

# ABSTRACTS

of current literature on the platinum metals and their alloys

## PROPERTIES

### Effect of Oxygen on the Diffusion of Ni in Pt in Pt-Ni-Pt Films

C.-A. CHANG and W. K. CHU, *J. Appl. Phys.*, 1981, **52**, (1), 512-514

Studies of the effect of O<sub>2</sub> on the diffusion of Ni into Pt in Pt-Ni-Pt films showed that below 400°C the diffusion rates of Ni into both Pt layers were greatly reduced by O<sub>2</sub>. Above 500°C Ni rapidly mixed with the Pt layers, which led to the formation of Ni oxide on the Pt surface in the presence of O<sub>2</sub>.

### High Pressure Hydrogen Absorption Study on YNi<sub>5</sub>, LaPt<sub>5</sub> and ThNi<sub>5</sub>

I. TAKESHITA, K. A. GSCHNEIDNER and J. F. LAKNER, *J. Less-Common Met.*, 1981, **78**, (2), P43-P47

High pressure H<sub>2</sub> gas (up to 1550 atm) was used to study H<sub>2</sub> absorption in the title compounds, which do not absorb H<sub>2</sub> at moderate pressures and room temperature. They were found to absorb a large amount of H<sub>2</sub> at high pressures. LaPt<sub>5</sub> and YNi<sub>5</sub> form hydride phases, while ThNi<sub>5</sub> dissolves H<sub>2</sub> as a continuous series of solid solutions to high H<sub>2</sub> concentrations. The LaPt<sub>5</sub> and YNi<sub>5</sub> hydride formation is thought to be controlled mainly by their lattice compressibility and not by the unit cell size.

### Electronic Structure and Ordering of Hydrogen in F.C.C. Transition Metals

M. A. KHAN, J. C. PARLEBAS and C. DEMANGEAT, *J. Less-Common Met.*, 1981, **77**, (1), P1-P8

The heats of formation of H atoms at octahedral and tetrahedral interstitial sites in f.c.c. Pd and Ni were estimated, and the octahedral sites were found to be more stable than tetrahedral sites. The chemical binding energies of nearest-neighbouring and next-nearest-neighbouring pairs of H atoms in  $\alpha$ -Pd were repulsive. The binding energies between d element substitutional impurities in Pd and H atoms as the first and second neighbours were also calculated.

### On the Possibility of an Increase in Titanium Corrosion Stability by Palladium Ion Implantation

N. D. TOMASHOV, M. I. GUSEVA, G. A. FEDOSEVA, A. E. GORODETSKI, A. P. ZAKHAROV, D. B. BOGOMOLOV, G. P. CHERNOVA, B. G. VLADIMIROV and S. M. IVANOV, *Dokl. Akad. Nauk SSSR*, 1981, **256**, (5), 1129-1133

Studies of the effect of Pd ion implantation on corrosion stability of Ti showed an increase in corrosion stability in the Pd implanted Ti. The highest corrosion stability was observed on samples containing  $5 \cdot 10^{16}$ - $10^{17}$  Pd ions/cm<sup>2</sup>, implanted by ion energies of 20-100 keV. This increased the Ti corrosion stability 103 times.

### Diffusion, Permeability and Solubility of Hydrogen in Pd-1at.%Er, Pd-1at.%Dy Alloys

A. D. SPECTOR, IU. D. KOZMANOV, G. E. KAGAN and V. V. LOBANOV, *Fiz. Met. Metalloved.*, 1981, **51**, (2), 354-356

Studies of the temperature dependence of the coefficients of diffusion, permeability and solubility of H<sub>2</sub> in 1at.%Er-Pd and 1at.%Dy-Pd alloys were performed at 590-1073K. The effect of internal oxidation on H<sub>2</sub> permeability was also studied.

### Electrical Resistivity of Fe-Rich Fe-Pd Alloys between 77 and 1250 K

Y. D. YAO and S. ARAJS, *Phys. Status Solidi A*, 1981, **64**, (1), 95-104

Electrical resistivity ( $\rho$ ) of Fe-Pd alloys containing 0.5, 1.0, 3.0, 7.9, 10.0 and 11.4 at.%Pd was studied at increasing and decreasing temperatures between 77 and 1250K. The  $\alpha$ - $\gamma$  transition exhibited hysteresis in the electrical resistivity. The temperature region for the  $\alpha$ - $\gamma$  transition can be slightly affected by the heating and cooling rates. The metastable phase in higher concentration Pd alloys is observed from an irreversible shift in the  $\rho$  data for Fe-Pd containing 7.9, 10.0 and 11.9 at.%Pd.

### In Vitro Corrosion and Tarnish Analysis of the Ag-Pd Binary System

T. K. VAIDY ANATHAN and A. PRASAD, *J. Dent. Res.*, 1981, **60**, (3), 707-715

Ag-Pd alloys were characterised by anodic polarisation in Ringer's solution and alternate immersion in 0.5% Na<sub>2</sub>S solution. Alloying with Pd reduces the chloride corrosion and sulphide tarnish of Ag, and the Pd rich compositions of the alloy show stable protection over a wide range of potentials. Intermediate compositions show a potential region for breakdown of protection and subsequent passivation at higher anodic overpotentials. The Ag rich compositions have little protection or passivation tendencies.

### High-Temperature Effects of Shape Memory in TiNi-TiPd Alloys

V. N. KHACHIN, N. M. MATVEEVA, V. P. SIVOKHA, D. B. CHERNOV and IU. K. KOVNERISTII, *Dokl. Akad. Nauk SSSR*, 1981, **257**, (1), 167-169

Studies were performed on high-temperature (to 500°C) effects of shape memory in TiNi-TiPd. The results showed a practically full shape memory at high temperatures, after significant (to 4-5%) preliminary deformation of the alloy. The discovered effect increased a number of possible applications of the appearance of shape memory and explains reversible deformation during martensitic conversions.

## CHEMICAL COMPOUNDS

### $\eta^3$ -Allyl(hydrido)phosphaneplatinum(II) Complexes

G. CARTURAN, A. SCRIVANTI and F. MORANDINI, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, (2), 112-113

Novel allyl(hydrido)Pt(II) complexes were synthesised and characterised. They alter the position of equilibrium between allyl (hydrido) and olefin complexes which could be a key step in selective hydrogenations.

### High Yield Preparation of $Pt_5(CO)_6 [P(C_6H_5)_3]_4$ ; Its Use in Mixed-Metal Cluster Synthesis. Preparation and Molecular Structure of $PtCo_2(CO)_8 [P(C_6H_5)_3]$

R. BENDER, P. BRAUNSTEIN, J. FISCHER, L. RICARD and A. MITSCHLER, *Nouv. J. Chim.*, 1981, **5**, (2), 81-83

A new and unexpected high yield synthesis for  $Pt_5(CO)_6(PPh_3)_4(A)$  is reported which can be utilised in preparing mixed-metal clusters. Some clusters, such as  $Pt_2Mo_2Cp_2(CO)_6(PPh_3)_2$  and  $Pt_2Co_2(CO)_8(PPh_3)_2$  have been synthesised previously, but the new Pt cluster  $PtCo_2(CO)_8PPh_3$  has only been obtained by reacting (A) with  $Co_2(CO)_8$ . It is the first Pt-Co triangulo cluster and has a semi-triply bridging CO ligand on a heterotrimetallic face.

### Carbon Dioxide Activation; Formation of *trans*-( $Ph_3P$ ) $_2$ Rh(CO)(OCO $_2$ H) in the Reaction of CO $_2$ with HRh(CO)(PPh $_3$ ) $_3$ -CO and the Determination of Its Structure by X-Ray Crystallography

S. FAZLEY-HOSSAIN, K. M. NICHOLAS, C. L. TEAS and R. E. DAVIS, *J. Chem. Soc., Chem. Commun.*, 1981, (6), 268-269

The intermediate produced from the interaction of  $HRh(CO)(PPh_3)_3$  with CO reacts with CO $_2$  to yield a novel hydrogen carbonate complex, *trans*-( $Ph_3P$ ) $_2$ Rh(CO)(OCO $_2$ H) which then undergoes a reversible loss of CO $_2$ .

## ELECTROCHEMISTRY

### The Effect of Anions on the Electrochemical Reduction of Thick Oxide Films on Platinum Electrode in Acidic Aqueous Solutions

S. SHIBATA and M. P. SUMINO, *Electrochim. Acta.*, 1981, **26**, (4), 517-523

The cathodic galvanostatic reduction of thick oxide films on Pt was studied in HF, HClO $_4$  and H $_2$ SO $_4$  solutions at 25°C as a function of the current density and acid concentrations. The thick oxide film was completely reduced at a single potential step of 0.6V in HF solution and also in very dilute HClO $_4$  and H $_2$ SO $_4$  solutions. The effect of HSO $_4^-$  on the reduction of the inner-layer oxide was stronger than that of ClO $_4^-$  and the effect of F $^-$  was very weak.

### An Investigation of Electrode Materials for the Anodic Oxidation of Sulfur Dioxide in Concentrated Sulphuric Acid

P. W. T. LU and R. L. AMMON, *J. Electrochem. Soc.*, 1980, **127**, (12), 2610-2616

Catalysts for the SO $_2$  oxidation reaction with H $_2$ O to produce H $_2$ SO $_4$  and H $_2$  were evaluated. Pd and Pd oxide were better catalysts than Pt. Increasing temperature remarkably improves the anodic overpotential for SO $_2$  oxidation on a preanodised Pd electrode; however, the reaction mechanism is independent of temperature. In the anodic sweep SO $_2$  oxidation begins at potentials where the formation of adsorbed O $_2$ -containing species is initiated. The Pd oxide covered electrode exhibits high electrocatalytic activity for SO $_2$  oxidation.

### Observation of Electrochromism in Solid-State Anodic Iridium Oxide Film Cells Using Fluoride Electrolytes

C. E. RIE and P. M. BRIDENBAUGH, *Appl. Phys. Lett.*, 1981, **38**, (1), 59-61

Thin film cells SnO $_2$ /AIROF/fluoride/Au were constructed; AIROF is anodic Ir oxide film and fluoride is PbF $_2$  on PbSnF $_4$ . The devices exhibit reversible electrocoloration and bleaching with response times as low as 0.1 s. These cells are simple to construct and show switching speeds superior to solid state electrochromic cells previously reported.

### Advances in Oxygen Evolution Catalysis in Solid Polymer Electrolyte Water Electrolysis

J. M. SEDLAK, R. J. LAWRENCE and J. F. ENOS, *Int. J. Hydrogen Energy*, 1981, **6**, (2), 159-165

Continuous polarisation of a stabilised RuO $_2$  O $_2$  anode in a solid polymer electrolyte water electrolysis cell at 1072 mA/cm $^2$  resulted in severe anode deterioration within 24-48 hours. In contrast, a new Ru-based mixed oxide catalyst, exhibited stability in O $_2$  evolution over a 6700 hr period. The activation energy for O $_2$  evolution in the new catalyst is comparable to that observed on new RuO $_2$  anodes.

### An Electrode-Supported Oxidation Catalyst Based on Ruthenium (IV) pH "Encapsulation" in a Polymer Film

G. J. SAMUELS and T. J. MEYER, *J. Am. Chem. Soc.*, 1981, **103**, (2), 307-312

The oxidative catalytic behaviour of (bpy) $_2$ (py)RuO $^{2+}$  and (trpy)(bpy)RuO $^{2+}$  (trpy is 2,2',2''-terpyridine) has been transferred to electrode surfaces by depositing thin polymeric films containing the (bpy) $_2$ (H $_2$ O)Ru $^{II}$  group bound to poly-4-vinylpyridine. Upon oxidation to Ru $^{IV}$  catalytic currents are observed. Below pH 4, potentials for the redox couples change with pH as expected, but not from pH 4-9.2 where the unbound pyridyl group becomes deprotonated. This allows the deposition to be observed, and the cyano ions were seen to be permanently bound in the films by a Fe-Ru dimer.

## PHOTOCONVERSION

### Hydrogen Production from Photolysis of Steam Adsorbed onto Platinized SrTiO<sub>3</sub>

R. G. CARR and G. A. SOMORJAI, *Nature*, 1981, **290**, (5807), 576-577

Photodissociation of ultrapure, high pressure (1-8 atm) H<sub>2</sub>O at high temperatures (100-160°C) occurred under vacuum conditions, with Ar gas as carrier, on a single crystal wafer of SrTiO<sub>3</sub> with a thin Pt coating, when illuminated by a Hg discharge lamp. The photoreaction was highest when the coating was transparent, and the photon energy was higher than the bandgap energy (3.1 eV). After ~ 10 hours the H<sub>2</sub> production rate drops because of equilibration of production and recombination rates and surface poisoning. This work did not involve an electrolyte and the surface is accessible to UHV analytical surface techniques for examining the reaction mechanisms.

### Visible Light Induced Water Cleavage in CdS Dispersions Loaded with Pt and RuO<sub>2</sub>, Hole Scavenging by RuO<sub>2</sub>

K. KALYANASUNDARAM, E. BORGARELLO and M. GRÄTZEL, *Helv. Chim. Acta*, 1981, **64**, (1), 362-366

Visible light illumination of aqueous CdS dispersions loaded with Pt and RuO<sub>2</sub> produces stoichiometric amounts of H<sub>2</sub> and O<sub>2</sub>. No photo catalyst degradation was noted after 60 hr irradiation. The RuO<sub>2</sub> deposit on the particle surface greatly accelerates the transfer of holes from the semiconductor valence band to the aqueous solution, thus inhibiting photocorrosion.

### Photocatalytic Reaction of Water with Carbon over Platinized Titania

S. SATO and J. M. WHITE, *J. Phys. Chem.*, 1981, **85**, (4), 336-341

The reaction of gaseous water with active C over illuminated platinized TiO<sub>2</sub> was studied at room temperature and 60°C. The products were H<sub>2</sub>, CO<sub>2</sub> and a little O<sub>2</sub>. Accumulation of H<sub>2</sub> decreases contact between catalyst and C and reaction rate declines. At room temperature the quantum efficiency is ~2% at the beginning of the reaction. With liquid H<sub>2</sub>O, the oxidation of C is inhibited and O<sub>2</sub> as well as H<sub>2</sub> evolves.

### Oxidative Substitution Reaction of the Osmochrome Os(OEP)[P(OMe)<sub>3</sub>]<sub>2</sub> in Chlorinated Solvents

N. SERPONE, M. J. JAMIESON and T. L. NETZEL, *J. Photochem.*, 1981, **15**, (4), 295-301

Photolysis of Os(OEP)[P(OMe)<sub>3</sub>]<sub>2</sub>, where OEP is octaethylporphine, in the chlorinated solvents CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub> at 365 and 405 nm and at 22°C, produced an Os(IV) porphyrin identified as Os(OEP)Cl<sub>2</sub>. The rate of the product formation increased in the order of solvents CH<sub>2</sub>Cl<sub>2</sub> < CHCl<sub>3</sub> < CCl<sub>4</sub> in the ratio 1 : 8 : 120. A possible mechanism involving radicals is suggested.

### Electrogenerated Chemiluminescence. 37. Aqueous Ecl Systems Based on Ru(2,2'-bipyridine)<sub>3</sub><sup>2+</sup> and Oxalate or Organic Acids

I. RUBINSSTEIN and A. J. BARD, *J. Am. Chem. Soc.*, 1981, **103**, (3), 512-516

A new aqueous chemiluminescent and ecl system based on Ru(bpy)<sub>3</sub><sup>2+</sup> and a suitable organic acid or salt (e.g. C<sub>2</sub>O<sub>4</sub><sup>2-</sup>) is described. The bright orange chemiluminescence, which could also be generated by reaction of chemically produced Ru(III) species with oxalate, corresponded to emission by Ru(bpy)<sub>3</sub><sup>2+</sup>; ecl efficiency (photons emitted/Ru(bpy)<sub>3</sub><sup>2+</sup> generated) was ~2% in deaerated solution. Ecl by reaction of the 1+ and 3+ Ru species was also obtained in partially aqueous solutions containing at least 20% acetonitrile. Chemiluminescence was observed with other organic acids.

### Photoredox Reactions in Functional Micellar Assemblies. Use of Amphiphilic Redox Relays to Achieve Light Energy Conversion and Charge Separation

P.-A. BRUGGER, P. P. INFELTA, A. M. BRAUN and M. GRÄTZEL, *J. Am. Chem. Soc.*, 1981, **103**, (2), 320-326

The photoreduction of a homologous series of amphiphilic viologens (C<sub>n</sub>MV<sup>2+</sup>) using Ru(bpy)<sub>3</sub><sup>2+</sup> and Zn tetrakis(N-methylpyridyl)porphyrin(ZnTMPyP<sup>4+</sup>) as sensitizer was studied in H<sub>2</sub>O and aqueous solution containing cationic micelles, to establish pathways preventing back reactions. On reduction the relay acquires hydrophobic properties leading to rapid solubilisation in the micelles, and the thermal back reaction is impaired at least 500 times. The intermediates had high stability and the lifetimes were long enough to allow the intervention of ultrafine Pt particles as the efficient catalyst to couple three relays C<sub>12</sub>MV<sup>2+</sup>-C<sub>16</sub>MV<sup>2+</sup> with light induced H<sub>2</sub> production from water.

## ELECTRODEPOSITION AND SURFACE COATING

### Studies of Processes of Electrodeposition of Palladium-Iridium Alloy from Ammonium-Trilog and Sulphamide Electrolytes

A. A. TIKHONOV, P. M. VIACHESLAVOV and G. K. BURKAT, *Zh. Prikl. Khim. (Leningrad)*, 1981, **54**, (2), 364-369

The effect of electrolyte composition and electrolysis parameters on the composition and quality of deposited Pd-Ir layers was studied. The Pd-Ir alloy layer from the ammonium-trilog electrolyte exhibited high wear resistance and low internal stress. Technological processes for depositing Pd-Ir alloys from ammonium-trilog electrolytes can be used in the production of coatings for the collector of d.c. electric motors and in contacts. The use of Pd-Ir alloys instead of Pd layers increases the reliability of electric contacts.

## LABORATORY APPARATUS AND TECHNIQUE

### A Titanium Dioxide Hydrogen Detector

L. A. HARRIS, *J. Electrochem. Soc.*, 1980, **127**, (12), 2657-2662

Sputtered films of TiO<sub>2</sub> several thousand angstroms thick and sandwiched between a layer of Ti and a layer of Pt are highly selective H<sub>2</sub> detectors. The Pt film is made negative with respect to Ti, providing a greater dynamic range and faster recovery when H<sub>2</sub> is removed. Above 0.5% H<sub>2</sub> in air the response of the detector is rapid and limited by lead resistance. At lower concentrations (a few hundred ppm in air) the response is proportional to concentration, but relatively slow at room temperature. Increasing temperature quickens the response. The detectors can be used as alarm devices at room temperature, with a.c. or d.c. circuitry that requires negligible power in the absence of H<sub>2</sub>.

### Brazing of Sensors for High-Temperature Steam Instrumentation Systems

A. J. MOORHEAD, C. S. MORGAN, J. J. WOODHOUSE and R. W. REED, *Weld. J. (Miami)*, 1981, **60**, (4), 17-28

The structure of a probe for high temperature detection in water-cooled nuclear reactors is discussed. The probe measures impedance between two electrodes in the space between three fuel rod simulators giving the steam:water ratio. Base materials for brazing including platinised Al<sub>2</sub>O<sub>3</sub>-Pt and platinised Al<sub>2</sub>O<sub>3</sub>-Ir which with 72Ti-28Ni and 49Ti-49Cu-2Be filler metal composition had excellent wetting with no visible cracks. Steam corrosion testing, including high temperature steam exposure of 304L stainless steel joined to Pt on Kovar sheet was examined. A ceramic-to-metal seal of platinised Al<sub>2</sub>O<sub>3</sub> cermet insulator brazed to a Pt transition material, with a filler of 49Ti-49Cu-2Be was used in the probe.

## HETEROGENEOUS CATALYSIS

### The Effects of SO<sub>2</sub> on the Oxidation of Hydrocarbons and Carbon Monoxide over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalysts

H. C. YAO, H. K. STEPIEN and H. S. GANDHI, *J. Catal.*, 1981, **67**, (1), 231-236

Propane and propylene were used to test the effects of SO<sub>2</sub> on the oxidation of saturated and unsaturated hydrocarbons over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts in a flow reactor. SO<sub>2</sub> in the feed gas enhanced propane oxidation but suppressed propylene and CO oxidations. This is due to the formation of surface sulphates on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> after the SO<sub>2</sub> adsorption and oxidation and their effects on the chemisorptive properties of the Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. These sulphates may enhance propane oxidation by increasing its dissociative adsorption on Pt and suppressing CO and propylene oxidations by decreasing the associative CO and propylene adsorptions on Pt.

### Study of the Factors Affecting the Stability of Supported Metals against Sulphur. I. Effect of the Nature of the Support on the Stability against Sulphur of Nickel-, Platinum- and Palladium-Containing Catalysts

G. V. ECHEVSKII, K. G. IONE, L. A. VOSTRIKOVA and L. S. EGOROVA, *Kinet. Katal.*, 1981, **22**, (1), 208-212

Studies of the stability of Pt, Pd and Ni supported catalysts against S were performed during 1-hexene hydrogenation. Stability of the catalysts did not depend on the Na content, the degree of dealuminisation of the Y type zeolites, mordenites, or on the nature of the support. The increase in activity of S containing metal catalysts with the increase of decationisation of the supports is connected with the stabilisation of more dispersed compounds.

### Design Factors of Dual Bed Catalysts

J. C. SUMMERS and D. R. MONROE, *Ind. Eng. Chem., Prod. Res. Dev.*, 1981, **20**, (1), 23-31

The effect of various design parameters on the performance of dual bed systems was studied. For front bed catalysts, in which Rh is very active, neither Pt nor Pd adds to the warmed up CO or HC conversions. Pt and Pd affect the NO conversion activity of Rh, deteriorating rich and enhancing lean conversions. Pt and Pd assist Rh for lightoff. The three-way durability performance of Pt and Pd is poorer than that of Rh. Increasing the noble metal loading of the rear bed increases the warmed up durability of the dual bed catalyst. Poisons are unequally distributed with P and Pb collecting heaviest on the front bed and S heaviest on the rear.

### Hydrocarbon Conversion Reactions over Platinum-Ruthenium Alloys Supported Catalysts

G. BLANCHARD, H. CHARCOSSET, M. GUENIN and L. TOURNAYAN, *Nouv. J. Chim.*, 1981, **51**, (2), 85-89

Poorly dispersed Pt-Ru/SiO<sub>2</sub> and well dispersed Pt-Ru/Al<sub>2</sub>O<sub>3</sub> were studied during hydrogenation of benzene, dehydrogenation of cyclohexane and conversion of n-heptane. For benzene hydrogenation the turnover number was a maximum for about 75at.% Ru/(Pt + Ru). In the two other reactions turnover number decreased as % Ru/(Pt + Ru) increased. The results are discussed in terms of the nearly identical mean and surface compositions of the Pt-Ru alloy particles, the dilute effects on Pt by Ru and the role of carbonaceous deposits.

### A Contribution of Catalysts for the Aromatising of Ethylene

O. V. BRAGIN, T. V. VASINA, A. V. PREOBRAZENSIIK, P. BIRKE, S. ENGELS and M. WILDE, *Z. Anorg. Allg. Chem.*, 1981, **472**, (1), 173-178

A series of monometallic, bimetallic and trimetallic platinum group metal catalysts supported on Al<sub>2</sub>O<sub>3</sub> were tested for the aromatisation of ethylene. The results were correlated with the composition and the metal dispersion of the catalysts.

### Palladium-Catalyzed Oxidation of Terminal Olefins to Methyl Ketones by Hydrogen Peroxide

M. ROUSSEL and H. MIMOUN, *J. Org. Chem.*, 1980, **45**, (26), 5387-5390

A very efficient catalytic procedure for the oxidation of terminal olefins to methyl ketones by  $H_2O_2$  using a Pd catalyst and operating in the absence of halogens and co-metals is discussed. A high selectivity for 2-octanone formation was observed, and a 90-95% conversion of 1-octene was obtained after 3 hours of reaction time. 3- and 4-octanone were the major by-products.

### Kinetics of Hydrogenation of Cyclic Butadiene Oligomers on Palladium Catalysts. I. Cyclooctadiene Isomers. II. 1,5,9-Cyclododecatriene Stereoisomers

J. HANIKA, I. SVOBODA and V. RŮŽIČKA, *Collect. Czech. Chem. Commun.*, 1981, **46**, (4), 1031-1038, 1039-1047

The kinetics of hydrogenation of 1,3- and 1,5-cyclooctadiene, cyclooctene and of 1,5,9-cyclododecatriene stereoisomers and cyclododecene were studied on Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/C and Pd/CaCO<sub>3</sub> catalysts in n-heptane solutions at 300K and H<sub>2</sub> at atmospheric pressure. The kinetic constants were obtained by relating the experimental data to a kinetic model in which the partial reactions are assumed to be first order.

### Selective Hydrogenation of Benzene over Platinum or Palladium Supported on Organic Polymer Catalysts. II. Characterisation of Palladium Deposited on Polyamide-66 by Hydrogen-Oxygen Titration and Electron Microscopy

C. MICHEL, C. HOANG-VAN and S. J. TEICHNER, *J. Chim. Phys. Phys.-Chim. Biol.*, 1981, **78**, (3), 241-245

The metal surface area of Pd/nylon-66 catalysts was measured by hydrogen-oxygen titration. The presence of Pd crystallites was observed inside the nylon carrier. Most of them had a mean diameter of ~30Å, thus confirming the Pd penetration during catalyst preparation into the bulk of the nylon carrier. Catalytic properties of Pd/nylon catalysts support the hypothesis of a modification of metallic sites resulting from an interaction between Pd and nylon.

### Chemical Oscillations of Methanol-Oxidation on a Pd-Supported Catalyst

N. I. JAEGER, P. J. PLATH and E. VAN RAAIJ, *Z. Naturforsch., A*, 1981, **36**, (4), 395-402

A periodic reaction was observed during the complete oxidation of MeOH to CO<sub>2</sub> and H<sub>2</sub>O over a Pd-supported catalyst. The temperature oscillations of the catalyst and the corresponding product distribution were measured and correlated with a chemical reaction scheme. This scheme is based on the monotonic behaviour of the pressure-concentration relationship in the Pd-H system.

### Study of the Effect of PdCu Zeolites Acidity on Their Catalytic Properties in Ethylene Oxidation to Acetaldehyde

KH. M. MINACHEV, N. IA. USACHEV, IA. I. ISAKOV, A. P. RODIN and V. P. KALININ, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, (4), 724-730

Catalytic properties of ion exchange PdCu catalyst supported on zeolites type A, X, Y, and mordenite during C<sub>2</sub>H<sub>4</sub> oxidation depended on their acidity. The increase in concentration of the acid OH group in PdCuNaY zeolites decreased the activity, selectivity and stability of the catalyst. Spectroscopic studies showed that NH<sub>3</sub>, which was added to zeolites in the Pd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> complex or by adsorption, reacted with acid H<sup>+</sup> centres in aluminosilicate and also with cations of transition metals.

### The Effects of Different Supports on the Formation and Reactivity of Surface Isocyanates on Pd, Ir, Ru and Rh

F. SOLYMOSI, L. VÖLGYESI and J. RASKÓ, *Magy. Kem. Foly.*, 1981, **87**, (1), 23-27

The effect of Al<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub> and SiO<sub>2</sub> supports for Pd, Rh, Ir and Ru catalysts was studied on the formation and stability of isocyanate species in the NO + CO reaction. Isocyanate formation occurred easily on TiO<sub>2</sub> supported metal, but very slowly on SiO<sub>2</sub>. The location of the isocyanate bond hardly depended on the metal, but was strongly influenced by the support. The isocyanate was relatively unstable on M/TiO<sub>2</sub> but was extremely stable on M/SiO<sub>2</sub>. The results were explained by assuming that isocyanate forms on the metal, but migrates rapidly onto the support, which thus determines its behaviour.

### Catalytic Synthesis of 3-Substituted Indoles Using CO as Building Block and Supported Rhodium as Catalyst

E. UCCIANI and A. BONFAND, *J. Chem. Soc., Chem. Commun.*, 1981, (3), 82-83

Under hydroformylation conditions, using Rh/C as catalyst, 2-nitrostyrene is directly converted into skatole in ~70% yield, by a reaction involving formation of 2-(o-nitrophenyl)propionaldehyde by homogeneous catalysis, reduction of the nitro-group by heterogeneous catalysis, then ring closure and thermal dehydration. Thus under severe hydroformylation conditions supported Rh can act as a reservoir of Rh carbonyl complexes and a mass contact able to activate H<sub>2</sub>, and a catalytic route to 3-substituted indoles from 2-nitrostyrenes and CO is available.

### Zeolite Support Effects on CO-Ru Interactions

D. G. BLACKMOND and J. G. GOODWIN, *J. Chem. Soc., Chem. Commun.*, 1981, (3), 125-126

An i.r. study of Co adsorption on a series of zeolite-supported Ru catalysts relates strong metal-support interactions to higher zeolite activity and lower Fischer-Tropsch/methanation activity.

## HOMOGENEOUS CATALYSIS

### Homogeneous Reduction of Nitrobenzene p-Chloronitrobenzene in Presence of Dichlorobis(phenylecyano)palladium(II) as Catalyst

T. K. BANERJEE and C. R. SAHA, *Indian J. Chem.*, 1980, **19A**, (10), 964-966

The complex  $\text{Pd}(\text{C}_6\text{H}_5\text{CH})_2\text{Cl}_2$  was prepared and used as a homogeneous catalyst for the reduction of  $\text{C}_6\text{H}_5\text{NO}_2$  and  $p\text{-ClC}_6\text{H}_4\text{NO}_2$  in a basic ethanolic medium. Reduction of  $\text{C}_6\text{H}_5\text{NO}_2$  produced only aniline (94%) under normal pressure and aniline and azoxybenzene (45% and 20%, respectively) under high pressure. The yield of  $p\text{-ClC}_6\text{H}_4\text{NH}_2$  from  $p\text{-ClC}_6\text{H}_4\text{NO}_2$  is highest (60%) at normal pressure and decreases with increasing pressure.

### A Chemist's Tool Kit

R. E. MERRILL, *Chemtech*, 1981, **11**, (2), 118-127

A review of biologically active compounds, most being optically active, is presented. Ways of synthesising them, especially by asymmetric syntheses are examined. The first asymmetric catalysis, including hydrogenation with Wilkinson's catalyst,  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ , is discussed, and asymmetric syntheses with chiral phosphine complexes are explained. Also discussed are asymmetric hydrosilylations, catalysed by Pt, Pd, Rh or Ni complexes and asymmetric alkylations.

### Kinetics and Selectivity of Homogeneous Hydroformylation of 1-Hexene with $\text{RhHCO}(\text{P}\phi_3)_3$

W. STROHMEIER and M. MICHEL, *Z. Phys. Chem. (Frankfurt am Main)*, 1981, **124**, (1), 23-31

Studies of the bulk hydroformylation of 1-hexene with  $\text{RhHCO}(\text{P}\phi_3)_3$  catalyst showed that the selectivity (*n*/isoaldehyde) increases with  $\text{P}\phi_3$  concentration as well as with decreasing total pressure and goes through a maximum at 90°C. The selectivity was practically independent of catalyst concentration when the rate was not controlled by gas diffusion. At constant pressure and catalyst concentration, the conversion of 1-hexene obeys a pseudo first order rate law.

### Catalytic Double Bond Isomerization by Polystyrene-Anchored $\text{RuCl}_2(\text{PPh}_3)_3$

A. ZORAN, Y. SASSON and J. BLUM, *J. Org. Chem.*, 1981, **46**, (2), 255-260

Dichlorotris(triphenylphosphine)Ru has been anchored to diphenylphosphinated styrene-divinylbenzene copolymer. The resulting catalyst has been successfully used for isomerising allylbenzenes and allyl alcohols in numerous turnovers. The catalyst stability was examined in several media and its performance compared with those of homogeneous  $\text{RuCl}_2(\text{PPh}_3)_3$  and with those of polymer-bound and free  $\text{RhCl}(\text{PPh}_3)_3$  and  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ .

### The Kinetics and Mechanism of Homogeneous Hydrogen Transfer upon Alcohols to Benzylideneacetone Catalyzed by Dichlorotris(Triphenylphosphine)Ruthenium(II)

G. SPEIER and I. MARKÓ, *J. Organomet. Chem.*, 1981, **210**, (2), 253-262

$\text{Ru}(\text{II})\text{Cl}_2(\text{PPh}_3)_3$  catalyses the transfer from alcohols to olefins. Kinetic studies were carried out at 170-190°C using the Ru(II) complex as homogeneous catalyst, benzyl alcohol, diphenylcarbinol, methylphenylcarbinol and benzoin as the H donors, benzylideneacetone as H acceptor and dibenzyl ether as a solvent. In the reaction mixture  $\text{RuCl}_2(\text{PPh}_3)_3$  is converted by the alcohols into  $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$  which then hydrogenates benzylideneacetone. The rate determining step is the transfer of H from the alcohol to a Ru species.

## FUEL CELLS

### Electrocatalytic Problems Associated with the Development of Direct Methanol-Air Fuel Cells

B. D. MCNICOL, *J. Electroanal. Chem. Interfacial Electrochem.*, 1981, **118**, 71-87

The potential advantages of the direct methanol-air fuel cell over conventional power sources are reviewed and in particular the area of noble metal catalytic electrodes is discussed in some detail. The role of the second component in bimetallic catalysts and the activity of such noble metal catalysts is also discussed. (41 Refs.)

## CHEMICAL TECHNOLOGY

### Production of Pd-Cu-Si Amorphous Wires by Melt Spinning Method Using Rotating Water

T. MASUMOTO, I. OHNKA, A. INOUE and M. HAGIWARA, *Scr. Metall.*, 1981, **15**, (3), 293-296

Continuous Pd-Cu-Si amorphous alloy wire has been produced by a melt spinning method directly from the liquid state. The wire was supercooled below the glass transition temperature of the alloy without breakup of the stable jet stream. The wires had good shape and uniformity.

## ELECTRICAL AND ELECTRONIC ENGINEERING

### Reaction at a Platinum-Gallium Arsenide Interface

D. L. BEGLEY, R. W. ALEXANDER, R. J. BELL and C. A. GOBEN, *Surf. Sci.*, 1981, **104**, (2/3), 341-353

The reaction at a Pt/n-GaAs interface after annealing at 400°C was investigated by various techniques. An increase in optical reflectivity was observed early in the annealing sequence, and a complex layered structure formed at the interface, but Ga was seen to

diffuse rapidly into the Pt film at apparent imperfections in the film. These areas are believed to be primary sites for premature IMPATT device failure.

### **An AES/XPS Study of the Chemistry of Palladium on Hydrogenated Amorphous Silicon Schottky Barrier Solar Cells**

J. H. THOMAS and D. E. CARLSON, *J. Electrochem. Soc.*, 1981, **128**, (2), 415-420

Thin layers of Pd (~100 Å thick) on hydrogenated amorphous Si have been used as diodes and photo-voltaic devices (solar cells). AES and XPS with ion-milling were used to characterise the interface region, where a thin oxide layer is observed along with possible Pd silicide. Pd and Pd silicides extend well into the Si substrate. Pd silicide is due in part to ion-mixing. The degradation is due to oxide formation at the Pd/a-Si:H interface.

### **Thin Palladium Silicide Contacts to Silicon**

S. KRITZINGER and K. N. TU, *J. Appl. Phys.*, 1981, **52**, (1), 305-310

A new approach to the development of very thin Pd<sub>2</sub>Si-to-Si contacts for possible future use in ultrasmall devices is described. It is based on the principle of diluting the silicide-forming Pd metal with Si, by codeposition of these two elements onto a single-crystal Si substrate. During annealing of the layered structure, Pd is extracted from the amorphous alloy to form the metal-rich and very stable compound Pd<sub>2</sub>Si at the surface. The decomposing Pd<sub>80</sub>Si<sub>20</sub> is also converted to Pd<sub>2</sub>Si. In this way, a silicide is formed for which only ~50% of the required Si need be supplied by the Si-substrate, resulting in a very shallow silicide contact.

## **NEW PATENTS**

### **METALS AND ALLOYS**

#### **Jewellery Alloys**

JOHNSON MATTHEY & CO. LTD.

*British Patent* 1,582,582

Pt alloys which may be cast by the lost-wax investment casting method contain a minimum of 95% Pt, 1.5-3.5% Ga and the balance Au or other specified metals. Around 0.1% Y may be added as a deoxidiser.

#### **Corrosion Resistant Amorphous Platinum Metal Alloys**

TOYO SODA MANUFACTURING CO. LTD.

*British Appl.* 2,051,128 A

Amorphous alloys, especially useful as electrode materials in brine cells, are prepared by rapid quenching from the liquid state, and contain 10-40 at.% P and/or Si with 0.7 at.% B and/or C, 90-60

### **A Comparison of Clad Inlay Gold, Palladium, and Palladium-Silver Contact Alloys**

R. J. RUSSELL and P. O. CAPP, *Insul./Circuits*, 1981, **27**, (3), 34-38

A comparison of contact resistance between Pd and 60%Pd-40%Ag and traditional Au alloys was performed. Pd and 60%Pd-40%Ag clad inlays had low, stable contact resistance under dry circuit conditions and with 100g load after artificial ageing. Au clad inlays had considerable contact resistance increases after artificial ageing. Their resistances were greater than those of Pd and 60%Pd-40%Ag at the same thickness. Pd and 60%Pd-40%Ag contact alloys were equal in performance to other precious metal alloys when subjected to a hostile gas environment.

### **MEDICAL USES**

#### **Pd-Co Dental Casting Ferromagnetic Alloys**

Y. KINOCHI, J. USHITA, H. TSUTSUI, Y. YOSHIDA, H. SASAKI and T. MIYAZAKI, *J. Dent. Res.*, 1981, **60**, (1), 50-58

Three dental alloys, 43wt.%Pd-57wt.%Co, 41wt.%Pd-54wt.%Co-5wt.%Cr and 43wt.%Pd-27wt.%Co-30wt.%Ni have been developed, and their magnetic and physical properties and corrosion resistances have been measured. The alloys were found to have magnetic properties suitable for generating an effective magnetic attraction in combination with the Sm-Co magnet. They have typical dental casting alloy properties, Pd-Co-Ni was the most easily melted and had the highest corrosion resistance.

at.%Pd, Rh and/or Pt or one of these metals combined with up to 80 at.% Ir and Ru and optionally up to 25 at.% Ti, Zr, Nb or Ta.

### **ELECTROCHEMISTRY**

#### **Electrochemical Cell**

NATIONAL RESEARCH DEVELOPMENT CORP.

*British Patent* 1,585,070

Electrochemical cells for detecting the presence of an oxidisable or reducible component, such as O<sub>2</sub> or H<sub>2</sub>, in a gas or a liquid suffer from background current flow which varies throughout the cell life. This is now overcome by using a Pt/Pt oxide counter electrode of surface area comparable to that of the working electrode, which may be formed from Pd, Ti, Zr, Y or Ni. The counter electrode used in the cell is preferably of Pd.