhibit enhanced H mobility compared to the corresponding crystalline hydrides. Measurements suggest that the electronic density of states at  $E_F$  is significantly lower in the amorphous hydride than in the crystalline hydride.

## Thermodynamics of Pd-Cu-H Solid Solutions

M. YOSHIHARA and R. B. McLELLAN, *Acta Metall.*, 1983, **31**, (1), 61-68

Solubility isobars at temperatures in the range 625-1250K were measured for Pd-Cu-H solid solutions containing 0-20 at.%Cu. The H concentration was always  $<10^{-4}$ at.%. The variation with Cu concentration of the partial molar thermodynamic functions of the H atoms exhibited singularities not observed in other Pd-noble metal-H systems. The observed behaviour is explained, and effects related to changes in the specific volume of the solution with Cu concentration have been calculated from elastic data measured in the same temperature range and composition.

## Phase Equilibrium and Corrosion Properties of Pd-Y-Cu Alloy Systems

A. MUSHAGI, M. V. RAEVSKAIA, T. P. LOBODA and O. I. BODAK, *Izv. Akad. Nauk SSSR, Met.*, 1983, (1), 200-203

Physico-chemical studies were made of ternary Pd-Y-Cu alloys at 600°C. Two new ternary intermediate phases at constant Y content of 25at.% were discovered. Studies of corrosion stability of some binary and ternary Cu based alloys in 10%  $HNO_3$  were performed.

## Cobalt, Rhodium and Iridium. Annual Survey Covering the Year 1981

J. T. MAGUE, *J. Organomet. Chem.*, 1983, **242**, 241-419

Published literature from many sources, including dissertations, covering the year 1981 is reviewed. Topics examined include Rh, Ir and Co metals-C  $\sigma$ -bonded complexes, metal carbene complexes, metal isocyanide complexes, metal carbonyl complexes and related compounds, metal nitrosyl and arylidiazole compounds, metal alkene compounds, metal alkyne compounds, metal  $\pi$ -allyl compounds, metal carbocyclic compounds and metal carbaborane compounds. (705 Refs.)

## Thorium Segregation to Grain Boundaries in Ir+0.3%W Alloys Containing 5-1000 ppm Thorium

C. L. WHITE, L. HEATHERLY and R. A. PADGETT, *Acta Metall.*, 1983, **31**, (1), 111-119

Segregation of Th to grain boundaries in Ir+0.3%W alloys containing 5-1000 ppm Th was observed by AES. Alloys with 5 ppm Th had grain boundary Th:Ir atomic ratios of 0.1 after a 1h, 1500°C vacuum anneal. The Th enriched region was only a few atomic layers thick. No additional increase in grain level Th levels was found as the overall Th level increased to 1000 ppm. This result indicates a solubility limit of Th in Ir+0.3%W of  $\leq 5$  ppm; and that significant improvements in high temperature impact ductility of Ir+0.3%W should be possible with Th additions of 5 ppm.

## Antiferromagnetic Ruthenium(III)

R. L. CARLIN, R. BURRIEL, K. R. SEDDON and R. I. CRISP, *Inorg. Chem.*, 1982, **21**, (12), 4337-4338

The first example of antiferromagnetism in a discrete Ru(III) co-ordination compound chloropentammineRu(III) chloride  $[Ru(NH_3)_5Cl]Cl_2$  is reported.

## Growth and Characterization of RuO<sub>2</sub> Single Crystals

*Mater. Res. Bull.*, 1982, **17**, (10), 1305-1312

Using the vapour transport technique in a flowing  $O_2$  system, the largest single crystal  $RuO_2$  ever reported, 10mm  $\times$  5mm  $\times$  5mm, has been grown. Starting materials, optimum growth conditions, morphology, stoichiometry and resistivity are reported.

## CHEMICAL COMPOUNDS

### Isolation of $\pi$ -Olefin Platinum(II) Complexes Formed in the Reaction of Saturated Hydrocarbons with $H_2PtCl_6$ in $CF_3COOH-H_2O$ Solution

G. V. NIZOVA, T. V. Z. KREVROR, A. N. KITAIGORODSKY and G. B. SHUL'PIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (12), 2805-2808

Heating of n-hexane and  $H_2PtCl_6$  in  $CF_3COOH-H_2O$  solution formed  $\pi$ -hexene Pt(II) complexes which after pyridine treatment were brought out on silica gel by chromatography as  $[(C_6H_{12})PtCl_2(C_3H_7N)]$ . Interaction of hexene-1, hexanol-1 and n-hexylacetate with  $H_2PtCl_6$  and  $CH_3COOH$  produced the same  $\pi$  complex of Pt(II) with hexene.

### Aspects of Ruthenium and Osmium Clusters Chemistry

B. F. G. JOHNSON and J. LEWIS, *Philos. Trans. A*, 1982, **308**, (1501), 5-15

A survey of synthesis, structure and bonding of a series of Ru and Os cluster carbonyl compounds, containing 3 to 10 metal atoms is presented. This series includes neutral, anionic hydride and carbido clusters all derived from  $[M_3(CO)_{12}]$ .

## ELECTROCHEMISTRY

### Corrosion and Electrochemical Properties of Plastic Chromium Doped with Platinum and Palladium

N. D. TOMASHOV, V. I. TREFILOV, G. P. CHERNOVA, A. N. RAKITSKI, N. E. PODRIADCHENKO and E. N. USTINSKI, *Zashch. Met.*, 1983, **19**, (1), 109-112

Studies of corrosion and electrochemical behaviour of Cr doped with cathodic additions of Pt and Pd were made in 50% H<sub>2</sub>SO<sub>4</sub>. The results showed that Cr alloys containing Pt and Pd were easily self-passivating even in concentrated H<sub>2</sub>SO<sub>4</sub> at higher temperatures. Adding into the solution a small amount of nitrate ions sharply increased the stability of the passive behaviour and the corrosion stability of the alloys in extremely aggressive solutions.

### Electrochemical Behaviour of the Hydrogen-Platinum-Crystallised Phosphate Uranyl Acid (HUP) System

P. DE LAMBERTERRE, M. FORESTIER and J. GUITTON, *Surf. Technol.*, 1982, **17**, (4), 357-367

The electrochemical behaviour of electrode H<sub>2</sub>/Pt/HUO<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O (HUP) was studied at room temperature. HUP is a fast proton conductor. The cathodic reaction was rapid and stable; the anodic reaction is also rapid, if it follows a cathodic treatment, otherwise a limiting anodic current is observed. It was concluded that in the H<sub>2</sub>/Pt/HUP/Pt/H<sub>2</sub> cell water is produced at the cathodic interface and is consumed slowly at the anodic interface.

### Comparative Study of LaNi<sub>5</sub>-Type Alloy Electrodes with and without Pd-Plated Layer by Means of Cyclic Voltammetry

T. KITAMURA, C. IWAKURA and H. TAMURA, *Electrochim. Acta*, 1982, **27**, (12), 1729-1731

Cyclic voltammetry was applied to the characterisation of LaNi<sub>5</sub>-type alloy electrodes with and without a Pd-plated layer, to obtain some mechanistic information of the oxidation of absorbed H<sub>2</sub>. As a result, this technique is found to be available not only for examining such alloy electrodes electrochemically but also estimating the equilibrium pressure of H<sub>2</sub> in alloys from a chemical point of view.

### Study of the Adsorption and Electrochemical Properties of Thin Palladium Films on Nickel

A. E. RIVERA GARSIAS, A. M. SKUNDIN, V. S. KONDRASHEVA and M. M. GRIAZNOV, *Elektrokhimiya*, 1982, **18**, (12), 1678-1680

Studies of the properties of thin Pd films on Ni were made at maximum desorption of O<sub>2</sub> at 0.74-0.75V in 1M H<sub>2</sub>SO<sub>4</sub> and 0.71-0.72V in 0.1M NaOH. Anodic polarisation curves on massive Pd and on Pd films on Ni in 1M CH<sub>3</sub>OH + 0.1M NaOH reached 25%. The results showed that Ni samples even with a very thin Pd layer obtained in 15s, behaved like pure Pd.

### Investigations on the Adsorption and Electrocatalytic Oxidation of Carbon Monoxide on Gold and Palladium Alloys

K. GOSSNER and E. MIZERA, *J. Electroanal. Chem. Interfacial Electrochem.*, 1982, **140**, (1), 35-45

A bifunctional mechanism of electrocatalysis was found for the CO oxidation at Au + Pd alloys. The synergetic effect worked best for the 20% Au alloys. The different behaviour of Au + Pd and Ag + Pd was assigned to the formation of CO induced ensembles of Pd-atoms in Au + Pd alloys with high Au content, due to a high mobility of Pd atoms at the surface.

## PHOTOCONVERSION

### Electrochemical and Surface Characteristics of the Photocatalytic Platinum Deposits on TiO<sub>2</sub>

M. KOUDELKA, J. SANCHEZ and J. AUGUSTYNSKI, *J. Phys. Chem.*, 1982, **86**, (22), 4277-4280

Polycrystalline TiO<sub>2</sub> partially or completely covered with a Pt deposit formed by two different modifications of a photocatalytic method were examined by cyclic voltammetry and XPS. Strong irreversible adsorption of Pt(IV) species occurred during the initial photocatalytic Pt deposition from a solution containing hexachloroplatinate and acetate ions. A steady-state Pt coverage occurs after several hours and is not significantly affected by illuminating the TiO<sub>2</sub> surface. Intermediates or products from acetate decarboxylation adsorbed on the TiO<sub>2</sub> surface may block Pt photodeposition.

### Hydrogen-Evolving Semiconductor Photocathodes. Nature of the Junction and Function of the Platinum Group Metal Catalyst

A. HELLER, E. AHARON-SHALOM, W. A. BONNER and B. MILLER, *J. Am. Chem. Soc.*, 1982, **104**, (25), 6942-6948

Pt, Rh, Ru incorporation in the surface of p-type semiconductor p-InP photocathodes to catalyse H<sub>2</sub> evolution gives efficient solar to chemical conversion.

### Fluorescence of Tris (2,2'-Bipyridyl)Ruthenium(II) in Sodium Dodecyl Sulfate Solutions below the Critical Micelle Concentration

J. H. BAXENDALE and M. A. J. RODGERS, *J. Phys. Chem.*, 1982, **86**, (25), 4906-4909

Ru(bpy)<sub>3</sub><sup>2+</sup> in solutions of Na dodecyl sulphate (SDS) below the critical micelle concentration is present entirely in the form of Ru(bpy)<sub>3</sub><sup>2+</sup>-SDS clusters which behave as micelles in that they incorporate aromatic molecules which act as quenchers for emission from Ru(bpy)<sub>3</sub><sup>2+</sup>. The cluster concentration was proportional to the Ru(bpy)<sub>3</sub><sup>2+</sup> concentration, and decreased as the SDS concentration increased. The Ru(bpy)<sub>3</sub><sup>2+</sup> in these clusters was found to be two phased at high exciting light intensities.

### Oxygen Evolution Improvement at a Cr-Doped SrTiO<sub>3</sub> Photoanode by a Ru-Oxide Coating

P. SALVADOR, V. M. FERNANDEZ and C. GUTIERREZ, *Solar Energy Mater.*, 1982, 7, (3), 323-329

The performance for water photo-oxidation of a Cr-doped SrTiO<sub>3</sub> photoanode covered with a Ru oxide film was studied. The Ru oxide films were quite good electrocatalysts for O<sub>2</sub> evolution and can facilitate the photoevolution of O<sub>2</sub> in those semiconductors with a valency band only slightly positive of the O<sub>2</sub>/H<sub>2</sub>O level. Another possible application is corrosion prevention in chalcogenide semiconductors.

### Simultaneous Evolution of Hydrogen and Oxygen by Water Photolysis with Prussian Blue and Tris (2,2'-Bipyridyl)-Ruthenium(II) Complex

M. KANEKO, N. TAKABAYASHI and A. YAMADA, *Chem. Lett.*, 1982, (10), 1647-1650

Simultaneous evolution of H<sub>2</sub> and O<sub>2</sub> was achieved by visible light irradiation of H<sub>2</sub>O containing prussian blue and tris (2,2'-bipyridyl)Ru(II) complex. The gases evolved were analysed by gas chromatography and mass spectroscopy.

### Photooxidation of Water in Colloidal Clay Suspensions and in Aqueous Solutions Using Ru(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> as Catalyst

H. NIJS, M. I. CRUZ, J. J. FRIPIAT and H. VAN DAMME, *Nouv. J. Chim.*, 1982, 6, (11), 551-557

The mechanism of catalytic activity of Ru(bpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> in the oxidation of H<sub>2</sub>O in homogeneous medium and in heterogeneous clay suspensions was investigated by comparing the *cis* and *trans* behaviour in various oxidations. O<sub>2</sub> is shown to be evolved by a true tetra-electronic oxidation process. The catalytically active isomer is the *cis* isomer. Several possible catalytic cycles are discussed. The system has high efficiency down to very acidic conditions (pH ~ 0), but is unstable.

## HETEROGENEOUS CATALYSIS

### Effect of Rhenium Addition to Pt-Al<sub>2</sub>O<sub>3</sub> Catalysts on Dehydrogenation of High Molecular Weight n-Paraffins

E. A. TIMOFEEVA, A. P. TIUPAEV and G. V. ISAGULIANTS, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (12), 2654-2658

Studies of the effect of Re on the selectivity and activity of 0.5%Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were made during dehydrogenation of high molecular weight n-paraffins in the presence of H<sub>2</sub>. Catalysts modified with Re showed higher catalytic activity but no changes in the selectivity occurred. The addition of 0.5-1%Li into 0.5%Pt-Re/γ-Al<sub>2</sub>O<sub>3</sub> catalysts increased the selectivity of n-mono-olefins, and no decrease in dehydrogenation activity occurred as it did in Pt/Al<sub>2</sub>O<sub>3</sub> catalysts without Re.

### New Metallic Catalysis Obtained by Supporting Platinum on AlPO<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> and AlPO<sub>4</sub>-SiO<sub>2</sub> Systems

M. A. ARAMENDIA, V. BORAU, C. JIMENEZ and J. M. MARINAS, *Acta. Chim. Acad. Sci. Hung.*, 1982, 110, (4), 97-101

The synthesis and catalytic performance of metallic systems obtained by supporting Pt on AlPO<sub>4</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and AlPO<sub>4</sub>/SiO<sub>2</sub> at low metallic loading is reported. Their performance in the reduction of alkenes at low H<sub>2</sub> pressures of 1-5bar is reported.

### Effect of the Nature of Supports on the Platinum State in Platinum Catalysts

L. IA. MOSTOVAIA, N. S. KOZLOV, A. F. YANCHUK and L. I. TITOVA, *Dokl. Akad. Nauk BSSR*, 1982, 26, (11), 1014-1016

Spectroscopic studies were made of 0.5wt.% Pt catalysts supported on γ-Al<sub>2</sub>O<sub>3</sub>, MgO and SiO<sub>2</sub> prepared by saturation of the supports by aqueous solutions of (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub>. Pt was found to be uniformly dispersed on the γ-Al<sub>2</sub>O<sub>3</sub> support whereas on the MgO and SiO<sub>2</sub> supports an agglomeration of metal particles was observed.

### The Role of Catalyst Presulfurization in Some Reactions of Catalytic Reforming and Hydrogenolysis

C. R. APESTEGUIA and J. BARBIER, *J. Catal.*, 1982, 78, (2), 352-359

Three reforming catalysts, Pt/Al<sub>2</sub>O<sub>3</sub>, Pt-Ir/Al<sub>2</sub>O<sub>3</sub> and Pt-Re/Al<sub>2</sub>O<sub>3</sub> were sulphurised by H<sub>2</sub>S. The S levels for each catalyst, localised on the metal, give atomic ratios S:Me near 0.5. For the same S coverage Pt-Re catalysts are more deactivated than Pt or Pt-Ir catalysts; but addition of small quantities of Ir to Pt increases S resistance.

### Cutbacks in Throughput May Encourage Revamps in Cat-Reformer Operations

P. J. NAT, *Oil Gas J.*, 1982, 80, (49), 136-138, 143

Changes which have brought about the reduction of operating pressures in reformers are discussed. These include Pt-Re catalysts with high Re content and enhanced stability; improved pretreatments and increasing the density of the catalyst bed. Figures for cycle life, throughput, fuel prices, etc., from a 1 year cycle are presented and evaluated.

### The Oscillatory Oxidation of Carbon Monoxide over Pt, Pd and Ir Catalysts: A Kinetic Model

J. C. TURNER, Ph.D. Thesis, University of California, San Diego, 1982, *Diss. Abstr. Int. B.*, 1982, 43, (3), 741

Oscillations in the rate of CO oxidation were studied over Pt, Pd and Ir using a flow reactor. The oscillations were found to occur between two branches of a Langmuir-Hinshelwood reaction. A time dependent model is proposed for the oscillations. Rates of oxide formation and CO reduction were also measured.

### Liquid Phase Hydrogenation of Furfural in the Presence of Palladium Catalyst

V. F. PECHENKINA, M. S. ERZHANOVA and N. A. ZIBROVA, *Khim. Khim. Tekhnol.*, 1982, **25**, (10), 1209–1212

Studies were made of liquid phase hydrogenation of furfural in the presence of PdCl<sub>2</sub> catalyst and Pd supported catalysts on Al<sub>2</sub>O<sub>3</sub>, C,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. The rate of hydrogenation was 5–7 times higher on supported catalysts; the most active were Pd catalysts supported on Al<sub>2</sub>O<sub>3</sub> and C.

### Hydrogenation of Cyclopentadiene to Cyclopentene on Alumina-Palladium-Sulphide Catalyst

S. G. GAGARIN, S. S. MAKAR'EV and A. A. KRICHKO, *Neftekhimiya*, 1982, **22**, (6), 735–742

Feasibility studies were made of the selective hydrogenation of cyclopentadiene to cyclopentene over 0.2% PdS/Al<sub>2</sub>O<sub>3</sub> catalysts at a pressure of 0.5MPa and temperature of 300–310K. Process conditions allowed production of cyclopentene to 99.99% purity.

### Reactivity of CO with a Rh/TiO<sub>2</sub> Catalyst

J. C. CONESA, M. T. SAINZ, J. SORIA, G. MUNUERA, V. RIVES-ARNAU and A. MUÑOZ, *J. Mol. Catal.*, 1982, **17**, (2–3), 231–240

The reactivity of CO with a RhCl<sub>3</sub>/TiO<sub>2</sub> catalyst was studied using ESR and i.r. Different results were found depending on the manner of contacting the catalyst with the gas. CO was adsorbed at low pressure and 300K, and heating at 373K caused CO dissociation forming C which reacted with H<sub>2</sub> to give alcohols. On carrying out the adsorption of CO at 77K and higher pressure, and subsequently heating the sample at 373K, a reversible reduction was observed on cooling to 77K.

### Hydrogenation of Coal-Derived Liquids in the Presence of Rhodium Complexes

I. W. RAJCA, V. V. ABALAYEVA and A. F. BOROWSKI, *Fuel*, 1982, **61**, (12), 1292–1294

Hydrogenation of the 473–573K distillate derived from the product of catalytic hydrogenation of coal in the presence of H<sub>2</sub> donor solvent and ethyl alcohol, and dimethyl-formamide extracts of the tar from low temperature coal carbonisation were investigated in the presence of Rh complexes. The Rh complexes in homogeneous and in immobilised forms are catalytically active for hydrogenation of these coal-derived liquids.

### Kinetics of the Fischer-Tropsch Synthesis

R. S. DIXIT and L. L. TAVLARIDES, *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 commercial 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, 0.6–10MPa and a weight hourly space velocity of 0.1–0.5/h.

### A Composite Zeolite Catalyst for Olefin Synthesis Prepared by a Novel Metal-Loading Method

T. INVI, G. TAKEUCHI and Y. TAKEGAMI, *Appl. Catal.*, 1982, **4**, (3), 211–221

Ru- and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts had considerably delayed deactivation due to coke formation and had longer catalyst lifespans compared with the lifespans of conventionally prepared catalysts. The catalysts were prepared by a new metal loading method—the crystallisation nuclei method. Metal-loaded Al<sub>2</sub>O<sub>3</sub> powder was suspended in an aqueous solution containing Na aluminate before the preparation of gel materials for crystallisation to zeolite. The particles acted as nuclei for zeolite growth and were highly dispersed on the zeolite crystals. The catalysts were used for selective olefin synthesis from methanol.

### CO-H<sub>2</sub> Reactions in Liquid Phase in Presence of Metals of Group 8

A. KLENNEMANN, G. JENNER, E. BAGHERZADAH and A. DELUZARCHE, *Ind. Eng. Chem., Prod. Res. Dev.*, 1982, **21**, (3), 418–424

The effect of Ru, Rh, Co, etc., catalysts in Group VIII was studied during synthesis of hydrocarbons and alcohols through hydrocondensation of CO. Rh, Ru and Co complexes were most active. The use of very high pressures of 3000bar leads to the successful synthesis of saturated long-chain alcohols C<sub>1</sub> to C<sub>8</sub> with Ru according to a Schulz-Flory distribution. The effects of temperature, CO:H<sub>2</sub> ratio, solvent, pH and additives were also studied.

### Methane Oxidative Chlorination Catalysed by Ruthenium and Platinum Compounds Supported on Al<sub>2</sub>O<sub>3</sub>

V. P. TREPIAKOV and A. N. OSETSKII, *Kinet. Katal.*, 1982, **23**, (5), 1126–1129

Studies of the catalytic activity of K<sub>2</sub>Ru<sub>2</sub>OCl<sub>10</sub> and K<sub>2</sub>PtCl<sub>4</sub> complexes deposited on Al<sub>2</sub>O<sub>3</sub> made during oxidative chlorination of CH<sub>4</sub> showed that under 350°C both catalysts were more active than CuCl<sub>2</sub> based catalysts. Mechanistic behaviours of Pt and Ru were different. Reaction in the presence of Pt included activation of alkane by formation of intermediate Pt-alkyl compounds.

## HOMOGENEOUS CATALYSIS

### Rh<sub>2</sub>(OAc)<sub>4</sub>-PPh<sub>3</sub> as a Catalyst for the Liquid-Phase Dehydrogenation of 2-Propanol

S. SHINODA, T. KOJIMA and Y. SAITO, *J. Mol. Catal.*, 1983, **18**, (1), 99–104

The most active homogeneous catalyst hitherto known for the selective dehydrogenation of 2-propanol was found to form Rh<sub>2</sub>(OAc)<sub>4</sub> by adding PPh<sub>3</sub> in situ. Drastic changes in catalytic properties occurred by replacing Rh<sub>2</sub>(OAc)<sub>4</sub> with Rh<sub>2</sub>(OCOCF<sub>3</sub>)<sub>4</sub> or PPh<sub>3</sub> with P(OPh)<sub>3</sub> which indicate prospects of tailor-making the catalyst.

## Ethylene Dimerisation in the Presence of Rhodium Complex with Tin Chloride Ligands

V. M. IGHATOV, N. V. BORUNOVA, C.-I. DZEN, A. F. LUNIN and L. KH. FREIDLIN, *Neftekhimiya*, 1982, **22**, (6), 749-753

Studies of the catalytic properties of Rh complexes with  $\text{SnCl}_3$ -ligands,  $[\text{Rh}_2\text{Cl}_2(\text{SnCl}_3)_4]^{4+}$ , were made during ethylene dimerisation. The catalyst was more active and stable than  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ . The most active complex had a ratio Sn:Rh=2 and concentration of HCl > 0.5 mole/l. Ethylene dimerisation reaction was first order for the catalyst and ethylene, and was highly selective, forming an equilibrium mixture of butene: butene-1(3%) and butene-2(97%).

## FUEL CELLS

### Oxidation of $\text{H}_2$ at Gas Diffusion Electrodes in $\text{H}_2\text{SO}_4$ and HBr

G. G. BARNA, S. N. FRANK and T. H. TEHERANI, *J. Electrochem. Soc.*, 1982, **129**, (11), 2464-2468

The oxidation of  $\text{H}_2$  at a Pt-black catalysed gas diffusion fuel cell electrode was found to be diffusion limited in  $\text{H}_2\text{SO}_4$ , but kinetically controlled in 48% HBr. The method to activate the anodes completely wets all the Pt in the anode. All of this wetted Pt then participates in the oxidation of  $\text{H}_2$ . This proves that the anodes are flooded and are operating at the theoretical current limit. Further improvements will be achieved through using Pt/C where the available surface area of Pt is maximised.

## NEW PATENTS

### METALS AND ALLOYS

#### High Chromium Superalloy

JOHNSON MATTHEY P.L.C. *European Appl.* 65,812  
Alloys having good high temperature 1000-1100°C resistance to molten glass and good mechanical properties, for use in centrifugal spinners for glass fibre production, are Ni-Cr alloys having less than 25 vol.% of  $\gamma'$  precipitate and containing up to 1.7% C, 0.3-4% Pt and/or Ru and up to 1.5% Ti and/or Al.

### ELECTROCHEMISTRY

#### Electrochemical Cell

THE ELECTRICITY COUNCIL *British Appl.* 2,098,238 A  
The efficiency of an electrochemical cell having  $\text{RuO}_2$ , Pt-Ir or platinised Ti electrodes is improved by positioning a turbulence promotor, such as a plastic mesh insert, in a flow path over one of the cell electrodes. The cell may be used for electrochemical reduction of oxidation.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Platinum Silicide Ohmic Contacts to Shallow Junctions in Silicon

S. S. COHEN, P. A. PIACENTE, G. GILDENBLAT and D. M. BROWN, *J. Appl. Phys.*, 1982, **53**, (12), 8856-8862

Ohmic contact to shallow  $\text{pn}^+$  and  $\text{pn}^+$  junctions in Si were studied. Thin layers ( $\sim 200\text{\AA}$ ) of Pt were sputter deposited and reacted with the Si substrate at 590°C to give a stable Pt silicide. A four terminal Kelvin-resistor structure was used to measure accurately the contact resistance. Pre-deposition and in situ etching resulted in considerable improvement in the measured specific contact resistance. Values well within the range required were obtained.

### An Evaluation of Palladium and Palladium-Silver Alloy in a Dual-in-Line Package Switch

W. R. HAIN, J. A. CLISURA and W. L. RUDLOFF, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1982, **CHMT-5**, (1), 16-22

Pd and 60%Pd-40%Ag were evaluated as potential substitutes for Au contacts in a dual-in-line package switch, of the rocker type. Switches were evaluated for thickness and hardness, formability and adhesion, porosity before and after 2000 cycles, wearability and contact resistance before and after 2000 cycles. Results show that Au to Pd or Au to 60%Pd-40%Ag will provide stable contact resistance with acceptable wear properties.

### Hydrogen Evolution Electrode

DIAMOND SHAMROCK CORP.

*European Appl.* 62,950/51

Cathodes for  $\text{H}_2$  evolution from aqueous electrolytes consist of a valve metal support coated with a catalyst finely dispersed in a matrix of semiconducting polymer. The polymer may be polyphenylene and the catalyst is a platinum group metal.

### Hydrogen by Electrolysis

WESTINGHOUSE ELECTRIC CORP.

*European Appl.* 63,420

An electrolyser for the production of  $\text{H}_2$  from dilute  $\text{H}_2\text{SO}_4$  saturated with  $\text{SO}_2$  consists of a series of half cells in which the anodes are preferably pellets of activated vegetable C mixed with 1-5% Pt powder.

### Improved Anode for Halogen Production

GENERAL ELECTRIC CO.

*U.S. Patent* 4,333,805

$\text{Cl}_2$  or another halogen is produced electrolytically in a cell having a new catalytic anode consisting of 90% Ru oxide and 10% Mn oxide.