

# ABSTRACTS

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

### PROPERTIES

#### The Surface Structure and Bonding of (2×2) Acetylene Overlayers on Platinum (III): LEED Intensity Analysis

L. L. KESMODEL, R. C. BAETZOLD and G. A. SOMORJAI, *Surface Sci.*, 1977, **66**, (1), 299-320

Two different bonding states of chemisorbed acetylene exist on the Pt(III) surface. The more weakly bound state involves co-ordination to one surface metal atom (Pt-C bond lengths of 2.5(1)Å) and the more strongly bound state has attachment to three metal atoms, of Pt-C bond lengths 2.2(1) and 2.6(1)Å.

#### Pt<sub>2</sub>Si and PtSi Formation with High-purity Pt Thin Films

C. CANALI, C. CATELLANI, M. PRUDENZATI, W. H. WADLIN and C. A. EVANS, *Appl. Phys. Lett.*, 1977, **31**, (1), 43-45

Formation rates of Pt<sub>2</sub>Si and PtSi were studied using 1.8 MeV <sup>4</sup>He<sup>+</sup> backscattering spectroscopy. The results showed that both silicide layers were grown with t<sup>1/2</sup> time dependence, but the formation of PtSi started only after all the available Pt had reacted to Pt<sub>2</sub>Si. The activation energies were found to be 1.5±0.1 eV. Spectroscopic data confirmed the deposited Pt purity. The contaminants contained in the sputter-deposited Pt layer segregated at the Pt<sub>2</sub>Si/Pt interface.

#### Effect of Palladium on the Hydrogen Permeability of Steel

L. A. CHIGIRINSKAYA, G. P. CHERNOVA and D. TOMASHOV, *Zashchita Metal.*, 1977, **13**, (4), 406-409

Studies of the effect of small amounts of Pd in the surface of carbon steels were carried out in 5-30% H<sub>2</sub>SO<sub>4</sub> at 20°C and 30-60 mA/cm<sup>2</sup> on samples prepared either by addition of 10<sup>-4</sup>-10<sup>-5</sup> g ion/l Pd<sup>2+</sup> ions to the electrolyte or by alloying with 0.5% Pd. It is shown that Pd in the steel decreases the hydrogen permeability rate in steel.

#### The Effect of the α-β Phase Change on the α Phase Solubility of Hydrogen in Palladium

J. F. LYNCH, J. D. CLEWLEY, T. CURRAN and T. B. FLANAGAN, *J. Less-Common Metals*, 1977, **55**, (2), 153-163

The α-β phase change in Pd causes greater solubility of H<sub>2</sub> within the low H<sub>2</sub> content α-phase. There are similarities between the absorption isotherms for H<sub>2</sub> following the phase change and those exhibited by heavily cold-worked Pd. Partial thermodynamic parameters

for H<sub>2</sub> absorption are reported for Pd plastically deformed by the phase change.

#### The New B-2 Alloy on the Palladium Base for Diffusion Hydrogen Filters

V. A. GOL'TSOV, V. V. LATYSHEV, N. I. TIMOFEEV and I. YU. MACHIKINA, *Izv. Vysshikh Ucheb. Zaved., Tsvetnaya Metallurgiya*, 1977, (4), 117-120

A new B-2 alloy containing Pd-15%Ag-1.5%In-0.2%Y was used in H<sub>2</sub> diffusion filters. The alloy was very effective at 600-300°C with an increase of H<sub>2</sub> permeability of 15-20% compared to that obtained by Pd-15%Ag-5%Pt alloy filters and 230-400% higher than for Pd-10%Ag-5%Ni alloys.

#### Mechanical Characteristics of Amorphous Metals

T. MASUMOTO, *Sci. Reports Res. Inst. Tohoku Univ.*, 1977, **26**, (4-5), 246-262

Pd-Si base alloys Pd<sub>80</sub>Si<sub>20</sub> and Pd<sub>77.5</sub>Cu<sub>8</sub>Si<sub>16.5</sub> and other amorphous alloy systems were tested for static and dynamic properties, plastic deformation, toughness and the effects of composition, structure and environment on their mechanical behaviour. In the Pd<sub>80</sub>Si<sub>20</sub> alloy system hardness (PDN) was 325, fracture strength was 136 kg/mm<sup>2</sup>, Young's modulus 6.8 × 10<sup>9</sup> kg/mm<sup>2</sup>, and the crystallisation temperature 380°C.

#### Kinetic Properties of Pd-Ni Alloys. 3. Transverse Magneto-resistance. 4. Anomalous Hall Effect of Pd-Ni alloys

V. A. MATVEEV, G. V. FEDOROV and N. V. VOLKENSHEIN, *Fiz. Metal. Metalloved.*, 1977, **43**, (6), 1185-1191

The transverse magneto-resistance of ferromagnetic Pd-Ni alloys (containing 3-99.3 at.% Ni) was measured at 4.2, 20.4, 77.8 and 293K, in variable magnetic fields. In the field range corresponding to true magnetisation, the magneto-resistance changes linearly with the increase in field strength. The observed anomaly in the transverse magneto-resistance of Pd-Ni alloys is due to the interaction of conduction electrons with magnetic heterogeneities.

#### Stability of PdO, RuO<sub>2</sub> and IrO<sub>2</sub> and the Change of Their Thermal Expansion Coefficient at Elevated Temperatures

G. BAYER and H. G. WIEDEMANN, *Arch. Hutn.*, 1977, **22**, (1), 3-13

The oxidation of Pd, Ru and Ir powders with different grain sizes was studied by TG, DTA and X-ray diffraction. The oxides, PdO, RuO<sub>2</sub> and

IrO<sub>2</sub>, formed on heating show different stabilities at elevated temperatures. The decomposition temperature vs. O<sub>2</sub> partial pressure was determined for PdO. The thermal expansion coefficients for RuO<sub>2</sub> and IrO<sub>2</sub> showed considerable anisotropy. The thermal expansion of these oxides was compared to that of other oxides with rutile structure.

## CHEMICAL COMPOUNDS

### Synthesis and Structure of BaPtO<sub>3</sub>

P. K. GALLAGHER, D. W. JOHNSON, JR., E. M. VOGEL, G. K. WERTHEIM and F. J. SCHNETTLER, *J. Solid State Chem.*, 1977, 21, (4), 277-282

BaPtO<sub>3</sub> was prepared by the reaction of BaO<sub>2</sub> with PtO<sub>2</sub> at high O<sub>2</sub> pressures, and by the thermal decomposition of BaPt(OH)<sub>6</sub> at 500-700°C in O<sub>2</sub> at 1 atmosphere pressure. The powder X-ray diffraction pattern fits a hexagonal perovskite cell with  $a=5.64$  and  $c=27.44\text{\AA}$ . The O<sub>2</sub> content of BaPtO<sub>3-x</sub> materials can be determined by weight change on heating the samples to 300°C in H<sub>2</sub> to form Ba(OH)<sub>2</sub>+Pt.

### Thermal Stability of Ethylenediamino Pt(II) Complexes

YU. N. KUKUSHKIN, V. P. KOTEL'NIKOV and V. N. SPEVAK, *Zh. Neorg. Khim.*, 1977, 22, (8), 2208-2210

The thermal characteristics of complex Pt(II) compounds of the type [Pt(LX)]X where L=dimethylsulphoxide, diethylsulphoxide, dipropylsulphoxide, dimethylsulphide, diethylsulphide and dipropylsulphide and X=Cl<sup>-</sup> and Br<sup>-</sup> were studied. It is shown that the first stage of the thermal transformation involves separation of the L ligand. The kinetic parameters are derived.

### Thermal Isomerisation of Phosphine Platinum(II) Complexes Containing Tin(II) Trichloride

YU. N. KUKUSHKIN, G. N. SEDOVA, P. G. ANTONOV and L. N. MITRONINA, *Zh. Neorg. Khim.*, 1977, 22, (10), 2785-2788

Studies showed that heating the solid-phase *cis*-[PtL<sub>2</sub>(SnCl<sub>3</sub>)Cl] complexes where L=(PPh<sub>3</sub>), (PPh<sub>2</sub>Et) and (PPhEt<sub>2</sub>) leads to the formation of thermodynamically more stable isomers of *trans*-configuration. The value  $\Delta H$  for the *cis*→*trans* isomerisation of the complexes was found to be -5, 11 and 10 kcal/mole, respectively.

### A New Synthesis of Platinum-Carbon Bonds

M. A. CAIRNS, K. R. DIXON and M. A. R. SMITH, *J. Organometal Chem.*, 1977, 135, (1), C33-C34

Pt-C bonds have been formed during the synthesis of *cis*-[PtCl(CH<sub>2</sub>COCH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>], *cis*-[PtCl(CH<sub>2</sub>NO<sub>2</sub>)(PEt<sub>3</sub>)<sub>2</sub>] and *trans*-[Pt(C≡CPh)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>]. The reaction of *cis*-[PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] with Ag<sub>2</sub>O and acidic C-H bonds precipitates AgCl and forms a Pt-C bond.

### LaRu<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> Perovskites

R. J. BOUCHARD, J. F. WEIHER and J. L. GILLSON, *J. Solid State Chem.*, 1977, 21, (2), 135-143

LaRu<sub>x</sub>Fe<sub>1-x</sub>O<sub>3</sub> solid solutions were prepared and electrical, magnetic, crystallographic and Mössbauer data were taken. Metallic conductivity is destroyed by substituting as little as 10% Fe for Ru. Mössbauer and magnetic data show the presence of only high-spin octahedral Fe<sup>3+</sup>. At the Fe-rich end, addition of Ru decreases the Néel temperature of LaFeO<sub>3</sub> by  $\approx 100^\circ\text{C}$  for every 10% of Ru.

## ELECTROCHEMISTRY

### An Investigation of the Thiourea Effect on the Properties of a Platinum Electrode

N. I. IL'CHENKO, A. A. CUTYAGINA and G. D. VOVCHEKNO, *Vest. Moskov. Univ. Ser. II, Khim.*, 1977, 18, (1), 72-75

Studies of the adsorption of thiourea and its effect on the adsorption properties of the Pt/Pt electrode in relation to H<sub>2</sub> and O<sub>2</sub> in 0.1N H<sub>2</sub>SO<sub>4</sub> solution were made. The regeneration conditions of this electrode are discussed.

### Obtaining Thin Layers of Pt Usable in Electrochemistry and in Polarographic-brometry by Sputtering

G. TOURILLON, J. E. DUBOIS and P. C. LACAZE, *J. Chem. Phys.*, 1977, 74, (6), 683-688

High purity thin-layer Pt electrodes were prepared by sputtering on a glass substrate. The results showed that by using sputtering the preparation of various types of electrodes used in several physical analyses could be limited to one electrode. In the case of the Kolbe reaction the catalytic and mechanical properties of these electrodes have the same behaviour as those of bulk Pt.

### Electrochemical Reduction of Pt(CN)<sub>4</sub><sup>2-</sup> Ions in Molten Sodium-Potassium Cyanide Eutectic

E. T. VAN DER KOUWE and A. VON GRUENEWALDT, *J. Appl. Electrochem.*, 1977, 7, (5), 407-416

Studies of the reduction of Pt(CN)<sub>4</sub><sup>2-</sup> ions in a NaCN-KCN eutectic melt were carried out at 510-580°C using chronopotentiometry and cyclic voltammetry. The reduction to Pt(CN)<sub>4</sub><sup>1-</sup> was found to be a reversible process. The density of the eutectic melt was determined as a function of temperature.

### Thin Film Solid Electrolyte Systems

J. H. KENNEDY, *Thin Solid Films*, 1977, 43, (1/2), 41-92

A comprehensive review is given of the materials useful for thin film electrochemical cells. Typical metal electrode materials such as Pt, Au and Ag are discussed and thin film cathode materials are reviewed. (183 Refs.)

### **An Investigation of Anodic Film Formation on Electrodeposited Ruthenium by Potential Sweep Techniques**

L. D. BURKE, J. K. MULCAHY and S. VENKATESAN, *J. Electroanal. Chem. Interfacial Electrochem.*, 1977, **81**, (2), 339-346

The anodic behaviour of reduced Ru surfaces prepared by electrodeposition on Au-plated substrates was studied by a potential sweep technique as a function of sweep rate, temperature and pH. The formation of thin oxide films on Ru at pH 3.5-9.5 was found to be due to the growth of a compact amorphous film. The effects of both sweep rate and temperature on anodic behaviour in strong acid are attributed to activation-controlled rearrangement of the oxide film.

### **An Investigation of the Electrochemistry of a Series of Metal Dioxides with Rutile-Type Structure: MoO<sub>2</sub>, WO<sub>2</sub>, ReO<sub>2</sub>, RuO<sub>2</sub>, OsO<sub>2</sub> and IrO<sub>2</sub>**

J. HORKANS and M. W. SHAFER, *J. Electrochem. Soc.*, 1977, **124**, (8), 1202-1207

Ru, Os, Ir and other metal dioxides were examined as electrodes in 1N H<sub>2</sub>SO<sub>4</sub> solution. RuO<sub>2</sub> had a broad current-potential profile indicating a surface layer existed for a range of compositions. Measurements of O<sub>2</sub> reductions showed lower catalytic activity than Pt but similarities to other oxide catalysts. RuO<sub>2</sub> was the only dioxide stable enough to allow measurements of O<sub>2</sub> evolution and reduction. The current-potential profiles of OsO<sub>2</sub> and IrO<sub>2</sub> had distinct peaks indicating changes in the oxidised surface layer.

### **On the State of Osmium(VIII) and Osmium(VII) in Alkaline Solutions**

G. M. DAKAR, B. Z. IOFA and A. N. NESMEYANOV, *Vest. Moskov. Univ., Ser. II, Khim.*, 1977, **18**, (1), 62-65

Studies of the state of Os(VIII) and Os(VII) in Na hydroxide solutions, n-tributylphosphate and CCl<sub>4</sub> were made by measuring the absorption spectra before and after extraction. The results show that Os(VIII) and Os(VII) exist in different forms in alkaline solutions. The spectrophotometric characteristics of these forms were determined.

## **ELECTRODEPOSITION AND SURFACE COATINGS**

### **High Temperature Oxidation Resistant Coatings for the Directionally Solidified Ni-Nb-Cr-Al Eutectic Superalloy**

T. E. STRANGMAN, E. J. FELTEN and N. E. ULION, *Am. Ceram. Soc. Bull.*, 1977, **56**, (8), 700-705

A NiCrAlY + Pt(5-10%) vapour deposited coating exhibited good oxidation resistance, diffusional stability, thermal fatigue and creep resistance when used as a protective coating for Ni-Nb-Cr-Al

directionally solidified eutectic superalloy. The useful life of a 127 $\mu$ m thick coating exceeded 1000 hours at 1366K, and the creep life at 1311K and stress 151.7 MN/m<sup>2</sup> of a coated specimen was greater than that of an uncoated specimen by a factor of 2.

### **Precision Circuit Repair With Selective Plating**

M. RUBINSTEIN, *Insulation/Circuits*, 1977, **23**, (8), 37-40

The 'styli' of brush plating equipment have been improved. One type, flat shim styli, are made of a 90%Pt-10%Ir alloy for extra hardness. Selective plating can repair Rh or Au plating on tabs of assembled circuit cards, and Au or Ni with Rh can be plated without endangering neighbouring parts.

### **Electrolytic Deposition of Thin Metal Films on Semiconductor Substrates**

P. BINDRA, H. GERISCHER and D. M. KOLB, *J. Electrochem. Soc.*, 1977, **124**, (7), 1012-1018

The deposition mechanism and deposit structure of Pd(metal ion concentration 10<sup>-3</sup>M) on various substrates were examined. The presence of n-GaAs in solutions containing Pd<sup>2+</sup> and Ag<sup>+</sup> showed that metal deposition occurred by dipping the electrode in solution. The systems can be split into three groups; metal-like substrate (Pd on SnO<sub>2</sub>), semiconductor—Pd on ZnO<sub>2</sub>, and chemical interaction with the substance—Pd on CdS, n-GaAs and n-GaP.

### **Metallic Barriers for Protection of Contacts in Electronic Circuits from Atmospheric Corrosion**

D. R. MARX, N. R. BITLER and H. W. PICKERING, *Plating*, 1977, **64**, (6), 69-72

Copper bars were plated with barrier metals Pt, Pd, Rh and others to a thickness of 1 and 2 $\mu$ m by electro- and electroless deposition. Pt and Pd specimens were given gold strikes and outgassed to prevent blistering and the samples were then examined for copper penetration. At 400 and 550°C the Cu penetration was considerable but at 175°C it was not measurable, whilst at 100°C in all three metals there was significant void formation and Cu penetration.

### **The Electrodeposition of Platinum Metals from Molten Salts**

W. B. HARDING, *Plating*, 1977, **64**, (9), 48-55

For Ir plating from cyanide mixtures a eutectic composition of 57 wt. % Na cyanide and 43 wt. % K cyanide is preferred. Ir can be introduced into the melt electrolytically, and soluble anodes should be used. Pt can be plated out of cyanide mixtures from a soluble Pt anode, giving deposits of 250  $\mu$ m thickness. Rh, Ru and Pd may also be deposited, giving thick deposits, from cyanide-based electrolytes.

## LABORATORY APPARATUS AND TECHNIQUE

### Poisoning Titration Technique for Determining the Number of Active Centers in a Supported Platinum Catalyst

L. GONZALEZ-TEJUCA, K. AIKA, S. NAMBA and J. TURKEVICH, *J. Phys. Chem.*, 1977, **81**, (14), 1399-1406

A method to determine the number of active centres on Pt responsible for the catalytic hydrogenation of olefins and equilibration of H<sub>2</sub>-D<sub>2</sub> mixtures was developed. Alternate poison (titrant) and reactant pulses were put into a H<sub>2</sub> stream which passed over the catalyst. CS<sub>2</sub> was the best titrant. The number of active centres equalled those found by H<sub>2</sub> chemisorption assuming one CS<sub>2</sub> molecule poisons two Pt atoms.

### Chemisorption on Molecular Sieve Supported Platinum. 1. Hydrogen, Oxygen and the Hydrogen-Oxygen Titration

E. ROCKOVA, *J. Catalysis*, 1977, **48**, (1-3), 137-149  
Chemisorption of H<sub>2</sub>, O<sub>2</sub> and the titration reaction on molecular sieve supported Pt were investigated to determine the specific surface of Pt. The Pt surface is saturated from an O<sub>2</sub> pulse for a molecular sieve 5Å supported Pt. Distribution curves of Pt crystallite size showed their mean diameter to be 46Å. The specific Pt surface in this material containing 0.3% Pt was 0.150 or 0.180 m<sup>2</sup>/g depending on the crystallite geometry.

### Comparison of Hydrogen-Oxygen Titration with Hydrogen-Alkene Titration for the Measurement of Platinum Surface Area in Supported Catalysts

G. LECLERCQ, J. BARBIER, C. BETIZEAU, R. MAUREL, H. CHARCOSSET, R. FRETY and L. TOURNAYAN, *J. Catalysis*, 1977, **47**, (3), 389-392

The Pt surface area was measured on clean and poisoned Pt/Al<sub>2</sub>O<sub>3</sub> catalysts by H<sub>2</sub>-O<sub>2</sub> titrations at room temperature and by alkene titration. The results show that the alkene titration method gives the same results as H<sub>2</sub>-O<sub>2</sub> titration with clean catalysts but not with poisoned ones. It is concluded that the results of alkene titration give the better correlation with catalytic activity.

## HETEROGENEOUS CATALYSIS

### On the Mechanism of Cyclopentanes Formation from Aliphatic Hydrocarbons on Platinum/Alumina Catalysts

O. V. BRAGIN, V. G. TOVMASYAN, I. V. GOSTUNSKAYA and A. L. LIBERMAN, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1977, (6), 1340-1344

Studies of the cyclopentane formation from aliphatic hydrocarbons over 0.6% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst

in the H<sub>2</sub> and gas carrier flow systems at 310-450°C showed that the cyclisation of alkanes and alkenes occurred in two different ways; by the direct dehydrocyclisation of initial alkanes or through formation of intermediate olefines.

### Valence State and Interaction of Platinum and Germanium on $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Investigated by X-Ray Photoelectron Spectroscopy

R. BOUWMAN and P. BILOEN, *J. Catalysis*, 1977, **48**, (1-3), 209-216

X-ray photoelectron spectroscopy of the reducibility of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ge/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Pt, Ge/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> systems shows that H<sub>2</sub> treatment at temperatures up to 650°C forms Pt-Ge alloys. Without Pt, Ge at 650°C seems to dissolve in the Al<sub>2</sub>O<sub>3</sub> matrix, but with Pt it remains exposed. "Pt atoms" in Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pt, and Ge/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> thus appear to be in an electron-deficient state.

### Formation of Superoxide Ion During the Decomposition of Hydrogen Peroxide on Supported Metals

Y. ONO, T. MATSUMURA, N. KITAJIMA and S.-I. FUKUZUMI, *J. Phys. Chem.*, 1977, **81**, (13), 1307-1311

Pt, Pd and Ag catalysts supported on Al<sub>2</sub>O<sub>3</sub> were used in the decomposition of H<sub>2</sub>O<sub>2</sub> at 275K. This produced the superoxide ion O<sub>2</sub><sup>-</sup>, the presence of which was determined by ESR. The conversion of H<sub>2</sub>O<sub>2</sub> was measured as a function of the amount of catalyst, and it was found that decomposition is first order with respect to H<sub>2</sub>O<sub>2</sub> concentration for the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst.

### Surface Acidity and Acid Strength Distribution of Modified Alumina Support and Platinum Reforming Catalysts

L. D. SHARMA, P. K. SINHAMAPATRA, H. R. SHARMA, R. P. MEHROTRA and G. BALAMALLIAH, *J. Catalysis*, 1977, **48**, (1-3), 404-407

The catalyst Pt-Ir/Al<sub>2</sub>O<sub>3</sub>-Cl containing Pt 0.35 wt.% and Ir 0.04 wt.%, prepared by the simultaneous impregnation of HCl, H<sub>2</sub>PtCl<sub>6</sub> and H<sub>2</sub>IrCl<sub>6</sub> on unchlorinated Al<sub>2</sub>O<sub>3</sub>, has high homogeneity and acidity in the range -5.6 < pK<sub>a</sub> ≤ -3.0. This is vital for isomerisation activity in the reforming process for upgrading motor gasoline.

### Determination of the Rate Limiting Step in the Hydrogenolysis of n-Butane on Supported Platinum/Rhenium Catalysts

I. H. B. HAINING, C. KEMBALL and D. A. WHAN, *J. Chem. Research*, 1977, (7), 170-171

The activity for the hydrogenolysis of n-butane increases to a maximum at ~60% Re : 40% Pt as Re is added to Pt on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The rate limiting step changes from C-C bond fission to methane desorption as the Re is increased.

### On the Mechanism of Liquid-Phase Hydrogenation of Benzofuran and Its Derivatives in the Presence of Platinum Catalysts

E. A. KARAKHANOV, A. G. DEDOV, I. I. PAKHOMOVA, L. G. SAGINOVA and E. A. VIKTOROVA, *Vest. Moskov. Univ., Ser. II, Khim.*, 1977, **18**, (3), 334-339

Studies of the hydrogenation of benzofuran and its alkyl and 2,3-dihydroderivatives over Pt catalysts, prepared by the reduction of  $H_2PtCl_6$  with an excess of  $NaBH_4$ , and 5% Pt/C catalysts were carried out in a vertical flow reactor at 30-120°C and in a static system at 20-60°C. The differences in conversions of benzofurans and 2,3-dihydrobenzofurans are discussed. The dissociative  $\pi$ -complex mechanism was suggested for hydrogenation of benzofuran and its derivatives.

### The Catalytic Decomposition of $H_2O_2$ on Platinum in the Presence of a Series of Organic Substances

T. M. SEMIONKINA, G. I. ELFIMOVA, G. A. BOGDANOVSKII and G. D. VOVCHEENKO, *Vest Moskov. Univ., Ser. II, Khim.*, 1977, **18**, (3), 365-367

The catalytic decomposition of  $H_2O_2$  on platinised Pt and Pt/C catalysts was carried out in the presence of acetic, butyric, isobutyric and isovaleric acids, and isopropyl alcohol and nitromethane. The organic substances were found to possess the inhibitor effect on decomposition.

### The Influence of Activation Conditions on the Performance of Platinum/Ruthenium Methanol Electro-Oxidation Catalysts. Surface Enrichment Phenomenon

B. D. MCNICOL and R. T. SHORT, *J. Electroanal. Chem. Interfacial Electrochem.*, 1977, **81**, (2), 249-260

The influence of activation conditions upon the performance of supported 70 wt.% Pt-Ru/C paper and unsupported finely divided 95 wt.% Pt-5 wt.% Ru and 70 wt.% Pt-30 wt.% Ru catalysts was studied during the electro-oxidation of methanol. The results showed that the low activity of C paper supported catalysts prepared in  $H_2$  could be increased by oxidation in air at 300°C.

### X-ray Photoelectron Spectroscopy and Electron Microscopy of Pt-Rh Gauzes Used for Catalytic Oxidation of Ammonia

J. P. CONTOUR, G. MOUVIER, M. HOGEWYS and C. LECLERE, *J. Catalysis*, 1977, **48**, (1-3), 217-228

Pt-Rh gauzes working in industrial burners for  $NH_3$  oxidation are examined by various techniques. During combustion Rh-rich and Pt-rich crystals form. Chemical analysis shows that catalyst deactivation may be caused by Rh segregation at the surface, resulting from the volatilisation of Pt oxide at high temperatures after the oxidation of Rh and Pt.

### Surface Morphology of Platinum Catalysts

M. FLYTZANI-STEPHANOPOULOS, S. WONG and L. D. SCHMIDT, *J. Catalysis*, 1977, **49**, (1), 51-82

Surface morphologies of small (<0.06 cm diameter) single crystal spheres of Pt, Rh, Pd and Pt-30% Rh were examined after use as catalysts in the oxidation of  $NH_3$ ,  $C_2H_6$  and CO and  $NH_3$  decomposition. For  $NH_3$  oxidation the facet formation rate is large on small spheres, and stable planes are influenced by sphere diameter and flow velocity. Metal transport may occur by surface diffusion or volatile oxide formation and minimum surface free energy can explain unstable and metastable regions and faceting rates.

### Kinetics of the Vapor-Phase Oxidation of Ethylene to Acetaldehyde over Pd- $V_2O_5$

L. FORNI and G. TERZONI, *Ind. Engng. Chem. Process Des. Dev.*, 1977, **16**, (3), 288-293

A kinetic study of the influence of external and internal diffusion, support surface area,  $V_2O_5$  concentration, and activation temperature on the life and regenerability of Pd-Ru/ $V_2O_5$  catalysts was carried out by both differential and integral reactor technique at 1 atm and 110-180°C. The partial reaction orders were determined with respect to ethylene,  $O_2$  and  $H_2O$  vapour, together with the apparent activation energies for the formation of acetaldehyde, acetic acid and  $CO_2$ .

### Water-promoted Oxidation of Carbon Monoxide Over Tin(IV) Oxide-supported Palladium

G. CROFT and M. J. FULLER, *Nature*, 1977, **269**, (5629), 585-586

The low-temperature activity of the Pd/ $SnO_2$  system is not poisoned by water vapour, but its presence enhances the oxidation of CO by  $O_2$  and NO. This is useful for automobile exhaust control in cold-start conditions and the removal of CO from tobacco smoke by a catalytic filter.

### The Effect of Medium Acidity on the Process of Liquid-Phase Hydrogenation of Eugenol in the Presence of Platinum Group Metals under the Hydrogen Pressure

D. V. SOKOLSKII, T. O. OMARKULOV, T. K. DZHARIKBAEV and K. KH. NURGOZHAEV, *Dokl. Akad. Nauk. S.S.S.R.*, 1977, **236**, (2), 397-399

The effect of medium acidity on the process of liquid-phase hydrogenation of eugenol was studied over Pt, Pd and Rh black catalysts at 1-80 atm  $H_2$  and pH 3.3, 7.5 and 12.7. An increase in the hydrogenation rates from 6 to 800 ml in 30s occurred over Pt catalysts in pH 3.3, from 20-138 ml in pH 7.5 and from 10-104 ml in pH 12.7 media followed by a decrease of energy. The results obtained on Rh catalysts showed that the reaction rates increased 3-4 fold with the increase of pH from 3.3-12.7.

### Electrochemical Investigations on Supported Palladium Catalysts

E. POLYÁNSZKY, T. MALLÁT and J. PETRÓ, *Acta Chim. Acad. Sci. Hung.*, 1977, **92**, (2), 147-156

The parameters of potentiodynamic measurements were determined on 5 wt.% Pd/C and Pd/BaSO<sub>4</sub> catalysts prepared under various conditions. The results showed that at low Pd content the character of H<sub>2</sub> sorption resembles that of pure C, and at higher metal contents that of pure Pd black. The amount of adsorbed H<sub>2</sub> increases with increasing metal content, as well as the ratio of weakly and strongly bonded hydrogen.

### Hydrogen Adsorption by Palladium Catalysts in Solutions

G. D. ZAKUMBAEVA, N. A. ZAKARINA, N. F. TOKTABAIEVA and N. V. MASLAK, *Kinet. Kataliz*, 1977, **18**, (4), 1007-1013

The adsorption behaviour of H<sub>2</sub> by Pd black and supported Pd catalysts containing 2, 5, 10 or 20% Pd were studied by a potentiodynamic method. The results showed that the increase of Pd content from 2 to 20% causes a decrease of H<sub>ads</sub>/Pd ratio from 0.47-0.09. The decrease in the amount of adsorbed H was due to high temperature treatment of the catalyst. The diffused: adsorbed H ratio was studied in terms of catalyst dispersity.

### The Hydrogenation of Hydrocarbons on Catalyst of the System Porous Glass-Metal

F. WOLF, F. JANOWSKI and W. HEYER, *Z. Anorg. Allgem. Chem.*, 1977, **432**, (5), 242-248

Studies of dependences of the pore structure of catalysts on their selectivity were made during the hydrogenation of hydrocarbons over Pd, Pt or Ni metal catalysts supported by porous glasses and zeolites, in the gas phase. The results showed that catalysts of the type porous glass/metal were able to shape a selective catalysis in the same way as zeolite catalysts.

### The Adsorption and Catalytic Properties of the Skeleton Rh-Os Catalyst

T. M. GRISHINA, V. V. ZHUCHKOVA and G. D. VOVCHEENKO, *Vest. Moskov. Univ., Ser. II, Khim.*, 1977, **18**, (3), 367-369

The adsorption ability of hydrogen was studied during hydrogenation of nitroethane over skeleton Rh-Os catalysts containing various amounts of Rh. The addition of Os to Rh increases catalytic activity, 35 at.% Os being most active.

### The Activity of Ruthenium, Rhodium, Iridium-Ruthenium and Iridium-Rhodium Adsorption Catalysts in the Dehydrogenation of Formic Acid

V. A. MIKHAILOV and I. A. ZUBOVICH, *Zh. Fiz. Khim.*, 1977, **51**, (4), 847-850

The activity of Ru-, Rh-, (Ir+nRu)- and (Ir+nRh)- catalysts supported on charcoal and SiO<sub>2</sub> was studied in the dehydrogenation of

HCOOH. The activity was found to change in the following order Ir<Ru<(Ir+nRu)<Rh<(Ir+nRh). The highest activity was observed for (Ir+nRh)/SiO<sub>2</sub> catalysts. It is shown that during the preparation of (Ir+nRh)- and (Ir+nRu)-catalysts, an interaction of Ir atoms with Ru or Rh atoms produces structures of variable composition.

### The Adsorption of Hydrogen on Skeleton Iridium-Osmium Catalysts at Different Temperatures

F. A. MAKHMUTOV, A. D. SEMENOVA and G. D. VOVCHEENKO, *Zh. Fiz. Khim.*, 1977, **51**, (6), 1520-1521

The galvanostatic charging curves vs. temperature dependence was used to determine the differential adsorption heats of H<sub>2</sub> on skeleton Ir-Os catalysts.

## HOMOGENEOUS CATALYSIS

### Non-Isomerising Hydroformylation by Rhodiumcarbonyl/tetr. Phosphine Catalyst Systems. II. Hydroformylation of Allyl Alcohols

B. FELL and M. BARL, *Chem. Z.*, 1977, **101**, (7/8), 343-350

Studies of the non-isomerising hydroformylation of unsaturated alcohols by Rh carbonyl/tetr. phosphine catalyst systems showed good yields of hydroxy-aldehydes. The primary hydroformylation product and the by-products can be hydrogenated to 2-methylpropane-1,3-diol and butane-1,4-diol. Unsaturated alcohols can be hydroformylated without isomerisation but only with small yields.

### Catalysis by Chlorohydridobis(triphenylphosphine)ruthenium(II) Species. Novel Kinetics and Their Implications for Activation of Saturated Hydrocarbons

B. R. JAMES and D. K. W. WANG, *J. Chem. Soc., D. Chem. Commun.*, 1977, (16), 550-551

The kinetics of hydrogenation of acrylamide catalysed by [HRuCl(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub> in solution indicate a mechanism which includes competitive oxidative addition reactions of H<sub>2</sub> and propionamide to Ru(I) centres.

## CHEMICAL TECHNOLOGY

### Effect of Spinneret Material on the Spinning of Rayon Textile Thread

R. V. EGOROVA, A. T. SERKOV, G. G. FINGER and A. F. TELYSHEVA, *Khim. Volokna*, 1977, (3), 70-71

Studies of Pt alloy spinnerets carried out during the production of rayon textile thread showed that the use of spinnerets made from Pt-Au alloys decreased the average weekly change of spinnerets by 9% and the quality of the produced fibres increased by 3.4% due to a decrease in the defects.

## The Sintering of Tantalum with Transition Metal Additions

R. M. GERMAN and Z. A. MUNIR, *Powder Metallurgy*, 1977, 20, (3), 145-150

The sintering behaviour of Ta powders with Rh, Pd, Ir and Pt was studied at 1250-1700°C. Pt, Pd and Rh caused densification by a slight shrinkage, but none was obtained with addition of Ir. Pd shrinkage was lower than expected due to a high surface diffusivity.

## Recovery of Solubilized Rhodium from Hydroformylated Vegetable Oils and Their Methyl Esters

E. J. DUFEK and G. R. LIST, *J. Am. Oil Chem. Soc.*, 1977, 54, (7), 276-278

The extraction of Rh from hydroformylated vegetable oils and methyl esters by different reagents was examined. Aqueous hydrogen cyanide with triethanolamine (TEA) was the most effective, and the effects of time, temperature and reagent concentration were studied. Over 98% of Rh was removed from methyl formylstearate at 100°C for 1 hour with 0.5% HCN, 5% H<sub>2</sub>O and 0.5% TEA. 98% of Rh was extracted from hydroformylated soya bean and safflower methyl esters with 1% HCN, 10% H<sub>2</sub>O and 0.62 TEA, and 90% Rh from hydroformylated soya bean oil.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Low as Fired Distribution Eliminate Most Thick Film Resistor Trimming

F. E. BUZAN, *Solid State Technol.*, 1977, 20, (8), 40, 42

A new Ru oxide resistor paste provides low as fired distributions typically 1 Sigma level of 2.5%. This eliminates the need for trimming resistors with tolerance levels greater than ±5%.

## MEDICAL USES

### On the Mechanisms of Action of Platinum Complexes as Anticancer Agents

B. ROSENBERG, *J. Clin. Hematol. Oncol.*, 1977, 7, (2), 817-827

Experiments with Pt drugs for anticancer properties show that they may act by enhancing the antigenicity of tumour cells, thus allowing the immune system to destroy the cancer without killing the cell. Only *cis* configurations are active, showing Pt does not simply act with non-specific toxicity, and Pt drugs act by causing a lesion on cellular DNA. A reaction to explain the anticancer activity is proposed.

## NEW PATENTS

### METALS AND ALLOYS

#### Rhodium Alloys

INTERNATIONAL BUSINESS MACHINES CORP.

*U.S. Patent 4,023,965*

The alloys, for use in magnetic devices and which enhance corrosion resistance, contain 65-90% Ni, 10-35% Fe and 1-25% Rh.

#### Titanium Alloy

JOHNSON MATTHEY & CO. LTD.

*Dutch Appl. 76.13127*

The corrosion resistance of Ti alloys is improved by the incorporation of 6-40% of one or more of Rh, Ru, Pt and Pd, although Ir may also be present. One alloy contains 6% Pt and 6% Ir.

### CHEMICAL COMPOUNDS

#### Platinum or Silver Hydroxymercaptan Salts

AMERICAN CYANAMID CO.

*U.S. Patent 4,018,807*

Certain metal salts, such as the Pt and Ag salts of aromatic o-hydroxymercaptans, are prepared by the reaction of an aromatic o-hydroxythiocyanate with a water-soluble salt of the metal in the

presence of a strong mineral acid. The salts can be incorporated into plastic lenses to afford eye protection against laser radiation.

### ELECTRODEPOSITION AND SURFACE COATINGS

#### Platinum Coating for Electrodes

EXXON RESEARCH & ENGINEERING CO.

*British Patent 1,484,645*

A photogalvanic device has a thin layer of Pt on a glass surface for use as an electrode.

#### Platinum Group Metals for Bipolar Press Cell

B.A.S.F. WYANDOTTE CORP.

*British Patent 1,487,237*

In the cell, a connection between the anode and cathode can be made of a Pd-Ti alloy and the anode may be coated with one or more Pt group metals or their oxides.

#### Platinum Group Layer for Electrodes

SIEMENS A.G.

*British Patent 1,487,485*

Electrodes for fuel cells are coated with a catalytic layer of an alloy of a Pt group metal and an Fe group metal, a suitable alloy being of Pt-Ni.