

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Effect of Evolution of Gases by High Temperature UHV Treatment of Rh, Pt, and Nb on the Formation of Highly Active Surface

S. NISHIYAMA, K. YOSHIOKA, S. TSURUYA and M. MASAI, *Vide*, 1987, **42**, (236), 47-49

The UHV treatment of Rh metal powder and  $H_2PtCl_6 \cdot 6H_2O$  powder and Nb(V) compounds is reported. The  $H_2PtCl_6 \cdot 6H_2O$  decomposed to metallic Pt. Gases evolved during Rh treatment consisted mostly of  $N_2O$ . For the Pt compound the gases evolved were mainly  $H_2O$  and HCl. XRD powder patterns were taken of the Rh and metallic Pt after UHV treatment, and results for the  $H_2$ - $D_2$  exchange reaction show low activation energies and indicate that the Pt and Rh surfaces were active for  $H_2$  molecular dissociation.

### Synthesis and Study of Binary Actinoid and Lanthanoid Compounds. IX. Thermal Decomposition of Intermetallides $Pt_3Sm$ , $Pt_3Gd$ and $Pt_3Am$

M. A. RYABININ, V. M. RADCHENKO, A. G. SESEZNEV, L. S. LEBEDEVA, V. D. SHUSHAKOV and V. YA. VASIL'EV, *Radiokhimiya*, 1987, **29**, (3), 276-279

Studies of the thermal decomposition of intermetallides  $Pt_3Sm$ ,  $Pt_3Gd$  and  $Pt_3Am$  in vacuum showed that they had high thermal stability in vacuum below the melting temperatures, but were quickly split up in liquid solutions. The high melting temperatures of the intermetallides studied makes it difficult to obtain pure lanthanoid and actinoid metals from intermetallides by thermal decomposition methods.

### Intergranular Embrittlement of Pt-Rh Alloys

YU. P. DENISOV, A. S. DRACHINSKII, YU. N. IVASHCHENKO, A. V. KRAINIKOV, A. V. PRONIN, N. I. TIMOFEEV and S. A. FIRSTOV, *Fiz. Met. Metalloved.*, 1987, **63**, (3), 604-609

Studies of the effect of aggressive media on the composition and structure of surface embrittled 13-18at.% Pt-Rh alloys were performed in molten glass at 1400°C. Continuous tempering resulted in brittle intergranular disintegration. Selective dissolution of Pt occurred along the grain boundaries due to electrochemical reduction. Corrosion results showed 2-3 times lower Pt content on grain boundaries in relation to Rh, while grain boundaries became enriched by  $O_2$ ,  $H_2$ , Al, Si and Mg. The depth of the layer of the chemical heterogeneity depended on the degree of proceeding of the reaction and is estimated to be several tenths of intermetallic spacing.

### Correlation of the Concentration Dependences of the Characteristics of Interdiffusion and Heat Resistance of Platinum Metals Alloys

B. S. DRILENOK, G. M. KUZNETSOV and E. I. RITVIN, *Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall.*, 1987, (2), 88-92

Studies were made of the coefficients of interdiffusion  $\bar{D}$ , and the values of the activation energies in the interdiffusion process were calculated for platinum alloys. The increased Rh concentration in Pt-Rh alloys resulted in a decrease in the  $\bar{D}$  coefficient from  $5 \cdot 10^{-11}$  to  $2 \cdot 10^{-12} \text{ cm}^2/\text{s}$ . In Pd-Rh alloys, an increase in Rh concentration resulted in a decrease of  $\bar{D}$  coefficient from  $3 \cdot 10^{-10}$  to  $6 \cdot 10^{-12} \text{ cm}^2/\text{s}$ . In the Rh concentration range of 30-70at.% the  $\bar{D}$  coefficient stays constant at  $4.5 \cdot 10^{-11} \text{ cm}^2/\text{s}$ .

### Study of the Surface Composition and Catalytic Properties of the System $Zr_2Pd-H$

E. N. ANISOCHKINA, V. V. LUNIN, P. A. ZHDAN, G. D. CHUKIN and I. I. SKARZOV, *Kinet. Katal.*, 1987, **28**, (2), 427-430

The mechanism of the formation of the active surface system  $Zr_2Pd-H$  was studied spectroscopically. The results showed that the presence of  $Pd^0$  on the surface of the catalyst was due to the catalytic activity of the initial  $Zr_2PdH_{2.7}$  during hydrocarbon conversion. The increase in catalytic activity and selectivity of  $Zr_2PdH_x$  after oxidation-reduction treatment is associated with Pd segregation in the near surface layer. The H dissolved in the crystal lattice of  $Zr_2PdH_x$  was found to affect the formation of the structure and composition of the surfaces.

### Phase Equilibria in the Ternary System Cu-Ni-Ru at 770K

I. E. YANSON, M. V. RAEVSKAYA and A. L. TATARKINA, *Vestn. Mosk. Univ., Ser. II. Khim.*, 1987, **28**, (2), 195-197

Phase equilibria in the ternary system Cu-Ni-Ru were studied by microstructural and X-ray analysis, and by measuring hardness and microhardness of the alloys at 770K. The isothermal section adjoining Cu-Ni showed a wide layer of solid solution  $\alpha$ , which became narrower with increased Cu content. In view of the absence of visible dissolution of Cu in Ru solid solution, Ru base phase  $\epsilon$  was practically unobserved in the ternary system and was badly attached to the Ru-Ni side up to 7at.%Ni. The biggest part of the isothermal section in the Cu-Ni-Ru system was taken up by binary phase section  $\alpha + \epsilon$ . A special feature of this section appears to be penetration of a dome of immiscibility of complexes on the Cu-Ru side in the centre of concentrations, up to 45at.%Ni.

## CHEMICAL COMPOUNDS

### A General Synthetic Route for Platinum Cluster Compounds Containing Carbonyl and Tertiary Phosphine Ligands and a Study of Their Reactions with Unsaturated Inorganic Molecules

D. G. EVANS, M. F. HALLAM, D. M. P. MINGOS and R. W. M. WARDLE, *J. Chem. Soc., Dalton Trans.*, 1987, (8), 1889-1895

The reduction of  $\text{cis-}[\text{PtCl}_2(\text{CO})(\text{PR}_3)]$  where R is a variety of alkyl or aryl groups, by Zn dust or by Na tetrahydroborate under a CO atmosphere is an efficient high yield method for the formation of tri-, tetra-, and penta-nuclear clusters. The method gives superior yields, greater convenience and has more generality than other methods.

### Platinocyclobutane Chemistry: Platina-cyclobutanes from Bicyclo[X.1.0] Hydrocarbons

E. J. PARSONS and P. W. JENNINGS, *J. Am. Chem. Soc.*, 1987, **109**, (13), 3973-3977

A method for the preparation, isolation and characterisation of platinacyclobutane complexes from substrates such as bicyclo[X.1.0] alkanes and alkenes (X=4, 6) is presented. In the absence of strongly co-ordinating solvents the 8 membered ring complex rearranges to a hydrocarbon containing 1-methylcyclooctene, the exocyclic methylene derivative, and cyclononene. Finally the platinacyclobutane from bicyclo[6.1.0]nonane rearranges to methylidynylcyclooctane via an initial  $\alpha$ -hydride transfer mechanism.

### Complexes of Iridium and Platinum Containing 5-Coordinated Phosphorus

A. J. BLAKE, R. W. COCKMAN, E. A. V. EBSWORTH, S. G. D. HENDERSON, J. H. HOLLOWAY, N. J. PILKINGTON and D. W. H. RANKIN, *Phosphorus Sulfur*, 1987, **30**, (1-2), 143-146

Complex  $\text{Ir}(\text{CO})\text{Cl}_2(\text{PEt}_3)_2(\text{P}^1\text{F}_4)$  has been prepared in high yield from  $\text{XeF}_2$  and  $\text{Ir}(\text{CO})\text{Cl}_2(\text{PEt}_3)_2(\text{P}^1\text{F}_2)$  and characterised by various techniques. Related species  $\text{Ir}(\text{CO})\text{BrH}(\text{PEt}_3)_2(\text{P}^1\text{F}_2\text{H}_2)$  and  $\text{PtCl}(\text{PEt}_3)_2(\text{P}^1\text{F}_4)$  which were also formed by reactions of  $\text{XeF}_2$  are reported.

### Half-Sandwich Chiral Ruthenium Complexes

G. CONSIGLIO and F. MORANDINI, *Chem. Rev.*, 1987, **87**, (4), 761-778

A summary of studies of the stereochemical course of selected metallorganic reactions, and the diastereomeric equilibria of compounds containing prochiral ligands is presented for reactions using half-sandwich chiral Ru complexes. Among reactions studied are alkylations, hydrido complex formation, halide ligand substitution reactions and acetonitrile complex substitution; olefin and alkylidenecarbene complexes are discussed (125 Refs.)

### Synthetic, Electrochemical, Optical, and Conductivity Studies of Coordination Polymers of Iron, Ruthenium and Osmium Octa-ethylporphyrin

J. P. COLLMAN, J. T. MCDEVITT, C. R. LEIDNER, G. T. YEE, J. B. TORRANCE and W. A. LITTLE, *J. Am. Chem. Soc.*, 1987, **109**, (15), 4606-4614

The synthesis and characterisation of a series of ligand-bridged metalloporphyrin polymers  $[\text{M}(\text{OEP})\text{L-L}]_n$ , where M=Ru, Os, Fe, L-L=pyrazines, 4,4'-bipyridine, 1,4-diazabicyclo[2.2.2.]octane, are reported. The polymers are highly conductive when partially oxidised; their conductivity depends on the doping, the nature of the central transition metal and the bridging ligand.

## ELECTROCHEMISTRY

### Electrochemistry at Pt Band Electrodes of Width Approaching Molecular Dimensions. Breakdown of Transport Equations at Very Small Electrodes

R. B. MORRIS, D. J. FRANTA and H. S. WHITE, *J. Phys. Chem.*, 1987, **91**, (13), 3559-3564

Pt and Au band electrodes, 0.5-1 cm long and 20-500 Å wide were constructed by evaporation techniques and their electrochemical behaviours observed. The qualitative behaviour of these electrodes in voltammetric experiments with ferrocene in acetonitrile and ferrocyanide in water was similar to that of larger microelectrodes.

### Ohmic Resistance of Polypyrrole-Modified Electrodes with Incorporated Pt Particles

F. T. A. VORK, L. J. J. JANSSEN and E. BARENDRECHT, *Electrochim. Acta*, 1987, **32**, (8), 1187-1190

The ohmic resistance of polypyrrole modified electrodes was studied as a function of the potential by the a.c. impedance method. When the potential was decreased from -0.2 to -0.3 V the ohmic resistance showed a sharp increase. The electrodeposition of Pt particles in the film did not change the resistance at high potentials but decreased the rise in ohmic resistance at low potentials. This decrease depends on the current density used for the deposition.

### Oxygen Evolution Reaction on Thermally Treated Iridium Oxide Films

M. VUKOVIĆ, *J. Appl. Electrochem.*, 1987, **17**, (4), 737-745

The properties of electrochemically grown and thermally treated oxide films on Ir were examined by cyclic voltammetry and potentiostatic polarisation at  $\text{O}_2$  evolution potentials in 0.5 mol/dm<sup>3</sup>  $\text{H}_2\text{SO}_4$ . The oxide was grown by square wave pulses from -0.25 to +1.25 V S.C.E., which is much faster than potentiodynamic activation at the same frequency. The activated electrode, with low corrosion resistance during  $\text{O}_2$  evolution, was then stabilised by heat treatment. Optimal conditions are at 200-300°C.

## The Oxidation of Chloride Ions and Bromide Ions on Ruthenium Dioxide Electrodes

J. A. HARRISON and S. D. HERMIJANTO, *J. Electroanal. Chem. Interfacial Electrochem.*, 1987, **225**, (1/2), 159-175

The oxidation of solutions containing chloride ions at RuO<sub>2</sub>/TiO<sub>2</sub> electrodes was studied using steady current-potential and impedance-potential measurements as a function of the chloride ion concentration. At chloride ion concentrations >0.1M, a 40 mV Tafel slope was observed at low potentials which increased at the higher potentials. At the lower chloride concentration of 0.1M, where the O<sub>2</sub> evolution reaction is significant, the Tafel slope for the Cl<sub>2</sub> evolution reaction appears to increase to 70mV.

## PHOTOCONVERSION

### Colloidal Platinum Catalyst Protected by Nonionic Monomeric and Polymerized Micelle for Photochemical Hydrogen Generation from Water

N. TOSHIMA, T. TAKAMASHI and H. HIRAI, *Chem. Lett. Jpn.*, 1987, (6), 1031-1034

A colloidal dispersion of Pt protected by nonionic polymerised micelles was prepared by visible light irradiation followed by  $\gamma$ -ray polymerisation of an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> and polyethylene glycol undecenoate. The colloidal Pt obtained showed higher catalytic activity in photochemical H<sub>2</sub> generation than when protected by the corresponding anionic polymerised micelle.

### Photocatalytic Production of Hydrogen from H<sub>2</sub>S Solutions over CdS/Pt Colloids

N. Z. MURADOV, M. I. RUSTAMOV, A. D. GUSEINOVA and YU. V. BAZHUTIN, *React. Kinet. Catal. Lett.*, 1987, **33**, (2), 279-283

Photocatalytic decomposition of H<sub>2</sub>S over Pt/CdS was studied on the catalysts prepared by CdS decomposition from CdSO<sub>4</sub> and Na<sub>2</sub>S solutions in the presence of Pt colloid obtained from H<sub>2</sub>PtCl<sub>6</sub> reduction by NaBH<sub>4</sub> in poly(vinyl alcohol). The CdS/Pt colloids sensitised the photodecomposition of H<sub>2</sub>S into H<sub>2</sub> and S in aqueous solutions under visible light.

### Photocatalytic Reduction of NO<sub>3</sub><sup>-</sup> to Form NH<sub>3</sub> over Pt-TiO<sub>2</sub>

A. KUDO, K. DOMEN, K.-I. MARUYA and T. ONISHI, *Chem. Lett. Jpn.*, 1987, (6), 1019-1022

Photocatalytic reduction of NO<sub>3</sub><sup>-</sup> to form NH<sub>3</sub> and the simultaneous evolution of O<sub>2</sub> were observed over 0.3wt.% Pt-TiO<sub>2</sub> in aqueous HNO<sub>3</sub> and Na nitrate solutions. The amounts of NH<sub>3</sub> and O<sub>2</sub> produced increased proportionally to the irradiation. The rate of NH<sub>3</sub> formation increased with the increase of HNO<sub>3</sub> concentration. The reaction also occurred over TiO<sub>2</sub> loaded with Rh and Pd. A small amount of H<sub>2</sub> (0.05 $\mu$ mol/h) was evolved on the 0.3wt.% Pd-TiO<sub>2</sub>.

## Photoassisted Hydrogen Generation: Pt and CdS Supported on Separate Particles

A. SOBCZYNSKI, A. J. BARD, A. CAMPION, M. A. FOX, T. MALLOUK, S. E. WEBBER and J. M. WHITE, *J. Phys. Chem.*, 1987, **91**, (12), 3316-3320

A comparison between the catalytic properties of platinised TiO<sub>2</sub>, ZnO, SnO<sub>2</sub> and WO<sub>3</sub>, all on SiO<sub>2</sub>, mixed CdS/SiO<sub>2</sub>, was performed for visible light photoassisted H<sub>2</sub> production from methanol-water solutions. Activity is higher for separately supported particles than for samples prepared by depositing the active materials on the SiO<sub>2</sub> particles.

### Photohydrogenation of Acetylenes in Water-Oil Two-Phase Systems: Application of Novel Metal Colloids and Mechanistic Aspects of the Process

D. MANDLER and I. WILLNER, *J. Phys. Chem.*, 1987, **91**, (13), 3600-3605

Photohydrogenation of phenylacetylene and methylphenylacetylene was accomplished in a water-cyclohexane system using Ru(bpy)<sub>3</sub><sup>2+</sup> as a photosensitiser, a charge relay, Na<sub>2</sub>EDTA as a sacrificial electron donor in the photosystem, and a Pt or Pd colloid stabilised in the organic phase as a hydrogenation catalyst. Pt is a superior catalyst to Pd in the generation of metal-bound H atoms, but Pd is better than Pt in activating the substrate for hydrogenation.

### Methanation and Photo-Methanation of Carbon Dioxide at Room Temperature and Atmospheric Pressure

K. R. THAMPI, J. KIWI and M. GRÄTZEL, *Nature*, 1987, **327**, (6122), 506-508

The selective conversion of CO<sub>2</sub> to CH<sub>4</sub> at room temperature and atmospheric pressure has been performed using a catalyst of highly dispersed Ru/RuO<sub>x</sub> loaded onto TiO<sub>2</sub>. If the support TiO<sub>2</sub> powder is photoexcited the reaction rate is sharply enhanced. A turnover number of 28 with respect to the surface Ru atoms was produced without a decline in activity.

## ELECTRODEPOSITION AND SURFACE COATING

### Layer-Selective Metallising of Paper by Electroless Plating Using Surfactant-Stabilized Palladium Sols

Y. NAKAO, T. IMAI and K. KAERIYAMA, *J. Polym. Sci. C*, 1987, **25**, (7), 293-295

Layer-selective metallising of paper was carried out by electroless plating using three types of surfactant-stabilised Pd sols Pd-SC, Pd-SD and Pd-PN, in the presence of surfactants stearyltrimethylammonium chloride (SC), sodium dodecylbenzene sulphonate (SD) and polyethylene glycol mono-p-nonylphenyl ether (PN), respectively. The surfactant-stabilised sols which were nearly neutral, could be applied to electroless plating without an acceleration treatment thus outer or middle layers were metallised.

## LABORATORY APPARATUS AND TECHNIQUE

### Antimony-Doped Stannic Oxide-Based Thick-Film Gas Sensors

L. N. YANNOPOULOS, *Sens. Actuators*, 1987, **12**, (1), 77-89

The use of stannic oxide thick films doped with Sb for detecting combustible gases in oxidising and water vapour containing atmospheres is described. The H<sub>2</sub> and CO responses were recorded. The reliability and accuracy of the gas response was ensured by the addition of 5wt.% Pd catalyst and/or other diluents, such as Mg oxide and Ni silicide. Data were obtained at 250-500°C.

### Ultrahigh Vacuum Studies of Pd Metal/Insulator/Semiconductor Diode H<sub>2</sub> Sensors

R. R. RYE and A. J. RICCO, *J. Appl. Phys.*, 1987, **62**, (3), 1084-1092

Steady state and kinetic results for diodes with clean Pd surfaces have been obtained for H<sub>2</sub> detection at H<sub>2</sub> pressures from 10<sup>-10</sup> to 10<sup>-1</sup> torr. This sensitivity limit is at least seven orders of magnitude greater than that obtained for devices with contaminated surfaces. Analysis of the results for clean Pd surfaces indicates that at least two binding states are required for H at the Pd/SiO<sub>2</sub> interface.

## HETEROGENEOUS CATALYSIS

### A Pt/Alumina Catalyst Coated on Aluminum Thin Plate for Oxidation Reaction on Heat Transfer Surface

T. HASHIOKA, S. KOSEDO, M. ITOH, K. YAMAMOTO, H. KAMEYAMA and T. KABE, *Chem. Lett. Jpn.*, 1987, (6), 1067-1070

Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by treatment of Al foil by anodic oxidation of the γ-Al<sub>2</sub>O<sub>3</sub> coating and by Pt impregnation which was performed in a 0.1% chloroplatinic acid solution whose pH was controlled by addition of NH<sub>4</sub>OH. Prepared catalysts showed high activity during the oxidation of acetone.

### Low-Concentration Supported Precious Metal Catalysts Prepared by Thermal Transport

Y. -F. YU-YAO and J. T. KUMMER, *J. Catal.*, 1987, **106**, (1), 313-317

The thermal transport of metal from a sheet of Pt, Pd, or Rh onto an Al<sub>2</sub>O<sub>3</sub> support surface was performed by heating both together in air, to prepare catalysts. The catalytic activity of the Al<sub>2</sub>O<sub>3</sub> powder was then evaluated by CO oxidation. The metal concentration was very low and highly dispersed. The effects of support additives, CeO<sub>2</sub>, temperature and preparation methods on the catalytic activities were assessed. CeO<sub>2</sub> greatly enhances the transfer from the Pt and Rh sheets to the support surface.

### Pt-Sn/Al<sub>2</sub>O<sub>3</sub> Bimetallic Catalysts Prepared by Solvated Metal Atom Dispersion (SMAD) Synthesis and Catalytic Performance

Y. -X. LI and K. J. KLABUNDE, *Langmuir*, 1987, **3**, (4), 558-562

Conventional Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were doped with Sn by using low-temperature organic solutions of Sn atoms/clusters in THF or toluene (solvated metal atom dispersion, SMAD). The resultant SMAD Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalysts showed unusual behaviour in HC conversions. Dehydrocyclisation activities were high when hydrogenolysis (multiple C-C bond cleavages) activities were low. Resistance to S poisoning was good. Alloy formation of Pt-Sn appears to be important.

### On the Selectivity of Bimetallic Catalysts Based on Platinum and Nickel

KH. SH. TKHOANG, KH. D. LAN and I. FEL'TER, *Kinet. Katal.*, 1987, **28**, (1), 137-151

Bimetallic Pt based catalysts Pt-M/Al<sub>2</sub>O<sub>3</sub> and Ni-M/Al<sub>2</sub>O<sub>3</sub> (M=Sn, Sb, Bi or Pb) containing 0.3wt.% Pt and ratio M: Pt of 0.5-5 were studied during cyclohexane dehydrogenation at 100-700°C. The results showed the stabilising effect of the addition of Sn, Pb, Sb, Bi to Pt base catalysts at 450-500°C. The effect of the second metal on the activity and selectivity of the catalyst depends on the nature and character of "metal-metal" and "metal-support" interactions. The explanation of a "bimetallic" effect as the dynamic factor in the reaction, being a regulator and stabiliser of the selectivity in the reaction, is given.

### Activity, Selectivity and Stability of Bimetallic Catalysts in n-Paraffin and Cyclopentane Reforming

J. M. PARERA, C. A. QUERINI, J. N. BELTRAMINI and N. S. FIGOLI, *Appl. Catal.*, 1987, **32**, (1-2), 117-132

Catalytic activity, selectivity and stability under commercial conditions for reforming n-C<sub>5</sub>-n-C<sub>10</sub> paraffins, cyclopentane and methylcyclopentane were studied for Pt/Al<sub>2</sub>O<sub>3</sub> (1) (30kg/cm<sup>2</sup>), Pt-Re-S/Al<sub>2</sub>O<sub>3</sub> (2) and Pt-Ge/Al<sub>2</sub>O<sub>3</sub> (3) (15kg/cm<sup>2</sup>). For n-paraffin transformation the order of activity was (1)>(2)>(3); (1) is most active for hydrocracking, (2) for aromatisation and (3) for isomerisation. (1) has a minimum in coke formation and deactivation with n-heptane as feed, but on (2) and (3) coke formation and deactivation increase from n-C<sub>5</sub> with increase in paraffin length.

### Promotion of Platinum-Based Catalysts for Methanol Synthesis from Syngas

P. MERIAUDEAU, K. ALBANO and C. NACCACHE, *J. Chem. Soc., Faraday Trans. I*, 1987, **83**, (7), 2113-2118

Addition of Mo compounds to SiO<sub>2</sub>-promoted Pt catalysts resulted in an increase in their activity for methanol formation. The Mo oxide promotion was found to partly cover the Pt surface. The respective roles of Pt and Mo are discussed.

## Hydroconversion and Diffusion of n-Heptane on Mordenite Catalysts

A. K. ABOUL-GHEIT, M. F. MENOUFY, A. K. EL-MORSI and S. M. ABDEL-HAMID, *Zeolites*, 1987, 7, (4), 353-359  
Hydroconversion of n-heptane was carried out in a high-pressure continuous plug-flow reactor system over Pt/HM, Re/HM, Pt-Re/HM and Pt-Th/HM catalysts containing hydrogen mordenite (HM). Pt/HM was most selective for n-heptane isomerisation, whereas Pt-Re/HM and Pt-Th/HM had comparable intrinsic isomerisation activities and excellent centric hydrocracking selectivities. Pt-Th/HM gave the highest i-C<sub>4</sub> : n-C<sub>4</sub> ratio.

## Silica-Supported Bis(trialkylphosphine)-platinum Oxalates. Photogenerated Catalysts for Hydrosilation of Olefins

A. L. PRIGNANO and W. C. TROGLER, *J. Am. Chem. Soc.*, 1987, 109, (12), 3586-3595

A heterogeneous hydrosilation catalyst has been prepared by linking a photoactive Pt(C<sub>2</sub>O<sub>4</sub>)L complex to SiO<sub>2</sub> using the functionalised ligand L = (OMe)<sub>2</sub>Si(CH<sub>2</sub>)<sub>2</sub>PEt<sub>2</sub>, and characterised. The catalyst differs from hydrosilation catalysts in its sensitivity to O<sub>2</sub>, lack of an induction period and inhibition by co-ordinating solvents or excess olefin. The catalyst precursor is thermally stable up to 180°C and can be stored for months.

## Hydrogenation of Unsaturated Hydrocarbons in the Presence of Palladium Complexes Fixed on Polymeric Support

L. I. GVINTER, V. M. IGNATOV, L. N. SUVOROVA and V. Z. SHARF, *Neftekhimiya*, 1987, 27, (3), 348-351

New metallocomplex Pd catalysts of Na<sub>2</sub>PdCl<sub>4</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and PdCl<sub>2</sub> fixed on polymeric supports were studied during hydrogenation of unsaturated hydrocarbons at 25°C and atmospheric pressure. The catalysts were highly active and stable during the reaction and did not require additional activation by NaBH<sub>4</sub>. Activity of the catalyst depended on the nature and composition of the solution. In mixed solutions of benzene-methanol, the reaction rate was higher than in pure benzene.

## Heterogeneous Olefin Hydrogenation Catalysis of Metal Cluster Compounds Consisting of Rhodium-Boron Cluster Anion and Rare Earth Cations

K. SAITO, A. NAKAMURA, H. TAKEI and B. WANG, *J. Catal.*, 1987, 106, (1), 292-294

Hydrogenation catalysts with much increased activity and prolonged life have been made by H<sub>2</sub> absorption onto single crystals of Ln[Rh<sub>4</sub>B<sub>4</sub>], Ln[Rh<sub>3</sub>B] and Ln[Rh<sub>3</sub>B<sub>3</sub>], where Ln = lanthanoid elements in the 3+ state. The preparation of the crystals is described, and it was found that they are unique in their potential for activation by H<sub>2</sub> at ambient temperature and atmospheric H<sub>2</sub> pressure. The crystals act under mild conditions with substrate selectivity.

## Methanol from Synthesis Gas over Iron-Rich Iron-Iridium on Silica Catalysts

D. C. KONINGSBERGER, C. P. J. H. BORGMANS, A. M. J. VAN ELDEREN, B. J. KIP and J. W. NIEMANTSVERDRIET, *J. Chem. Soc., Chem. Commun.*, 1987, (12), 892-894  
Under steady state conditions Fe-Ir/SiO<sub>2</sub> catalysts with Fe : Ir = 0.1-5 produce methanol from CO + 3H<sub>2</sub> at 542k and 4.0MPa, with selectivities of 75% and higher.

## Hydroprocessing of Shale Oil Using Ruthenium-Based Catalysts

T. G. HARVEY, T. W. MATHESON, K. C. PRATT and M. S. STANBOROUGH, *Fuel*, 1987, 66, (6), 766-770

Retorted shale oils from the Rundle (Queensland) deposit were hydrotreated in both batch and continuous modes. Two catalysts, a commercial Ni-Mo/Al<sub>2</sub>O<sub>3</sub> and a novel 3.3wt.%Ru/Y zeolite catalyst, were used. The new Ru catalyst displayed N removal and its hydrocracking abilities were far in excess of the commercial system.

## HOMOGENEOUS CATALYSIS

### Platinum Complex-Catalysed Carbonylation of Acetylenic Compounds

Y. TSUJI, T. KONDO and Y. WATANABE, *J. Mol. Catal.*, 1987, 40, (3), 295-304

The carbonylation of acetylenic compounds is effectively catalysed by homogeneous Pt catalysts PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, PtH(SnCl<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub> and Pt(PPh<sub>3</sub>)<sub>4</sub> and Sn(II) (or Sn(IV)) chloride in alcoholic media. During the carbonylation of propargyl alcohol, ethyl-2-methylene-3-hydroxypropanoate was obtained in 68% yield at 100°C under 80kg/cm<sup>2</sup> of initial CO pressure. 3-Butyn-1-ol was selectively cyclocarbonylated to α-methylene-γ-butyrolactone.

### A Novel Palladium-Catalysed Reductive Cyclization

B. M. TROST and R. WALCHLI, *J. Am. Chem. Soc.*, 1987, 109, (11), 3487-3488

A novel chemoselective reductive cyclisation catalysed by Pd is reported. The substrate was readily prepared from cyclohexanone and when treated with 1 equivalent of (tri-n-butylstannyl)diethylalane, 10mol% of Pd(0) catalyst and 4-6 equivalents of Ph<sub>3</sub>P per Pd in THF, at room temperature, then 60°C and finally at 100°C the desired cyclisation product was achieved, at 60% yield.

### The Direct Conversion of Synthesis Gas into Ethylene Glycol Catalysed by RhX(CO)L<sub>2</sub> [X = Anionic Ligand, L = P(cyclo-C<sub>6</sub>H<sub>11</sub>)<sub>3</sub> or PPr<sub>3</sub>]

Y. OHGOMORI, S. -I. YOSHIDA and Y. WATANABE, *J. Chem. Soc., Chem. Commun.*, 1987, (11), 829-831

Higher catalytic activities for the direct conversion of syngas into ethylene glycol have been found for RhX(CO)L<sub>2</sub> complexes.

### Mechanism of Deactivation of Phosphine-Modified Rhodium-Catalysed Hydroformylation: A CIR-FTIR Study

W. R. MOSER, C. J. PAPILE and S. J. WEININGER, *J. Mol. Catal.*, 1987, **41**, (3), 293-302

The deactivation mechanism for the hydroformylation of 1-hexene was studied by cylindrical internal reflectance i.r. spectroscopy (CIR-FTIR) under autogenous conditions. The initial deactivation was found to involve the conversion of the most active catalytic intermediate,  $\text{RhH}(\text{CO})_2(\text{PR}_3)_2$ , to a less active orange dimer  $[\text{Rh}(\text{CO})(\text{PR}_3)_2]_2$  which was followed by the formation of a totally inactive binuclear complex with a bridged phosphido ligand. A series of hydroformylation reactions was performed, in which the triphenylphosphine ligands carried a variety of para-substituents on the phenyl rings.

### Hydroformylation of Formaldehyde to Give Glycolaldehyde with Halide-Promoted $\text{Rh}_4(\text{CO})_{12}$

M. MARCHIONNA and G. LONGONI, *J. Chem. Soc., Chem. Commun.*, 1987, (14), 1097-1098

Hydroformylation of paraformaldehyde and 37% aqueous formaldehyde to give glycolaldehyde with selectivity up to ~ 90% was carried out in acetone at 90-140°C and 100-140 atm CO-H<sub>2</sub>, using  $\text{Rh}_4(\text{CO})_{12}$  promoted with halide as the catalyst precursor.

### Chemo-Selectivity of Group-VIII Metal Catalysts in Hydrogenation of Nonconjugated Enones

J.-I. ISHIYAMA, S. MAEDA, K. TAKAHASHI, Y. SENDA and S. IMAIZUMI, *Bull. Chem. Soc. Jpn.*, 1987, **60**, (5), 1721-1726

The chemo-selectivity of Group VIII metal catalysts was studied during hydrogenation of non-conjugated enones at ambient temperature and atmospheric H<sub>2</sub> pressure. Os showed the highest selectivity among the platinum metal catalysts for the reduction of the carbonyl bond in the hydrogenation of trialkylated olefinic ketones. The hydrogenation of 4-methylene- and 4-ethylidenecyclohexanone was accompanied by the formation of diethyl acetals over Ru, Rh and Pd black catalysts in an ethanol solvent.

### Homogeneous Catalysis by Metal Clusters. 2. Tetranuclear Osmium Complexes as Catalyst Precursors in the Hydrogenation of Styrene

R. A. SÁNCHEZ-DELGADO, A. ANDRIOLLO, J. PUGA and G. MARTÍN, *Inorg. Chem.*, 1987, **26**, (12), 1867-1870

Styrene was efficiently hydrogenated by osmium complexes  $\text{H}_3\text{Os}_4(\text{CO})_{12}(\text{I})$ ,  $\text{H}_4\text{Os}_4(\text{CO})_{12}$ ,  $[\text{H}_2\text{Os}_4(\text{CO})_{12}(\text{I})]^-$  and  $[\text{H}_3\text{Os}_4(\text{CO})_{12}]^-$  in decalin solution at 140°C and 800 torr of H<sub>2</sub>. The reaction rate is dependent on the structure of the cluster and is first order with respect to styrene and hydrogen concentrations. However turnover frequency increases with decreasing cluster concentration. The results are interpreted by cluster fragmentation.

### The Selective Oxidation of Primary Alcohols to Aldehydes by O<sub>2</sub> Employing a Trinuclear Ruthenium Carboxylate Catalyst

C. BILGRIEN, S. DAVIS and R. S. DRAGO, *J. Am. Chem. Soc.*, 1987, **109**, (12), 3786-3787

$\text{Ru}_3\text{O}(\text{O}_2\text{CR})_2\text{L}_3^n$ , (where R=CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>, L=H<sub>2</sub>O or PPh<sub>3</sub>, and n=0 or +1) was found to be an efficient catalyst for the selective oxidation of primary alcohols to aldehydes and of secondary alcohols to ketones by O<sub>2</sub> under mild conditions. Primary alcohol, can be oxidised more rapidly than secondary, but tertiary alcohols were unreactive.

## FUEL CELLS

### Sputtered Fuel Cell Electrodes

M. F. WEBER, S. MAMICHE-AFARA, M. J. DIGNAM, L. PATAKI and R. D. VENTER, *J. Electrochem. Soc.*, 1987, **134**, (6), 1416-1419

H and O fuel cell electrodes were fabricated by sputtering Pt onto wet-proofed porous C and Ni substrates. The H electrodes were diffusion limited at 5-20mA/cm<sup>2</sup>, but the O electrodes performed to 500mA/cm<sup>2</sup> at potentials above 0.7V<sub>H.E.</sub>. Data indicate that at current densities >100mA/cm<sup>2</sup> the reaction was catalysed partly by the high surface area C.

### The Catalytic Activity of Tungsten Carbide Modified by Ion Implantation and Ion Beam Mixing

G. K. WOLF, R. SPIEGEL and K. ZUCHOLL, *Nucl. Instrum. Methods Phys. Res.*, 1987, **B19/20**, (11), 1030-1033

Ion implantation and ion beam mixing were used to dope WC substrates with finely dispersed Pt in an attempt to produce active catalysts for fuel cell electrodes. The catalysts produced were tested for their activity for the electrochemical H redox reaction and the oxidation of formic acid and methanol. Results indicate that the implanted substrate catalysts were much more active than untreated ones, and above a dose of 10<sup>16</sup> Pt<sup>+</sup>/cm<sup>2</sup> the activity even exceeds that of smooth Pt metal. Ion beam mixing was less effective.

### Preparation and Characterisation of Carbon-Based Fuel-Cell Electrodes with Platinum-Group Bimetallic Catalysts

K. V. RAMESHI, P. R. SARODE, S. VASULDEVAN and A. K. SHUKLA, *J. Electroanal. Chem. Interfacial Electrochem.*, 1987, **223**, (1/2), 91-106

Electrochemical activities for H<sub>2</sub> oxidation on porous C electrodes with platinum group bimetallic catalysts Pt+Ru, Pt+Pd and Pd+Ru in acid and alkali electrolytes were measured as a function of composition. Carbon electrodes containing 4wt.%Pt+6wt.%Ru showed the maximum activity, which is also higher than that for the individual metal catalysts. This catalyst was also active for the indirect oxidation of NH<sub>3</sub>, as well as for the reduction of O<sub>2</sub>.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### In Situ Examination of Segregation and Wear Processes of Precious Metal Electrical Contact Alloys

L. E. POPE and D. E. PEEBLES, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1987, **CHMT-10**, 47-55

An UHV pin-on-plate device was assembled to measure simultaneously and continuously the friction coefficient and the electrical contact resistance of a Pd based alloy pin sliding on a Au-based alloy plate, by scanning Auger microscopy. The wear process was of adhesive wear. Initially a prow formed on the pin and subsequently debris was transferred back and forth between pin and plate.

### Metallographic Research on Extruded Copper/Palladium Composite Materials

D. STÖCKEL, K. MÜLLER and H. CLAUS, *Metall*, 1987, **41**, (7), 702-706

Using Cu/Pd composite materials instead of Cu-Pd alloys improves the performance of electrical contacts and reduces their costs. However, the formation of solid solutions at the Cu/Pd interface during composite production must be avoided. The best composite is made by indirect extrusion of a billet formed by rolling together Cu and Pd strips. Mechanical properties, methods of production, recrystallisations, electrical properties, crystal structure are studied.

### Os-Coated Cathode for Very High Emission-Density Applications

A. SHIH, A. BERRY, C. R. K. MARRIAN and G. A. HAAS, *IEEE Trans. Electron Devices*, 1987, **ED-34**, (5), 1193-1200

Os-coated cathodes were prepared by coating "B" type W dispenser cathodes by thermal decomposition of Os(CO)<sub>5</sub> onto cathodes held at 205°C using CVD. The coatings had good adhesion and rapid activation. The activation process involves the formation of a BaO surface layer and also the formation of an optimum surface alloy of 50%Os-50%W. The cathodes had excellent emission capabilities and at 1085°C<sub>p</sub> a zero-field emission density near 50A/cm<sup>2</sup> was obtained. At 1085°C<sub>p</sub> an emission level of 40-50A/cm<sup>2</sup> for over 800h of life is obtainable. The pulsed emission density and surface composition were monitored.

### Effects of Surface Modification on n-CdTe Photoelectrochemical Solar Cells

K. C. MANDAL, S. BASU and D. N. BOSE, *J. Phys. Chem.*, 1987, **91**, (15), 4011-4013

When Ru was used to modify large grain n-CdTe the properties of the n-CdTe photoelectrochemical solar cells were improved. The dark I-V characteristic decreased for J<sub>0</sub> from 8.6 × 10<sup>-3</sup> to 4.2 × 10<sup>-3</sup> A/cm<sup>2</sup> and in ideality factor n from 2.12 to 1.16. Under AM1 illumination V<sub>oc</sub> increased from 0.52 to 0.78V vs.S.C.E., J(short-circuit current density) increased from 3.4 to 5.2mA/cm<sup>2</sup>.

### Characterization of Reactively Sputtered Ruthenium Dioxide for Very Large Scale Integrated Metallization

L. KRUSIN-ELBAUM, M. WITTMER and D. S. YEE, *Appl. Phys. Lett.*, 1987, **50**, (26), 1879-1881

Reactively sputtered films of RuO<sub>2</sub> have been examined for use in VLSI circuits. Sputtering yields stoichiometric RuO<sub>2</sub> in a large window of O<sub>2</sub> pressures and the films are reasonably low stressed in the 10<sup>9</sup> dyn/cm<sup>2</sup> range. The resistivity of as-deposited films is 40μΩcm. The films are excellent barriers against interdiffusion of Si and Al.

## TEMPERATURE MEASUREMENT

### Platinum Resistance Thermometers for Industrial Applications

H. J. A. KLAPPE, *Tech. Mess.*, 1987, **54**, (4), 130-140

The stability, precision and range of uses of commercially available Pt resistance thermometers are discussed. Such thermometers can measure temperatures from -200°C to 850°C. Thin film technology for manufacturing the thermometers has improved the reaction times and reduced the cost. For example, thin films of resistance 1000Ω at 0°C can be used in the car and the heating industries.

### Temperature Coefficients of Resistivity of Rh-Fe Thin Films for Cryogenic Thermometer Use

O. TAMURA and H. SAKURAI, *Jpn. J. Appl. Phys., Part 2. Lett.*, 1987, **26**, L947-L950

The temperature coefficients of electrical resistivity were measured on Rh-Fe thin films sputter deposited onto sapphire substrates from a Rh-0.5at.%Fe target, at temperatures from 4.2K to room temperature, to estimate their thermodynamic sensitivity. The temperature coefficients are close to those of high purity well annealed Rh-0.5at.%Fe wires, although the resistivity is higher than that of the wires. The dilute Fe in the films is as effective as in wires.

## MEDICAL USES

### Radiosensitizers Targeted to DNA Using Platinum. Synthesis, Characterisation, and DNA Binding of cis-[PtCl<sub>2</sub>(NH<sub>3</sub>)(Nitroimidazole)]

N. FARRELL and K. A. SKOV, *J. Chem. Soc., Chem. Commun.*, 1987, (13), 1043-1044

The preparation and characterisation of cis-[PtCl<sub>2</sub>(NH<sub>3</sub>)(misonidazole)] and cis-[PtCl<sub>2</sub>(NH<sub>3</sub>)(metronidazole)] are reported. These complexes bind to DNA and radiosensitise more efficiently than their analogues containing two nitroimidazole groups, and the results confirm the possibility of targeting radiosensitising ligands to DNA by complexation with Pt.