

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Structure of Platinum Aggregates Encaged in Y-Type Zeolite. Effect of CO Adsorption and of CO-H<sub>2</sub> Co-adsorption

P. GALLETZOT, *Zeolites*, 1982, **2**, (2), 103-108

The structure of 10 Å Pt particles encaged in Y-type zeolite was determined from the radial electron distribution method from X-ray diffraction data. CO adsorption at 300K on bare Pt leads to an average f.c.c. lattice with normal bond lengths, but with a displacement disorder of the Pt atoms around the nodes. Thus Pt-Pt distances are contracted or elongated compared to their average lattice. Similar observations in molecular Pt carbonyl clusters could provide good modes for these defects appearing in response to CO bonding.

### Strength and Plasticity of Palladium-Platinum-Hydrogen Alloys

N. T. TIMOFEEV, F. N. BERSENEVA and V. I. GROMOV, *Fiz. Met. Metalloved.*, 1982, **53**, (6), 1189-1193

Studies of the changes in mechanical characteristics of 5-60at.% Pt-Pd alloys under H<sub>2</sub> saturation showed an increase in strength and plasticity for 5at.% Pt-Pd alloys with an occurrence of phase conversion by H<sub>2</sub> saturation. Alloys containing ≥15at.% Pt showed increased strength and some increase in relative pressure during elongation tests of H<sub>2</sub> saturated material.

### Overview 19: Hydrogen in Amorphous Metals—I

R. KIRCHHEIM, F. SOMMER and G. SCHLUCKEBIER, *Acta Metall.*, 1982, **30**, (6), 1059-1068

The solubility and diffusivity of H<sub>2</sub> in amorphous Pd<sub>77.5</sub>Cu<sub>6</sub>Si<sub>16.5</sub> and Ni<sub>49.9</sub>Pd<sub>31.8</sub>P<sub>18.3</sub> were measured electrochemically. The pressure-concentration isotherms had remarkable deviations from Sievert's Law, while the amount of H<sub>2</sub> dissolved lies in-between the solubility of the alloy components. H<sub>2</sub> diffusivity is high (10<sup>-8</sup>cm<sup>2</sup>/s) and depends on temperature and concentration, even at very low H<sub>2</sub>.

### Wear Characteristic of the Sandwich System Nickel-Palladium-Gold

H. GROSSMAN, M. HUCK and G. SCHAUDT, *Metall.*, 1982, **36**, (7), 746-752

Microscopic, microanalysis and X-ray diffraction studies of friction-wear of sandwiched Ni-Pd-Au electrodeposits on connectors with thin Au layers between 0.05-0.5 μm were performed. Hard gold alloy (Au-Co) on Pd with a Ni underlayer shows more favourable friction and wear conditions even as a

thin layer, than pure Au. With hard gold the insertion forces are nearly independent of thickness of the Au deposit, whereas with fine Au the insertion forces become more pronounced with increasing thickness of the pure Au layer.

### Growth Mechanisms and Thermal Stability of Ion-Beam-Induced Epitaxial Pd<sub>2</sub>Si Films

H. ISHIWARA, *Thin Solid Films*, 1982, **92**, (1/2), 147-153

Growth mechanisms and thermal stability of ion-beam-induced epitaxial Pd<sub>2</sub>Si films were studied by Rutherford backscattering and channelling techniques. Epitaxial growth of Pd<sub>2</sub>Si films was observed at room temperature by Ar ion implantation into as-deposited Pd/Si(III) structures and furnace-annealed Pd<sub>2</sub>Si(polycrystalline) / Pd<sub>2</sub>Si(epitaxial) / Si(III) structures. The stability of the ion-beam-induced epitaxial Pd<sub>2</sub>Si films on subsequent furnace annealing is studied.

### The Diffusion of Hydrogen through Palladium-Titanium and Palladium-Vanadium Solid Solutions

M. YOSHIHARA and R. B. MCLELLAN, *J. Phys. Chem. Solids*, 1982, **43**, (6), 539-545

An electrolytic method was used to measure the diffusivity of H<sub>2</sub> through substitutional Pd-Ti and Pd-V alloys containing up to 10at.% Ti or V in the temperature range 273-350K. The diffusivity obeyed the Arrhenius relation. Both Ti and V atoms create trapping sites for H and the mobility of H decreases as the Ti or V increases.

### Paramagnetism in High-Nuclearity Osmium Clusters

R. E. BENFIELD, P. P. EDWARDS and A. M. STACY, *J. Chem. Soc., Chem. Commun.*, 1982, (10), 525-526

The cluster H<sub>2</sub>O<sub>8</sub>Os<sub>10</sub>C(CO)<sub>24</sub> exhibits intrinsic paramagnetism at temperatures below 70K; such behaviour is characteristic of a particulate metal in the quantum size effect regime.

## ELECTROCHEMISTRY

### Platinum Corrosion in Alkaline Solution in the Presence of Ba<sup>2+</sup> and Cl<sup>-</sup> ions

E. I. KHRUSHCHEVA, M. P. TARASEVICH, G. P. SAMOILOV and N. A. SHUMILOVA, *Elektrokhimiya*, 1982, **18**, (6), 848-850

Studies of the corrosion behaviour of Pt black in alkaline solutions were made at 0.85-1.37V. The dependence of the rate of corrosion of Pt on the potentials, and the effect of preliminary treatment

and electrochemical reduction of Pt on the rate of corrosion were studied. O<sub>2</sub> adsorption and desorption data on Pt in alkaline solution showed that the process of Pt dissolution proceeds through the formation of intermediate surface oxides.

### Reduction of Surface Oxide of Platinum and Gold Electrodes in Aqueous Sulfuric Acid. Local Cell Mechanism and Reactive Species

Z. H. GUO, T. MASUDA and K. SASAKI, *Nippon Kagaku Kaishi*, 1982, (4), 574-578

The surface oxides of Pt and Au electrodes, formed anodically, were gradually reduced at open circuit in aqueous H<sub>2</sub>SO<sub>4</sub>. The reaction proceeds by the galvanic cell mechanism when the bare surface of the metal acts as an anode which oxidises certain contaminants, and the oxide covered surface acts as a cathode. The formaldehyde used as a contaminant was effective for Pt oxide, but not for Au oxide.

### Activation of RuO<sub>2</sub> and PtO Electrode Surface for Immobilization Reactions Using Thionyl Chloride

K. N. KUO and R. W. MURRAY, *J. Electrochem. Soc.*, 1982, **129**, (4), 756-761

RuO<sub>2</sub> and superficially oxidised Pt electrodes are reacted with thionyl chloride in an attempt to produce activated chlorinated surfaces which bind and immobilise appropriately substituted reagents. The activated surfaces stably bind reagents such as aminophenylferrocene, tetra(p-aminophenyl)-porphyrin and [Ru(bpy)<sub>3</sub>4,4'-bipyridine]<sup>2+</sup>, which then display electrochemical reactions similar to those of the surfaces. (43 Refs.)

## PHOTOCONVERSION

### Photocatalytic Hydrogen Evolution from Alcohols Using Dodecawolfram-silicic Acid and Colloidal Platinum

J. R. DARWENT, *J. Chem. Soc., Chem. Commun.*, 1982, (14), 798-799

Photocatalytic H<sub>2</sub> evolution from alcohols using SiW<sub>12</sub><sup>-</sup> and colloidal Pt, prepared by boiling aqueous Na citrate and H<sub>2</sub>PtCl<sub>6</sub> for 4h, and illuminated with a 900W xenon lamp was studied. Illumination of SiW<sub>12</sub><sup>-</sup> and colloidal Pt leads to photocatalytic H<sub>2</sub> evolution with a quantum yield for H<sub>2</sub> of 0.1mol/einstein.

### A Rechargeable Photo-Electrochemical Solar Cell

M. SHARON and A. SINHA, *Int. J. Hydrogen Energy*, 1982, **7**, (7), 557-562

A rechargeable photoelectrochemical solar cell based on the n-type BaTiO<sub>3</sub>/Ce<sup>3+</sup>, Ce<sup>4+</sup>/Fe<sup>2+</sup>, Fe<sup>3+</sup>/Pt system has been made. The cell has 0.6V open circuit voltage and 0.12mA/cm<sup>2</sup> short-circuit current when fully charged. The power conversion efficiency of the

cell is 0.01% under AM2-sunlight irradiation (75mW/cm<sup>2</sup>). The fill factor of the cell is 0.26. Charging and discharging were characterised; flat-band potential and carrier concentrations of the BaTiO<sub>3</sub> were calculated and effects of pH and different electrolytes were studied.

### Visible Light Induced Water Cleavage in Colloidal Solution of Chromium-Doped Titanium Dioxide Particles

E. BORGARELLO, J. KIWI, M. GRÄTZEL, E. PELIZZETTI and M. VISCA, *J. Am. Chem. Soc.*, 1982, **104**, (11), 2996-3002

Surface doping of colloidal TiO<sub>2</sub> particles with Cr ions precipitated from aqueous H<sub>2</sub>SO<sub>4</sub> solution produces very small (<0.1 μm) mixed-oxide particles which absorb light in the 400-500nm region in addition to the band-gap adsorption of anatase. Ultrafine deposits of Pt or RuO<sub>2</sub> are necessary to promote H<sub>2</sub>O decomposition. A pronounced synergistic effect in catalytic activity is noted when both RuO<sub>2</sub> and Pt are co-deposited onto the particles.

## HETEROGENEOUS CATALYSIS

### Study of the Effect of Hydrogen on C<sub>6</sub>-Hydrocarbon Transformations in the Presence of Platinum-Alumina Catalysts

S. A. KRASAVIN and O. V. BRAGIN, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (6), 1314-1320

Studies of the effect of H<sub>2</sub> on the conversion of C<sub>6</sub>-hydrocarbons in the presence of 0.6%Pt/Al<sub>2</sub>O<sub>3</sub> and 0.55% Pt-0.002% Re-0.3%F/Al<sub>2</sub>O<sub>3</sub> catalysts showed that activity, selectivity and conversion mechanism depend on partial H<sub>2</sub> pressure in the gaseous phase. Skeletal isomerisation of alkanes proceeds through a predominantly C<sub>7</sub>-cyclic mechanism at high H<sub>2</sub> concentration and through a bifunctional mechanism at low H<sub>2</sub> concentrations.

### n-Heptane Transformations on Modified Reforming Catalysts

I. M. KOLESNIKOV, S. G. GORLOV, N. N. BELOV, A. P. FEDOROV and E. A. SHKURATOVA, *Neftekhimiya*, 1982, **22**, (3), 335-338

Studies of the effects of additions of small amounts of metal containing Si organic compounds on the catalytic activity of Pt/Al<sub>2</sub>O<sub>3</sub> reforming catalysts were made during n-heptane transformation. Modification of the catalysts by Si-organic compounds was found to increase their activity, selectivity and stability.

### Ceria-Promoted Three-Way Catalysts for Auto Exhaust Emission Control

G. KIM, *Ind. Eng. Chem., Prod. Res. Dev.*, 1982, **21**, (2), 267-274

Studies were made of the effects of Ba, Mg, Cr, Mn, Co, Ni and Ce promoters on the performance of a typical three-way catalyst (TWC) Pt-Pd-Rh/Al<sub>2</sub>O<sub>3</sub>

during CO removal under O<sub>2</sub> deficient conditions. Ce was found to be the best promoter largely because it increased the water gas shift reaction (CO + H<sub>2</sub>O = CO<sub>2</sub> + H<sub>2</sub>) and possibly also due to the additional O<sub>2</sub> storage it provides to the TWC.

### Heterogeneous Water Gas Shift Reaction Catalyzed by Titanium Dioxide Supported Noble Metals

R. RUPPERT, J.-P. SAUVAGE, J.-M. LEHN and R. ZIESSEL, *Nouv. J. Chim.*, 1982, 6, (5), 235-239

Various transition metal catalysts supported on SiO<sub>2</sub>, PVA, TiO<sub>2</sub> and zeolite were studied for the water gas shift reaction in the liquid and gas phases at 100 to 285°C and CO pressures ≤ 1 atm. Parameters such as pH, temperature and preparation method have a drastic effect on catalytic activity. The catalyst Pt<sub>2</sub>K<sub>2</sub>CO<sub>3</sub>/TiO<sub>2</sub> was the most efficient catalyst for the reaction, its turnover frequency varied from 360/h at 200°C to 3600/h at 268°C.

### Catalytic Combustion of Hydrogen. II. An Experimental Investigation of Fundamental Conditions for Burner Design

M. HARUTA, Y. SOUMA and H. SANO, *Int. J. Hydrogen Energy*, 1982, 7, (9), 729-736

The performances of catalysts, consisting of a ceramic honeycomb impregnated with Pt, Ni metal foams coated with Pd powder, and ceramic foam coated with Co-Mn-Ag oxide powder, were studied for the design of a catalytic combustor using H<sub>2</sub> fuel. In the diffusive mode of operation the Pd coated Ni foam with larger pores exhibited the highest combustion efficiency. Combustion efficiency was improved by increasing the amount of premixed air.

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

H. MIURA and R. D. GONZALEZ, *Ind. Eng. Chem., Prod. Res. Dev.*, 1982, 21, (2), 274-278

A Fischer-Tropsch (F-T) study over a well-characterised series of SiO<sub>2</sub> supported Pt-Ru bimetallic clusters showed that the increase in surface concentration of Pt has a marked effect on methane selectivity. The F-T reaction was shown to be structure sensitive, occurring predominantly on Ru surface sites. It is concluded that Pt surface sites are inactive in the CO-H<sub>2</sub> reaction under the studied conditions and the role of Pt is, therefore, reduced to that of a surface diluent.

### Transformation of 1,3-Pentadiene on Membrane Catalysts Made of Binary Palladium Alloys

A. P. MISHCHENKO, V. M. GRYAZNOV and M. E. SARYLOVA, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (7), 1471-1473

Studies of catalytic conversion of 1,3-pentadiene under H<sub>2</sub> pressure through membrane catalysts made of Pd-9.8% Ru and Pd-2.0% Sm alloys showed an

increase in rate of H<sub>2</sub> transfer through the catalyst. The effect of α- and β-hydride phases on selectivity of the hydrogenation process is discussed.

### AlPO<sub>4</sub>-Supported Rhodium Catalysts. I. Effect of the Preparation Variables on Cyclohexene Hydrogenation

J. M. CAMPELO, A. GARCIA, D. LUNA and J. M. MARINAS, *Gazz. Chim. Ital.*, 1982, 112, (5-6), 221-225

The liquid phase catalytic hydrogenation of cyclohexene over Rh/AlPO<sub>4</sub>-SiO<sub>2</sub> catalysts in 1 wt.% methanol solvent and initial H<sub>2</sub> pressure of 5.6 bar and 40°C is reported. Catalytic activity was strictly dependent on the conditions of reduction of the precursors. The highest catalytic activity was obtained when the precursor was reduced under mild conditions; at higher temperatures, or if the precursor was calcined, activity was lower.

### Hydrogenation of CO and CO<sub>2</sub> over Rhodium Catalysts Supported on Various Metal Oxides

T. IIZUKA, Y. TANAKA and K. TANABE, *J. Catal.*, 1982, 76, 1-8

The formation of hydrocarbons in the reaction of CO+H<sub>2</sub> and CO<sub>2</sub>+H<sub>2</sub> was studied over Rh catalyst supported on ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and MgO. In the studied reaction, Rh/ZrO<sub>2</sub> was the most active and Rh/MgO was least active. The activity for the CO+H<sub>2</sub> reaction over the oxidised Rh/ZrO<sub>2</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts was 2-10 times higher than that on the reduced catalyst.

### Improvement of the Catalytic Performance of an Osmium Powder in Ammonia Synthesis by the Use of a Cyclic Procedure

G. RAMBEAU, A. JORTI and H. AMARIGLIO, *Appl. Catal.*, 1982, 3, (3), 273-282

The catalytic activity of Os in NH<sub>3</sub> synthesis is greatly impeded by H<sub>2</sub> under the usual reaction conditions. Decreasing the H<sub>2</sub> content of the reactant mixture reduces inhibition and increases the reaction rate. The reaction is also inhibited by NH<sub>3</sub>. Decreasing the H<sub>2</sub> shifts the synthesis equilibrium to lower NH<sub>3</sub> contents. Cycling with pure N<sub>2</sub> and H<sub>2</sub> increases Os activity and the best average rate is 5-50 times higher than the best steady rate, depending on temperature in the range 400-250°C.

### Mechanistic Study of Carbon Monoxide Hydrogenation over Ruthenium Catalysts

Y. KOBORI, H. YAMASAKI, S. HAITO, T. ONISHI and K. TAMARU, *J. Chem. Soc., Faraday Trans. 1*, 1982, 78, (5), 1473-1490

The mechanism of the hydrogenation of CO over 4.5 wt.% Ru/SiO<sub>2</sub> catalyst prepared by impregnation of SiO<sub>2</sub> with an aqueous solution of RuCl<sub>3</sub> hydrate was studied. It is concluded that all the hydrocarbon products are produced via dissociatively adsorbed CO with no CO insertion. The rate-determining step comprises the conversion of C<sub>3</sub> intermediates.

## HOMOGENEOUS CATALYSIS

### Novel Palladium(II)—Catalyzed Copolymerization of Carbon Monoxide with Olefins

A. SEN and T.-W. LAI, *J. Am. Chem. Soc.*, 1982, **104**, (12), 3520–3522

The series of cationic Pd(II) compounds  $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_{2n} \text{PPh}_3$  ( $n = 1-3$ ) which catalyse the co-polymerisation of CO with a range of olefins under unusually mild conditions is reported. The species prepared by reactions of  $\text{AgBF}_4$  with  $\text{Pd}(\text{PPh}_3)_2\text{MeI}$  and  $\text{Pd}(\text{Ph}_3)_2(\text{C}(\text{O})\text{Me})\text{Cl}$  and  $\text{Pd}(\text{PPh}_3)_2(\text{C}(\text{O})\text{Me})(\text{solvent})^+$  were also active catalysts for the co-polymerisation of CO and  $\text{C}_2\text{H}_4$  under similar conditions. Catalysts prepared with a  $\text{PPh}_3 : \text{Pd}^{2+}$  ratio of 1–3 were active but those with ratios 4 and 6 were found to be inactive, which shows the need for easily accessible co-ordination sites.

### Activation of Molecular Hydrogen by Transition Metal Complexes. 6. Role of Molecular Oxygen in Formation of Palladium Complexes Active in Hydrogenation of Unsaturated Compounds

A. S. BERENBLIUM, A. G. KAIZHNIK, S. I. MUND and I. I. MOISEEV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (6), 1249–1253

Studies of the interaction of  $[\text{Ph}_3\text{PPd}(\text{OAc})_2]_2$  with  $\text{H}_2$  showed the formation of intermediate complexes  $(\text{Ph}_3\text{P})_2\text{Pd}_2(\text{OAc})_2$  and final yields of  $(\text{Ph}_3\text{P})_2\text{Pd}_2$  and  $(\text{Ph}_3\text{P})_2\text{Pd}_2\text{H}_2$ . The cluster  $[(\text{PPh}_3)_2\text{Pd}_3]_n$  was found to be active in the hydrogenation of unsaturated hydrocarbons.

### Mechanism and Stereoselectivity of Asymmetric Hydrogenation

J. HALPERN, *Science*, 1982, **217**, (4558), 401–407

Rh complexes containing chiral phosphine ligands catalyse the hydrogenation of olefinic substrates such as  $\alpha$ -aminoacrylic acid derivatives, giving chiral products with very high optical yields. It is concluded that the stereoselection is dictated by the much higher reactivity of the minor diastereomer of the catalyst-substrate adduct, corresponding to the less favoured binding mode.

### Selective Homogeneous Transfer Hydrogenolysis of Trihalomethyl Compounds by Alcohols and Ruthenium-Phosphine Catalysts

J. BLUM, S. SHTELZER, P. ALBIN and Y. SASSON, *J. Mol. Catal.*, 1982, **16**, (2), 167–174

$\text{RuCl}_2(\text{PPh}_3)_3$  was shown to catalyse  $\text{H}_2$  transfer from halogen-free alcohols to  $\alpha$ -trichloromethyl- and  $\alpha$ -tribromomethyl carbinols and to give selectively dihalomethyl derivatives. Benzyl alcohols proved to be very efficient  $\text{H}_2$  donors. The catalytic process was affected by the electronic structure of the catalyst and of the  $\text{H}_2$  acceptor but not by  $\text{H}_2$  donor.

### The Cluster Anion $[\text{HRu}_3(\text{CO})_{11}]^-$ as Catalyst in Hydroformylation, Hydrogenation, Silacarbonylation and Hydrosilylation Reductions of Ethylene and Propylene

G. SÜSS-FINK and J. REINER, *J. Mol. Catal.*, 1982, **16**,

The trinuclear cluster anion  $[\text{HRu}_3(\text{CO})_{11}]^-$  was found to catalyse hydroformylation, hydrogenation, silacarbonylation and hydrosilylation reactions. Ethylene and propylene were hydroformylated with CO and  $\text{H}_2$  to give the corresponding aldehydes; in the case of propylene a high yield of the unbranched butyraldehyde was obtained. The catalytic turnover of these reactions was observed to be 50–400.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Dynamics of Interfacial Electron-Transfer Processes in Colloidal Semiconductor Systems

D. DUONGHONG, J. RAMSDEN and M. GRÄTZEL, *J. Am. Chem. Soc.*, 1982, **104**, (11), 2977–2985

The dynamics of interfacial electron-transfer reactions were studied with colloidal  $\text{TiO}_2$  and CdS particles, which form transparent aqueous dispersions. Experiments with Pt-loaded CdS established catalytic  $\text{H}_2$  production by conduction-band electron with electron transfer to adsorbed  $\text{MV}^{2+}$ .  $\text{RuO}_2$  deposits enhance hole transfer from the valence band to solution species.

### Hydrogen Detection by Schottky Diodes

K. ITO and K. KOJIMA, *Int. J. Hydrogen Energy*, 1982, **7**, (6), 495–497

A Schottky diode was made from a 20 nm evaporated Pd film, a very thin  $\text{SiO}_2$  film and n-type Si substrate. Two diodes were obtained on the Si substrate, one was used for  $\text{H}_2$  detection and the other as a reference diode. The detector, operating at room temperature was able to detect 2000 ppm  $\text{H}_2$  in air within 10s. There was no degradation found over an 8 month operating period.

## TEMPERATURE MEASUREMENT

### Measuring Low Temperature in the 13 through 80K Range Using ZPA, MT-100 Platinum Temperature Sensors

J. VEPŘEK, *Slaboproud. Obzor*, 1982, **43**, (5), 216–220

The basic thermometric properties of the ZPA Pt temperature sensors of the MT-100 type are described for the temperature range 13–80K. The dependence of electrical resistance, sensitivity and temperature resistance coefficients on temperature are described. The dynamic stability of the electrical resistance is tested by the cycling method.