

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### XPS and UPS Study of the Reaction of Carbon Monoxide with Oxygen and Nitrogen Monoxide on Platinum-Rhenium Alloy

M. ALNOT, A. CASSUTO, R. DUCROS, J. J. EHRHARDT and B. WEBER, *Surf. Sci.*, 1982, **114**, (2/3), L48-L56

Room temperature interactions between CO with O<sub>2</sub> and NO were studied on a 40%Pt-60%Re alloy by XPS and UPS. There was a total removal of adsorbed CO by gaseous O<sub>2</sub> (which is not possible on Pt and difficult on Re); partial removal of adsorbed O<sub>2</sub> by CO from the gas phase (impossible on Re); and total removal of adsorbed CO gas, NO and total reversibility of this reaction (impossible on both Pt and Re).

### The Interaction of CO and O<sub>2</sub> with Thin Islands of Pd

H. POPPA and F. SORIA, *Surf. Sci.*, 1982, **115**, (2), L105-L110

The adsorption and co-adsorption of CO and O<sub>2</sub> on Pd islands ~7 monolayers thick was investigated by TPD and AES. CO decomposed much less on Pd islands grown on W(110)-(14 × 7)-o than on small Pd particles on bulk oxide substrates (mica, sapphire). O<sub>2</sub> interacted unusually strongly with the island surfaces at 600K. These results are attributed to a strong metal-support interaction.

### Glass-Forming Ability and Crystallization Kinetics of Amorphous Palladium-Boron Alloys

A. LUCCI and L. BATTIZZATI, *Thermochim. Acta*, 1982, **54**, (3), 343-348

Pd-B alloys were prepared to check their ability to produce metallic glasses when spun from the melt. The alloys were able to produce amorphous ribbons by melt spinning. The crystallisation kinetics of Pd<sub>68.5</sub>B<sub>31.5</sub> metallic glass were found to follow the Avrami rate equation over a wide range of transformed fractions (5-95%); and the Avrami coefficient indicated that the crystals grow in a spherulite form.

### Low Temperature Alloying in the Pd/Au System

H. D. SHIH, E. BAUER and H. POPPA, *Thin Solid Films*, 1982, **88**, (2), L21-L24

AES studies of low temperature alloying in the Pd-Au system were made on one to two monolayers of Pd deposited onto Au(III) at room temperature. The results showed that the surface alloying between Pd and Au occurs at room temperature, while massive alloying takes place by 530K.

### Are VPd<sub>3</sub> and NbPd<sub>3</sub> Itinerant Ferromagnets

W. L. BURMESTER and D. J. SELLMYER, *J. Appl. Phys.*, 1982, **53**, (3), 2024-2026

Low-field magnetic susceptibility and high field magnetisation results are reported for polycrystalline samples of NbPd<sub>3</sub>, VPd<sub>3</sub> and Fe doped VPd<sub>3</sub>. Recent self-consistent, spin-polarised band calculations have predicted that the pure compounds are itinerant ferromagnets. The Fe-doped alloys exhibit a low temperature transition to a magnetic cluster-glass state.

### Temperature Dependence of the Sensitivities of Metal-TiO<sub>2</sub> Junctions to Various Reducing Gases

N. YAMAMOTO, S. TONOMURA and H. TSUBOMURA, *J. Electrochem. Soc.*, 1982, **129**, (2), 444-446

The current through a Pd-TiO<sub>2</sub> diode is sensitive to H<sub>2</sub> at room temperature and becomes sensitive to other reducing gases and vapours such as CO, C<sub>2</sub>H<sub>5</sub>OH and propylene at high temperatures. Experiments were performed with TiO<sub>2</sub> and Pt, Au, Al, Ni, Cu, Mg and Zn. Pt-TiO<sub>2</sub> and Au-TiO<sub>2</sub> diodes are also sensitive to H<sub>2</sub>, the sensitivity being in the order Pd > Pt > Au. The diode sensitivity depends on the catalytic properties of the metal to the reduction between O<sub>2</sub> adsorbed on the metal surface and reducing gases, resulting in a lowered potential barrier height at the interface.

### Crystal Structure, Superconducting and Magnetic Properties of New Ternary Silicides LaRhSi, LaIrSi and NdIrSi

B. CHEVALIER, P. LEJAY, A. COLE, M. VLASSE and J. E. TOURNEAU, *Solid State Commun.*, 1982, **41**, (11), 801-804

New ternary silicides LaRhSi, LaIrSi and NdIrSi were synthesised by arc melting, and their powder patterns were indexed. LaRhSi and LaIrSi have a superconducting transition at 4.35K and 2.3K, respectively. NdIrSi has spontaneous magnetisation below T<sub>c</sub> = 10K.

### Low Temperature Specific Heats of H(NbIrO) and R(NbPtO)

B. CORTI, A. L. GIORGI and G. R. STEWART, *J. Low Temp. Phys.*, 1982, **4**, (1/2), 179-185

The specific heats of hexagonal structures H(NbIrO) and R(NbPtO) were measured from 1.2 to 15K. The R-phase compound was superconducting with T<sub>c</sub> = 3.8K. The reduction in T<sub>c</sub> from 10.1 to 3.8K between the two phases is accounted for by corresponding reductions in the density of states and Debye temperature using the BCS theory.

## Chemical Vapour Transport of Transition Metal Oxides (I) Crystal Growth of RuO<sub>2</sub>, IrO<sub>2</sub> and Ru<sub>1-x</sub>O<sub>2</sub>

C. A. GEORG, P. TRIGGS and F. LÉVY, *Mater. Res. Bull.*, 1982, **17**, (1), 105-110

Single crystals of RuO<sub>2</sub>, IrO<sub>2</sub> and the mixtures RuO<sub>2</sub>:IrO<sub>2</sub> have been prepared from the vapour phase. This is the first time it has been possible to grow single crystals of different concentrations of RuO<sub>2</sub>:IrO<sub>2</sub>.

## The Interaction of Coadsorbed Hydrogen and Carbon Monoxide on Ru(001)

D. E. PEEBLES, J. A. SCHREIFELS and J. M. WHITE, *Surf. Sci.*, 1982, **116**, (1), 117-134

The co-adsorption of H<sub>2</sub> and D<sub>2</sub> with CO on Ru(001) at 100K was studied by various techniques. Pre-adsorbed CO strongly blocks H<sub>2</sub> adsorption. Pre-adsorbed H<sub>2</sub> blocks CO adsorption, but less strongly. The desorption of pre-dosed H<sub>2</sub> from a co-adsorbed layer shows strong long-range CO-H repulsive interactions. The CO sticking coefficient decreases in proportion to the amount of uncovered Ru sites.

## Phase Transformations in Rapidly Quenched Aluminium-Ruthenium Alloys

Z. A. CHAUDHURY, G. V. S. SASTRY and C. SURYANARAYANA, *Z. Metallkd.*, 1982, **73**, (4), 201-206

Rapid quenching of two Al-Ru melts containing 10 and 15wt.% Ru formed supersaturated solid solutions. Subsequent annealing above room temperature indicated a metastable Al<sub>3</sub>Ru phase with a cubic CaF<sub>2</sub>-type structure, and an equilibrium Al<sub>6</sub>Ru phase.

## CHEMICAL COMPOUNDS

### Cobalt, Rhodium and Iridium: Annual Survey Covering the Year 1979; Cobalt, Rhodium and Iridium: Annual Survey Covering the Year 1980

R. D. W. KEMMITT and D. R. RUSSELL; T. J. MAGUE, *J. Organomet. Chem.*, 1982, **230**, 1-98; 99-260

Two annual surveys covering metal C  $\sigma$ -bonded compounds, carbene, isocyanide and carbonyl complexes; homonuclear carbonyl compounds, heteronuclear metal-metal bonded carbonyl compounds metal (I), (II) and (III) compounds, nitrosyl, aryldiazo compounds, metal alkene, alkyne, allyl, cyclo- and other compounds are presented. (421 Refs.; 551 Refs.)

### Structure and Chemistry of Some Carbonyl Cluster Compounds of Osmium and Ruthenium

J. LEWIS and B. F. G. JOHNSON, *Pure Appl. Chem.*, 1982, **54**, (1), 97-112

A review of the cluster compounds of Ru and Os with particular reference to the alternative ways of the bond breaking process. A survey of carbido derivatives and Au-Os complexes is presented. (31 Refs.)

## ELECTROCHEMISTRY

### Structural Effects in Electrocatalysis

R. R. ADŽIĆ, A. V. TRIPKOVIĆ and W. E. O'GRADY, *Nature (London)*, 1982, **296**, (5853), 137-138

The oxidation kinetics of HCOOH, CH<sub>3</sub>OH and CH<sub>2</sub>O on single crystal Pt electrodes with (100), (110) and (111) orientations are reported. Pronounced dependence of the kinetics of these reactions on the crystallographic orientation of the surface was observed. The intermediate completely blocks the Pt(100) surface; the smallest adsorption was at the (111) plane. On activation, the (100) surface had the highest activity. The results suggest that electrocatalytic reactions exhibit structural sensitivity.

### Electroreduction of Oxygen on Reduced Platinum in 85% Phosphoric Acid

W. E. O'GRADY, E. J. TAYLOR and S. SRINIVASAN, *J. Electroanal. Chem. Interfacial Electrochem.*, 1982, **132**, 137-150

Oxygen reduction in highly purified 85% H<sub>3</sub>PO<sub>4</sub> was studied on reduced Pt by rotating ring-disc techniques. The data suggest that the O<sub>2</sub> reduction proceeds by the parallel mechanisms of direct four-electron transfer to H<sub>2</sub>O and through the multistep mechanism involving peroxide intermediate. A value of  $7.6 \times 10^{-7}$  cm<sup>2</sup>/s was determined for the diffusion coefficient in 85% H<sub>3</sub>PO<sub>4</sub> at 25°C.

### The Study of Electrode Processes of Sulphur Dioxide on Platinized Electrode by the Radiochemical Method

M. SZKILARCZYK, A. CZERWINSKI and T. SOBKOWSKI, *J. Electroanal. Chem. Interfacial Electrochem.*, 1982, **132**, 263-271

The adsorption of SO<sub>2</sub> and the electrode reactions of adsorbed molecules at a platinized Pt electrode were studied by potentiodynamic and radiometric techniques. The surface concentration of adsorbed species as well as the charges of their reduction and oxidation were determined. Sulphur adatoms and Pt sulphides as products of SO<sub>2</sub> adsorption in "double-layer" and H<sub>2</sub> regions of potentials are proposed.

### The Development of an Energy-Efficient Insoluble Anode for Nickel Electrowinning. I. Single Layer Precious Metal Coatings. II. Multilayer Precious Metal Coatings

A. J. SCARPELLINO and G. I. FISHER, *J. Electrochem. Soc.*, 1982, **129**, (3), 515-521, 522-525

Precious metal-coated Ti insoluble anodes with increased energy efficiency over conventional Pb electrowinning anodes were developed. Precious metal microlayers extended the life of the Ru-4% Ir coating and made it economical to use at electrowinning temperatures up to 70°C. Several of the multilayered precious metal Ti coatings could operate efficiently as anodes for Ni electrowinning for at least 20,000 h at operating current densities.

### Electrocatalytic Activation of Ruthenium Electrode for the Cl<sub>2</sub> and O<sub>2</sub> Evolution Reactions by Anodic/Cathodic Cycling

M. VUKOVIĆ, H. ANGERSTEIN-KOZŁOWSKA and B. E. CONWAY, *J. Appl. Electrochem.*, 1982, **12**, (2), 193-204

The kinetics of Cl<sub>2</sub> and O<sub>2</sub> evolution on two types of oxidised Ru electrode surfaces subjected to an anodic/cathodic cycling regime from 0.06 to 1.4VE<sub>H</sub> were studied by a steady-state polarisation technique. Current densities for Cl<sub>2</sub> evolution at the cycled Ru surface oxide are ~30 times greater than those at the original Ru surface. O<sub>2</sub> evolution current densities are increased by ~8 times.

### Kinetics of Secondary Processes on Ruthenium-Titanium Anodes in Chloride Solutions

M. M. PECHERSKII, V. V. GORODETSKII, N. IA. BUNE and V. V. LOSEV, *Electrokhimiya*, 1982, **18**, (3), 415-422

The effect of current density and acidity of the solution on corrosion and electrochemical behaviour was studied on treated Ru-Ti anodes prepared by electrodeposition of Ru on Ti in 5M NaCl at 80°C. After thermal and anodic treatment, the secondary processes of Ru dissolving and evolution of O<sub>2</sub> were observed in the surface layer of the electrode without any changes in Cl<sub>2</sub> evolution.

### Reactivities of Ruthenium Cluster Anions: Implications for Catalysis of the Water-Gas Shift Reaction

J. C. BRICKER, C. C. NAGEL and S. G. SHORE, *J. Am. Chem. Soc.*, 1982, **104**, (5), 1444-1445

[HRu<sub>3</sub>(CO)<sub>11</sub>]<sup>-</sup> was used in catalysis in the water-gas shift reaction and its functions were observed. The anion functioned as an apparent hydride donor in the presence of CO at atmospheric pressure and room temperature. Three reactions were observed with CO, [Ph<sub>3</sub>C][BF<sub>4</sub>]<sup>-</sup> and CO, and with H<sub>2</sub>O and CO. All suggest hydridic behaviour for the anion. A new mechanism for the water-gas shift reaction is proposed, whereby [HRu<sub>3</sub>(CO)<sub>11</sub>]<sup>-</sup>-Ru<sub>3</sub>(CO)<sub>12</sub> plays the major role for the reaction in basic media, irrespective of whether the reaction is initiated by tetranuclear or trinuclear Ru carbonylates.

## PHOTOCONVERSION

### Photochemical Diode Model of Pt/TiO<sub>2</sub> Particle and Its Photocatalytic Activity

T. SAKATA, T. KAWAI and K. HASHIMOTO, *Chem. Phys. Lett.*, 1982, **88**, (1), 50-54

The photocatalytic properties of a powdered semiconductor loaded with Pt catalyst are discussed using a photochemical diode model. The rate of H<sub>2</sub> evolution depends on particle size and correlates with the irreversibility of the oxidation of the reactants. Only a small amount of Pt, smaller than 1/100 monolayer on TiO<sub>2</sub>, is required to produce a remarkable effect on photocatalytic activity.

### Photoelectrochemical Behaviour of Ruthenium Disulphide Electrodes in Contact with Aqueous Electrolytes

R. HEINDL, R. PARSONS, A. M. REDON, H. TRIBUTSCH and J. VIGNERON, *Surf. Sci.*, 1982, **115**, (1), 91-103

The photoreaction of a RuS<sub>2</sub> electrode with water for catalytic O<sub>2</sub> evolution was studied as a function of photon energy, electrolyte pH and electrochemical history of the electrode.

### Mechanism of the Uncatalyzed Formation of Dihydrogen in the Radiolytically Induced Reduction of Tris(2,2'-bipyridine)rhodium(III) Ion in Aqueous Solution

Q. G. MULAZZANI, M. VENTURI and M. Z. HOFFMAN, *J. Phys. Chem.*, 1982, **86**, (2), 242-247

The reaction of Rh(bpy)<sub>3</sub><sup>3+</sup> with radiation generated e<sub>aq</sub><sup>-</sup> and (CH<sub>3</sub>)<sub>2</sub>COH in deaerated aqueous solutions containing 0.1M 2-propanol generates H<sub>2</sub> in the absence of any catalyst. The H<sub>2</sub> yield above the background from the radiolytic act is greatest at pH 4.2, but diminishes to zero at pH 2 and 7. A mechanism for uncatalysed H<sub>2</sub> production is postulated with RhH(bpy)<sub>2</sub> as the direct precursor. This arises from reduction of RhH(bpy)<sub>2</sub><sup>2+</sup> by Rh(bpy)<sub>3</sub><sup>2+</sup>. The maximum turnover number for H<sub>2</sub> generation is ~12.

### In Vitro Analogues of Photosystem. II. Combined Flash Photolytic and Conductometric Study of Light-Induced Oxygen Evolution from Water Mediated by Colloidal RuO<sub>2</sub>/TiO<sub>2</sub>

R. HUMPHRY-BAKER, J. LILIE and M. GRÄTZEL, *J. Am. Chem. Soc.*, 1982, **104**, (2), 422-425

Colloidal TiO<sub>2</sub> particles when charged with ultrafine RuO<sub>2</sub> deposits are extremely active catalysts for water oxidation. A photochemical model system of aqueous Ru(bpy)<sub>3</sub><sup>2+</sup> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup> solutions was used to examine the details of the O<sub>2</sub> evolution reaction 4Ru(bpy)<sub>3</sub><sup>3+</sup> + 2H<sub>2</sub>O → 4H<sup>+</sup> + O<sub>2</sub> + 4Ru(bpy)<sub>3</sub><sup>2+</sup>. Flash photolysis and conductance techniques show that hole transfer from Ru(bpy)<sub>3</sub><sup>3+</sup> to the catalyst and proton release from water decomposition occur simultaneously within milliseconds at 3mg RuO<sub>2</sub>/l.

### Visible Light Induced Generation of Hydrogen from H<sub>2</sub>S in CdS-Dispersions, Hole Transfer Catalysis by RuO<sub>2</sub>

E. BORGARELLO, K. KALYANASUNDARAM, M. GRÄTZEL and E. PELIZZETT, *Helv. Chim. Acta*, 1982, **65**, (1), 243-248

Studies of illumination of CdS dispersions by visible light in solutions containing H<sub>2</sub>S or sulphide ions leading to efficient generation of H<sub>2</sub> and S showed that very small quantities of RuO<sub>2</sub> deposited on the CdS particles greatly improve the quantum yield of H<sub>2</sub> formation, for which the optimum value obtained so far is φ = 0.35 ± 0.1. The effect of RuO<sub>2</sub> is attributed to catalysis of hole transfer from the valence band of CdS to H<sub>2</sub>S or sulphide in solution.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Electrodeposition of Precious Metals 1966–January, 1982 (Citations from the Metals Abstracts Data Base)

National Technical Information Service, Springfield, VA. Jan. 1982, PB82-860289, *Materials Science, NTIS*, March 30, 1982, p. 131

A bibliography on electrodeposition of precious metals is discussed including both pure metals and alloys. Plating conditions and substrate materials for Pt, Pd, Rh, Ir, Ru are discussed. Emphasis is placed on fused salt electrolytes. The properties of the plated surface are discussed. (176 Refs.)

## FUEL CELLS

### Design of a Cell for Electrode Kinetic Investigations of Fuel Cell Reactions

H. OLENDER, J. McBREEN, W. E. O'GRADY, S. SRINIVASAN and K. V. KORDESCH, *J. Electrochem. Soc.*, 1982, **129**, (1), 135–137

Two designs of cell for investigating the electrode kinetics of fuel cell reactions in acid media are described. The cells, simulating a phosphoric acid fuel cell at elevated temperature and pressure are used to evaluate Pt/C electrodes.

## HETEROGENEOUS CATALYSIS

### Bifunctional Oxidation of Ammonia with Metal Oxide-Pt/Al<sub>2</sub>O<sub>3</sub> Mechanical Mixtures

Y. KOSAKI, A. MIYAMOTO and Y. MURAKAMI, *Bull. Chem. Soc. Jpn.*, 1982, **55**, (1), 63–68

Selectivity to N<sub>2</sub> in the reaction of NH<sub>3</sub> with metal oxides was greatly increased by the addition of Pt/Al<sub>2</sub>O<sub>3</sub> to the metal oxides. In the oxidation of NH<sub>3</sub> with metal oxide-Pt/Al<sub>2</sub>O<sub>3</sub> mixtures, NH<sub>3</sub> was at first oxidised by metal oxides to form NO<sub>x</sub> and N<sub>2</sub> and then the NO<sub>x</sub> components were transferred through the gas phase from the metal oxides to Pt particles on Al<sub>2</sub>O<sub>3</sub>. Finally, the NO<sub>x</sub> components reacted with NH<sub>3</sub> on Pt particles to form N<sub>2</sub> selectively.

### Effect of Sulfur Poisoning on the Hydrogenolysis Activity of Pt in Pt-Al<sub>2</sub>O<sub>3</sub> Catalysts

P. G. MENON, G. B. MARIN and G. F. FROMENT, *Ind. Eng. Chem., Prod. Res. Dev.*, 1982, **21**, (1), 52–56

The S poisoning of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts was studied during the hydrogenolysis of *n*-pentane by the gas chromatographic pulse titration technique at 300–380°C. The hydrogenolysis activity was reduced to zero only when the atomic ratio of S per exposed Pt atom, S/Pt<sub>s</sub> ≈ 1. The suppression of hydrogenolysis and increase in isomerisation and aromatisation can be achieved only by reversibly adsorbed S on the Pt above that held irreversibly.

### Self-Sustained Oscillations during CO Oxidation on a Pt/γ-Al<sub>2</sub>O<sub>3</sub> Catalyst

P. C. LIAO and E. E. WOLF, *Chem. Eng. Commun.*, 1982, **13**, (4–6), 315–326

A study of the reaction environment and catalyst surface effects on self-sustained oscillations during CO oxidation on Pt/γ-Al<sub>2</sub>O<sub>3</sub> catalysts is presented. The oscillations occurred in a narrow temperature range and low O<sub>2</sub>:CO ratios. Oscillation pattern depended upon catalyst pretreatment; amplitude and frequency varied with surface pretreatment, and decreased as temperature and O<sub>2</sub>:CO ratio increased. There was an overshoot of CO<sub>2</sub> outlet concentration in excess to the 100% conversion, which indicated the participation of surface stored CO.

### Selective Steam Reforming of Aromatic Hydrocarbons.III. Interaction of CO and Toluene in Steam and Hydrodealkylation over RhPt Bimetallic Catalysts

D. DUPREZ, R. MAUREL, A. MILOUDI and P. PEREIRA, *Nouv. J. Chim.*, 1982, **6**, (3), 163–169

Well dispersed RhPt/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared and characterised, and their activities in benzene hydrogenation, steam dealkylation (SDA) and hydrodealkylation (HDA) were studied. The surface compositions were richer in Rh at each composition. During steam dealkylation an inhibiting effect of CO on Rh is ascribed. Hydrodealkylation, a side-reaction in SDA, is more sensitive to CO than the main reaction. This is related to the metallic specificity of the HDA. A reaction scheme is proposed. (33 Refs.)

### Methanation Studies over Well-Characterized Silica-Supported Pt-Ru Bimetallic Clusters

H. MIURA and R. D. GONZALEZ, *J. Catal.*, 1982, **74**, (2), 216–224

A methanation study over a well-characterised series of SiO<sub>2</sub> supported Pt-Ru bimetallic clusters was performed. Turnover numbers and activation energies for CH<sub>4</sub> formation were determined for Pt-Ru bimetallic cluster catalysts with the following Pt surface composition: 17.9, 50, 73 and 99%. The results suggest that Ru ensembles are necessary to catalyse the methanation reaction as Pt-Ru dual sites show a catalytic behaviour characteristic of Pt. A temperature programmed pulse technique was used to study C formation by pulsing CO over each catalyst as the temperature was increased, in He.

### Carbon Monoxide Oxidation on Copper Chromite and Platinum-Copper Chromite Catalysts

G. K. CHITNIS, Ph.D. Thesis, University of Notre Dame, 1982, *Diss. Abstr. Int. B*, 1982, **42**, (7), 2918

CO oxidation was investigated on a Pt-CuO.Cr<sub>2</sub>O<sub>3</sub> bimodal catalyst. The most active catalysts resulted after a reduction which led to the formation of Cu crystallites (200–350Å) supported on amorphous Cr<sub>2</sub>O<sub>3</sub>. The catalyst activity was found to be a combination of Pt and CuO.Cr<sub>2</sub>O<sub>3</sub> functionality.

## Hydrogenated Amination of Aldehydes by Nitrobenzene in the Presence of Complexes of Platinum Group Metals with Chloroanilic Acid

M. V. KLYUEV, S. I. KONDRATEV and M. I. KHIDEKEL, *Kinet. Katal.*, 1982, **23**, (1), 71-76

Complexes of platinum group metals with chloroanilic acid fixed on supports catalyse hydrogenated amination of nitrobenzene. The catalytic activity of the complexes increased in the order: Pt>Pd>Rh>Ir.

## Colloidal Platinum and Palladium Catalysts in the Hydrogenation of Alkyne under Hydrogen Pressure

D. V. SOKOL'SKII and A. ULIKHANOVA, *Zh. Obshch. Khim.*, 1982, **52**, (1), 186-190

Studies of the catalytic properties of colloidal Pt and Pd made during hydrogenation of isomeric hexyne under H<sub>2</sub> pressure, showed that specific activity and general selectivity on Pd particles was higher than that on Pt. The C≡C bond migrates on Pd into C<sup>2</sup>-C<sup>3</sup> and C<sup>3</sup>-C<sup>4</sup> positions. Both on Pt and Pd *cis-trans* isomerisation occurs. Catalysts were stable during saturation of the triple bond of the hexyne. The gradual decrease in activity was observed during hydrogenation of the olefin reaction.

## Preparation of Permanent Pd-Catalysts for Petrochemistry

S. YAMAGUCHI, *Mater. Chem.*, 1982, **7**, (1), 137-142

An aqueous suspension containing  $\alpha$ - and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> served as an abrasive for rubbing Pd plate and Si ingots. The rubbing sludge obtained with Pd and Si particles in even dispersion was an active and durable contact catalyst for the low temperature oxidation of hydrocarbons. Aluminosilicate formed and solidified.

## Effect of Titania on Activity of Alumina Supported Palladium Catalyst during Hydrogenation of Benzene

L. S. KRAVCHUK, E. A. MAKAROVA, I. A. YURSHA, T. I. LARIONOVA, N. I. IVASHCHENKO and S. V. MARKEVICH, *Neftekhimiya*, 1982, **22**, (1), 42-45

The effect of TiO<sub>2</sub> addition on the activity of a 0.3%Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was studied during benzene hydrogenation. Samples reduced in H<sub>2</sub> at atmospheric pressure retained their activity after calcination at 600-800°C. The increase of H<sub>2</sub> pressure to 1.5MPa decreases activity of the catalyst.

## Spectrophotometric Study of Alumina Supported Palladium Catalysts

L. S. KRAVCHUK and S. V. VALIEVA, *Vest. Akad. Nauk BSSR, Ser. Khim. Nauk*, 1982, (2), 50-54

The solubility of oxidised Pd catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> containing 0.1-1.0wt.% Pd was studied in dilute HCl by u.v. spectroscopy. A decrease in Pd solubility was observed in samples containing  $\geq$ 0.5wt.% Pd. This was due to the substantial aggregation occurring during PdO phase formation.

## Methane and Methanol Synthesis over Supported Palladium Catalysts

F. FAJULA, R. G. ANTHONY and J. H. LUNSFORD, *J. Catal.*, 1982, **73**, (2), 237-256

Hydrogenation of CO over Pd supported on three different SiO<sub>2</sub> and on HY and NaY zeolites was studied at 260-340°C and 5 and 50 atm pressure. The selectivity and activity of the catalysts are strongly dependent on the nature of the support and on the state of the metal on its surface. Methanol is produced on the catalysts with small size crystallites on which CO is weakly adsorbed, whereas the formation of methane is directly related to the density of acidic sites at the surface of the support. Pd undergoes structural and electronic modifications due to transformation into hydride phases.

## Selective Hydrogenation of Carbon Monoxide on Supported Rh Catalysts Prereduced in Situ with H<sub>2</sub>O and CO or H<sub>2</sub>

Y. IWASAWA, T. HAYASAKA and S. OGASAWARA, *Chem. Lett.*, 1982, (1), 131-134

CO was selectively converted to ethylene and propylene (>80% of C<sub>1</sub>-C<sub>6</sub> hydrocarbons produced) at 433-447K over Rh/SiO<sub>2</sub> catalysts prereduced in situ with a CO-H<sub>2</sub>O mixture; while other Rh catalysts, obtained by pretreatment in situ with a H<sub>2</sub>-H<sub>2</sub>O mixture yielded ethanol and acetaldehyde at a higher selectivity, by a factor of about 100 at 453K, than a usual Rh(o) catalyst reduced by H<sub>2</sub>.

## Magnetic Resonance Studies on Catalytic Adsorption on Rhodium on Titanium Dioxide

T. M. APPLE, Ph.D. Thesis, University of Delaware, 1981, *Diss. Abstr. Int. B*, 1982, **42**, (7), 2846

The adsorption of H<sub>2</sub> and CO on Rh/TiO<sub>2</sub> was studied by NMR. The spectra of the surface species formed upon H adsorption revealed the presence of four types of H, three of which are irreversibly bound, and one is reversibly bound and formed by spillover from the Rh metal. Upon co-adsorption of CO this spillover H is not formed. There is an interaction between adsorbed CO and adsorbed H at room temperature.

## Support Effects on the Catalytic Activity and Selectivity of Ruthenium on CO and N<sub>2</sub> Activation

A. BOSSI, F. GARBASSI and G. PETRINI, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, (4), 1029-1038

CO and N<sub>2</sub> isotopic equilibration reactions were studied on Ru catalysts supported on Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and MgO. The reactivity in CO equilibration was found to follow the order: Al<sub>2</sub>O<sub>3</sub> > MgO > SiO<sub>2</sub>. Ru/MgO catalysts heated in vacuum at 673K and then reduced showed the highest activity. The Fischer-Tropsch reaction carried out on samples supported on Al<sub>2</sub>O<sub>3</sub> or MgO at ~50 atm and 530K produced a great amount of oxygenated components.

## Structure and Physico-Chemical Properties of Skeletal Ruthenium Catalysts

G. A. KIL'DIBEKOVA, A. B. FASMAN, A. I. LIASHENKO and V. N. ERMOLAEV, *Zh. Prikl. Khim. (Leningrad)*, 1982, **55**, (1), 72-76.

Studies of the structure and physico-chemical properties of Ru catalysts made from Ru-Fe, Ru-Co and Ru-Ni alloys containing 1 wt.% Ru showed that the products of their electrochemical disintegration were finely dispersed amorphous powders. Ru-Ni slurry contained metallic Ru and Ni oxides, Ru-Co-Ru,  $\text{Co}_2\text{RuO}_4$  and  $\alpha$ -Co. Selectivity of the catalysts during hydrogenation of industrial acetylene was first order.

## Hydrogenation of Benzene to Cyclohexene on a Ruthenium Catalyst. Physical and Chemical Characterisation of the Catalyst and Its Precursors

C. U. I. OBENBRAND and S. L. T. ANDERSSON, *J. Chem. Technol. Biotechnol.*, 1982, **32**, (2), 365-375

The chemical and physical characteristics of a Ru catalyst, consisting of metallic Ru obtained by  $\text{H}_2$  reduction of the precursor suspended in the alkaline aqueous phase, were studied during the hydrogenation of benzene. The precursor consists of hydrous oxides of Ru with a surface area of  $27\text{m}^2/\text{g}$ . After reduction the surface area increases to  $112\text{m}^2/\text{g}$  and the average pore diameter decreases from 28 to 13 nm and the number of pores <8nm increases substantially. The macroscopic particle size (25-40  $\mu\text{m}$ ) decreases along with decreasing Ru concentration.

## Homologation of Methanol by Cobalt-Ruthenium Mixed Catalysts

K. KUDO and N. SUGITA, *Nippon Kagaku Kaishi*, 1982, (3), 462-471

The homologation of methanol to ethanol was performed by a Ru-Co catalyst containing iodide promoters using ( $\text{H}_2$ -CO) gas under pressure. Reaction variables were examined; yield and selectivity of ethanol depend significantly on the Ru:Co ratio and the  $\text{H}_2$ :CO ratio. Yield increased with the charge ratio  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}:\text{Co}_2(\text{CO})_8$  reached a maximum, then decreased at larger ratios. The optimum Ru:Co ratio was 0.2-0.4.

## An Infrared Study of Supported Ruthenium Catalysts Prepared from $\text{Ru}_3(\text{CO})_{12}$

T. KIMURA, T. OKUHARA, M. MISONO and Y. YONEDA, *Nippon Kagaku Kaishi*, 1982, (2), 162-169

The structure and decomposition of  $\text{Ru}_3(\text{CO})_{12}$  dispersed on  $\text{SiO}_2$ , ZnO,  $\gamma\text{-Al}_2\text{O}_3$  and MgO was examined by i.r. spectroscopy. With  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{Ru}_3(\text{CO})_{12}$  strongly interacted, forming a very stable species. Thermal decomposition of  $\text{Ru}_3(\text{CO})_{12}/\gamma\text{-Al}_2\text{O}_3$ , followed by  $\text{H}_2$  reduction at  $450^\circ\text{C}$  formed Ru catalysts with high dispersion. CO was adsorbed in linear- and twin-types on  $\text{Ru}/\text{Al}_2\text{O}_3$ .

## Effect of Preparation Procedure on the Properties of Ruthenium Black

G. Z. ZAKUMBAEVA, B. K. KARAKEEV, L. B. SHAPOVALOVA and KH. G. OMASHEV, *Kinet. Katal.*, 1982, **23**, (2), 474-480

Studies of the effect of preparation procedure for Ru black on the adsorption of  $\text{H}_2\text{O}$  in liquid and gaseous phases showed that dispersion of the catalyst depends on the nature of complex salts used during its preparation, on  $\text{H}_2$  pressure, temperature and time of reduction. Temperature of  $\text{H}_2\text{O}$  adsorption on Ru-black was measured.

## HOMOGENEOUS CATALYSIS

### Rh(I) Complexes Containing Fully Alkylated Mono- and Diphosphine Ligands as Highly Active Hydrogenation Catalysts for Carbonyl Compounds

K. TANI, K. SUWA, E. TANIGAWA, T. YOSHIDA, T. OKANO and S. OTSUKA, *Chem. Lett.*, 1982, (3), 261-264

Cationic Rh(I) complexes with fully alkylated diphosphine ligands  $[\text{Rh}(\text{i-Pr})_2\text{P}(\text{CH}_2)_n\text{P}(\text{i-Pr})_2](\text{NBD})\text{ClO}_4$  ( $n=3, 4$ ) have been produced. These have been found to be versatile and efficient catalysts for the hydrogenation of a variety of carbonyl compounds, including aldehydes.

### Catalytic Hydrogenation of 3,4-Epoxybut-1-ene with Cationic Rhodium Complexes

H. FUJITSU, E. MATSUMURA, S. SHIRAHAMA, K. TAKESHITA and I. MOCHIDA, *J. Chem. Soc., Perkin Trans. I*, 1982, (3), 855-859

Catalytic hydrogenation of 3,4-epoxybut-1-ene with cationic Rh complexes was studied under 1 atm of  $\text{H}_2$  at  $30^\circ\text{C}$ . The catalytic activity of the epoxide depended on the nature of the P ligands of the catalyst. The order of activity of the ligands for the formation of alcohols was different from that observed for hydrogenation of 1,2-epoxy-1-phenylethane. It is noted that the diphos- and  $\text{PPh}_3$  catalysts which showed quite limited activity for both the carbonyl compound and 1,2-epoxy-1-phenylethane, exhibited considerable activity for the title compound.

### Oxidation of Unsaturated and Hydroxy Fatty Acids by Ruthenium Tetroxide and Ruthenium Oxyanions

Y. NAKANO and T. A. FOGLIA, *J. Am. Oil Chem. Soc.*, 1982, **59**, (4), 163-166

The reactions of  $\text{RuO}_4$ ,  $\text{RuO}_4^-$  and  $\text{RuO}_4^{2-}$  with hydroxy substituted and unsaturated fatty acids were studied. At a 1 : 1 molar ratio,  $\text{RuO}_4$  and both oxyanions oxidised 12-hydroxystearic acid to 12-kerostearic acid. With 9-10-dihydroxystearic acid the type of oxidation products depended on the amount of Ru used. Oxidation of oleic acid with excess  $\text{RuO}_4$  or  $\text{RuO}_4^-$  gave pelargonic and azelaic acid.  $\text{RuO}_4^{2-}$  did not react with oleic acid.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### A Comparison of the Performance of Gold and Platinum Killed Power Diodes

S. D. BROTHERTON and P. BRADLEY, *Solid-State Electron.*, 1982, **25**, (2), 119-125

Measurement of leakage current, switching time and forward voltage drop are presented for Pt and Au killed diodes. Under specified conditions improved switching is obtained from Pt killed devices due to the life time profile produced at elevated temperatures by the shallow recombination centre.

### Auger Electron Spectroscopy Analysis of the Contact Reaction of Pt-Si Codeposited Films and Silicon

M. EIZENBERG and R. BRENER, *Thin Solid Films*, 1982, **88**, (1), 41-48

Codeposited alloy films of Pt-Si on Si, used for the formation of shallow Schottky contacts, were studied by AES. The coat depth after annealing was larger than expected. An accumulation of Si and depletion of Pt in the outer 200-300Å of the film was also observed. Studies of the line shape for Auger transitions showed that the outer Si-rich region consists of a mixture of PtSi and elemental Si.

## MEDICAL USES

### High-Performance Liquid Chromatography Studies on Platinum Thymine Blue

J. D. WOOLLINS and B. ROSENBERG, *Inorg. Chem.*, 1982, **21**, (3), 1280-1282

Platinum thymine blue, PTB which has antitumour properties was examined by high-performance liquid chromatography. This revealed that typical preparations of PTB contain several colourless Pt compounds ("whites") as well as a number of blue species. This is the first time that the various blue components in PTB have been separated.

### Osmium-Carbohydrate Polymers as Anti-Arthritic Drugs

C. C. HINCKLEY, J. N. BEMILLER, L. E. STRACK and L. D. RUSSELL, *Book of Abstracts*, 183rd Am. Chem. Soc. Natl. Meeting, Las Vegas, Na., 1982, Inorganic Paper 68

Osmium-carbohydrate polymers (osmarins) have been prepared and characterised, and are now being investigated as potential anti-inflammatory agents for some forms of arthritis. When dilute osmarin solutions are injected into the synovial space of a joint they bind irreversibly to articular cartilage and to the joint capsule.

## NEW PATENTS

### ELECTROCHEMISTRY

#### Recombination Device for Storage Batteries

ATOMIC ENERGY OF CANADA LTD.

*British Appl.* 2,084,388 A

The amount of H<sub>2</sub>O lost in a recombination process is reduced by using a water-resistant PTFE supported platinised C catalyst which is not degraded when recombined H<sub>2</sub>O is drained over the catalyst particles.

#### Platinum Metal Coated Electrodes

DIAMOND SHAMROCK CORP. *European Appls.* 46,447/9

A Ti or other valve metal substrate is coated with a platinum group metal or platinum group metal oxide coating by application of a dilute solution containing an Ir, Rh, Ru or other platinum group metal salt and HCl or another agent which will attack the Ti base.

#### New Ion Exchange Resins

HOECHST A.G.

*European Appls.* 47,945/50

New ion exchange resins are made from perfluorocarbonyl sulphonic acid fluorides which are obtained by the electrolysis of monohydroperfluoroalkane sulphonic halides against a Pt wire electrode. Os and Ir electrodes are also claimed.

#### Activated Cathode for Aqueous Solution Electrolysis

HODOGAYA CHEMICAL CO. LTD. *U.S. Patent* 4,300,992

An electrode which controls the amount of hypochlorous ion formed in electrolysis reactions and which has excellent corrosion resistance is made from a valve metal or alloy substrate, and an oxide coating containing a Ru, Rh, Pd, Os, Ir and/or Pt oxide.

#### Photochemical Electrode for Water Decomposition

NATIONAL RESEARCH DEVELOPMENT CORP.

*U.S. Patent* 4,305,794

A photochemical electrode which can decompose H<sub>2</sub>O when irradiated with visible light is obtained by treating a Pt mesh with red mercuric sulphide blackened by iodide treatment.

#### Catalysed Chloralkali Cathode

JOHNSON MATTHEY & CO. LTD. *French Appl.* 2,480,795

A cathode for use in brine or H<sub>2</sub>O electrolysis cells is made from an electrically conductive matrix carrying a surface deposit of a platinum group metal, Au or Ag catalyst, preferably Pt and/or Ru. The matrix may be made of Ni, Cu, austenitic steel or another base metal on to which the catalyst is deposited by chemical displacement.