

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Specificity of Hydrogen Adsorption on Chromium-Supported Platinum Group Metal Catalysts

J. ADAMIEC, *React. Kinet. Catal. Lett.*, 1986, **30**, (1), 143-147

H₂ adsorption on Cr₂O₃ supported Pt, Pd and Rh was studied under various pretreatment conditions. The reduction temperature strongly influences the H₂ uptake for all these metals. Pt/Cr₂O₃ shows an unusually high H₂ adsorption stoichiometry.

Magneto-Optical Properties of Vacuum-Deposited PtMnSb Thin Films

T. INUKAI, M. MATSUOKA and K. ONO, *Appl. Phys. Lett.*, 1986, **49**, (1), 52-53

Magneto-optical properties of PtMnSb thin films, prepared by sequential vacuum deposition and annealing have been examined. Films annealed at 500°C exhibit a large Faraday rotation and a large polar Kerr rotation. They transmit light well in the 400-900nm wavelength range with an absorption coefficient of $3.2 \times 10^3 \text{ cm}^{-1}$ at 633nm.

Electrical and Structural Properties of Thin Palladium Films

R. ANTON, K. HÜPL, P. RUDOLF and P. WISSMANN, *Z. Naturforsch., A*, 1986, **41a**, (4), 665-670

The electrical resistivity of thin Pd films deposited on amorphous substrates was measured as a function of film thickness. Structural information was obtained from AES, TEM and X-ray diffraction studies. The steep decrease of resistivity in the ultra thin region can be correlated with the formation of coherent areas in the film. A more flattened course occurs at ~8nm film thickness when a continuous film develops.

Solubility of Helium in Melts of the Metallic Glass System Pd-Ni-P and in Related Systems

J. DIETRICH and G. H. FRISCHAT, *J. Mater. Sci.*, 1986, **21**, (7), 2535-2539

Glass melts of Pd₁₀₋₇₀Ni₁₀₋₇₀P₁₄₋₂₆ were saturated with He gas during the melt-spinning process. Pt was substituted for Pd, Mn, Fe and Co for Ni and B for P and these could also be saturated. The He could be extracted from the glasses. The He solubilities between 750 and 1250°C varied between 2 and 45 (μl He/mol glass). This method can measure very low gas solubilities in metallic glass melts where the solubilities obtained depend on the free volume and thus on the structure of the glasses and glass melts.

Synthesis, Lattice Parameters and Thermal Expansion Coefficients of Rhodium Arsenide Rh₂As and Some Substituted Compounds

M. SECOUE, P. AUVRAY, Y. TOUDIC, Y. BALLINI and R. GUERIN, *J. Cryst. Growth*, 1986, **76**, (1), 135-141

The lattice parameters of α-Rh₂As obtained by direct synthesis was measured between 295 and 956K. Its thermal expansion coefficient was practically constant within this temperature range. α-Rh₂As has numerous features in common with GaAs and seems to be favourable for coherent metal/semiconductor heteroepitaxy.

Preparation and Characterization of Conductive IrO_x Thin Films by Reactive Sputtering

S.-I. KAWATE, R. FUJIWARA, S. ODA and I. SHIMIZU, *Nippon Kagaku Kaishi*, 1986, (3), 249-254

Transparent conductive IrO_x films were prepared by reactive sputtering of an Ir target in O₂. IrO_x films of 500Å thickness have 85% transmittance in visible light, 60 S/cm conductivity at room temperature and sheet resistivity of 300 Ω. Optical, electrical and electrochemical properties of IrO_x films prepared under various sputtering conditions are described and bonding structures and valence bond profiles studied.

On 1/f Noise in RuO₂-Based Thick Film Resistive Films

A. KUSY and A. SZPYTMA, *Solid-State Electron.*, 1986, **29**, (6), 657-665

Results of 1/f noise power spectral density measurements on RuO₂-based thick resistive films are presented. A model of 1/f noise is proposed based on the results. Films made of RuO₂ of average particle size slightly smaller than 100Å have 1/f noise relative power spectral density 4-6 orders of magnitude smaller than RuO₂ films of average particle size 3000Å.

CHEMICAL COMPOUNDS

Water Soluble cis-Platinum(II) Complexes

S. A. HAROUTOUNIAN, M. P. GEORGIADIS and J. C. BAILAR, *Inorg. Chim. Acta, Bioinorg. Chem.*, 1986, **124**, (b16), (3), 137-139

Extremely water soluble complexes of cis-Pt(II) and 2-desoxytremptamine, D-glucosamine and 1-amino-2-methyl-2-propanol have been prepared; thus they may be less toxic than cis-DPP.

Crystal Growth of CsCl-Type $\text{Rh}_{50}\text{Al}_{50-x}\text{Cu}_x$ from Copper Solution

T. SHISHIDO and H. TAKEI, *J. Less-Common Met.*, 1986, **119**, (1), 75-82

Single crystals of $\text{Rh}_{50}\text{Al}_{50-x}\text{Cu}_x$ ($0 \leq x \leq 9$) have been prepared by the solution growth method, using Cu as solvent. The structure is the same as that of RhAl (CsCl-type) with space group B2.

ELECTROCHEMISTRY

The Electrochemistry of $[\text{PtH}(\text{PEt}_3)_3]^+$; Inverted and Amplified Cyclic Voltammetric Waves and Catalytic Hydrogen Production at a Mercury Electrode

R. G. COMPTON and D. J. COLE-HAMILTON, *J. Chem. Soc., Dalton Trans.*, 1986, (6), 1225-1229

The electrochemistry of $[\text{PtH}(\text{PEt}_3)_3]^+$ at a Hg drop electrode has been investigated by cyclic voltammetry. The inverted and amplified waves in the voltammograms are interpreted by catalytic cycles for H_2 production from water. The sweeps of the voltammograms and variations in peak shape and position are discussed and interpreted. By sweeping anodically to -1.7V it has been possible to observe catalytic H_2 production over 16 hours, which corresponds to an extremely efficient catalytic reaction with a turnover number of $\sim 2 \times 10^4$ /hour.

Characteristics and Stability of n-Si/SnO₂ and n-Si/SnO₂/Pt Photoanodes

D. BÉLANGER, J. P. DODELET and B. A. LOMBOS, *J. Electrochem. Soc.*, 1986, **133**, (6), 1113-1119

The photoanodic behaviour of the SIS solid-state heterojunction n-Si/SiO_x/SnO₂ was analysed in aqueous solution using various redox systems. The charge transfer at Ti/SnO₂ and Ti/SnO₂/Pt interfaces was determined, and for all the redox used, platinisation increased the heterogeneous rate constant by 1-2 orders of magnitude. Platinising n-Si/SnO₂ had no influence on J/V curves when $\text{Fe}(\text{CN})_6^{4-}$ was used. The most dramatic improvement upon platinisation was with I^-/I_2^- and $\text{Fe}^{2+}/\text{Fe}^{3+}$. The performance of the platinised photoanodes decreased with time.

Remarkable Enhancement of the Rate of Cathodic Reduction of Hydrocarbonate Anions at Palladium in the Presence of Caesium Ions

M. SPICHTER-ULMANN and J. AUGUSTYNSKI, *Helv. Chim. Acta*, 1986, **69**, (3), 632-634

Steady state polarisation curves obtained during electrochemical reduction of HCO_3^- ions at a smooth Pd electrode, obtained in CsHCO_3 and NaHCO_3 solutions were compared. For 1.0M CsHCO_3 the net current densities were up to 9 times larger than those observed in 1.0M NaHCO_3 solution. The Cs^+ cation may take part directly in the reaction at the cathode.

Anodic Characteristics of Amorphous Palladium-Base Alloys in Sodium Chloride Solutions

N. KUMAGAI, A. KAWASHIMA, K. ASAMI and K. HASHIMOTO, *J. Appl. Electrochem.*, 1986, **16**, (4), 565-574

The anodic characteristics of a variety of Pd-based alloys were examined for use in dilute NaCl solutions at 30°C. The corrosion resistance necessary for the Pd-metalloid anode was provided by alloying it with other platinum group metals and/or valve metals. Rh containing alloys showed high electrocatalytic activities for Cl_2 evolution. Surface activation was necessary to achieve sufficiently high activities for Cl_2 evolution at low overpotentials. The alloys had higher efficiency for Cl_2 evolution than existing anodes.

The Electrochemistry of Hexacyanoruthenate at Carbon Electrodes and the Use of Ruthenium Compounds as Mediators in the Glucose/Glucose Oxidase System

A. L. CRUMBLISS, H. A. O. HILL and D. J. PAGE, *J. Electroanal. Chem. Interfacial Electrochem.*, 1986, **206**, (1 and 2), 327-331

The reversible electrochemistry of the mediating couple $\text{Ru}(\text{CN})_6^{4-}/\text{Ru}(\text{CN})_6^{3-}$ at graphite rod, pyrolytic graphite edge plane and glassy C electrodes for possible use in glucose sensors and fuel cells is reported. The use of $\text{Ru}(\text{CN})_6^{4-}$ and $\text{Ru}(\text{NH}_3)_6^{2+}$ as mediators for the electrochemical oxidation of glucose oxidase in a glucose/glucose oxidase system is studied.

PHOTOCONVERSION

Optically Transparent Metallic Catalysts on Semiconductors

A. HELLER, *Pure Appl. Chem.*, 1986, **58**, (9), 1189-1192

Films consisting of 5nm Pt particles, which are substantially transparent, have been prepared by photoelectrodeposition of Pt onto p-InP under mass transport limited conditions. The resulting H evolving photocathodes convert sunlight to stored energy with a 13% Gibbs free-energy efficiency.

Strikingly High Photovoltages of Photoelectrochemical Solar Cells Equipped with Platinum-Coated and Alkali-Etched n-Si Electrodes

Y. NAKATO, H. YANO and H. TSUBOMURA, *Chem. Lett. Jpn.*, 1986, (6), 987-990

The open circuit photovoltages, V_{oc} , of photoelectrochemical cells with a Pt coated n-Si electrode in aqueous redox solution have been increased by etching the Pt coat in alkali solutions. The maximum V_{oc} obtained was 0.685V, $\sim 15\%$ higher than that on normal p-n junction Si solar cells (0.59V), indicating use as highly efficient solar energy converters.

Photoinduced Oxidation of Bromide to Bromine on Irradiated Platinized TiO₂ Powders and Platinized TiO₂ Particles Supported in Nafion Films

R. DABESTANI, X. WANG, A. J. BARD, A. CAMPION, M. A. FOX, S. E. WEBBER and J. M. WHITE, *J. Phys. Chem.*, 1986, **90**, (12), 2729-2732

The photoelectrochemical oxidation of bromide ion in O₂-saturated solutions of irradiated TiO₂ powders and TiO₂ in Nafion films with and without Pt was studied. K₂PtBr₆ appears to form when platinized TiO₂ powder or platinized TiO₂-Nafion interact with oxygenated aqueous KBr in light or darkness. Br₂ formation occurs efficiently only after the Pt has been totally converted to PtBr₆²⁻. The TiO₂/Nafion films produce Br₂ faster than TiO₂ powders.

Photo-Oxygenation of Alkylbenzenes by a Platinum Catalytic System

A. MONACI, *Gazz. Chim. Ital.*, 1986, **116**, (6), 339-340
Alkylbenzenes were photooxygenated under bubbling air at room temperature in the presence of a PtN₂S₂ complex as catalyst precursor. The wavelength of 254nm was effective for the reaction.

Water Photolysis over Metallized SrTiO₃ Catalysts

K. YAMAGUTI and S. SATO, *Nouv. J. Chim.*, 1986, **10**, (4 and 5), 217-221

Gas- and liquid-phase water photolysis was carried out on metal-free or Pt or Rh loaded SrTiO₃ powders. Metal-free SrTiO₃ produced an amount of H₂, but no O₂. However the Pt or Rh greatly enhanced the H₂ production rate with accompanying O₂ evolution. The Rh loading had higher photocatalytic activity than the Pt loading; maximum yield was ~1.2%. The effect of coatings of NaOH on metallized SrTiO₃ and metallized TiO₂ was also observed. Liquid-phase photolysis in 1.0N NaOH or 0.1N H₂SO₄ was significantly enhanced on reducing the thickness of the solution on the catalysts.

Interfacial Electron Transfer in Colloidal Metal and Semiconductor Dispersions and Photodecomposition of Water

K. KALYANASUNDARAM, M. GRÄTZEL and E. PELIZZETTI, *Coord. Chem. Rev.*, 1986, **69**, 57-125

An updated survey of literature on the photodecomposition of water is presented. The review is divided into sections covering photodecomposition in homogeneous dye-based systems using heterogeneous redox catalysts, homogeneous systems using homogeneous redox catalysts, heterogeneous redox catalysis, cleavage by u.v. and visible light in semiconductor-based systems and photochemistry and photoelectrochemistry in colloidal semiconductor systems. Platinum group metals contribute as sensitizers, catalysts and electrodes. Over 10% solar-to-chemical conversion efficiency for H₂ photogeneration is now achievable. (338 Refs.)

Photocatalyzed Transformation of Cyanide to Thiocyanate by Rhodium-Loaded Cadmium Sulfide in Alkaline Aqueous Sulfide Media

E. BORGARELLO, R. TERZIAN, N. SERPONE, E. PELIZZETTI and M. BARBENI, *Inorg. Chem.*, 1986, **25**, (13), 2135-2137

A process for totally disposing of CN⁻ by photocatalytic transformation to SCN⁻, which is 100 times less toxic is described. The process uses a 0.2wt.% Rh/CdS dispersion catalyst with light of λ ≥ 405nm or simulated AM1 solar radiation and an alkaline aqueous sulphide medium. H₂ is a byproduct. The quantum efficiency is ≥ 0.25.

Efficient Photochemical Conversion of Aqueous Sulphides and Sulphites to Hydrogen Using a Rhodium-Loaded CdS Photocatalyst

E. BORGARELLO, N. SERPONE, E. PELIZZETTI and M. BARBENI, *J. Photochem.*, 1986, **33**, (1), 35-48

An efficient photocatalytic dispersion has been developed from CdS and a 0.2wt.% Rh(III) salt via photodeposition. The catalyst is presumed to contain Rh species on the surface of the CdS particles, and can photocleave H₂S in the absence and presence of SO₂ in alkaline media, to produce H₂ and S or H and S₂O₃²⁻, respectively. The thermodynamic energy conversion efficiency is 0.17% or more.

Photoredox-Induced Polymerization of Microemulsion Droplets

C. K. GRÄTZEL, M. JIROUSEK and M. GRÄTZEL, *Langmuir*, 1986, **2**, (3), 292-296

Photoinduced polymerisations in cetyltrimethylammonium persulphate containing oil-in-water microemulsions were performed. Various monomers, including styrene, divinylbenzene, methyl methacrylate, etc., were polymerised highly efficiently under visible light by using Ru(bpy)₃²⁺ or eosin Y as a sensitizer. The morphology and size of the aggregates formed were examined.

Photogeneration of Carbon Monoxide and of Hydrogen via Simultaneous Photochemical Reduction of Carbon Dioxide and Water by Visible-Light Irradiation of Organic Solutions Containing Tris(2,2'-bipyridine)ruthenium(II) and Cobalt(II) Species as Homogeneous Catalysts

R. ZIESSEL, J. HAWECKER and J.-M. LEHN, *Helv. Chim. Acta.*, 1986, **69**, (5), 1065-1084

CO and H₂ are generated simultaneously by visible-light irradiation of a system containing the [Ru(bpy)₃]²⁺ complex and a Co(II) homogeneous catalyst, which mediate CO₂ and H₂O reduction by intermediate formation of Co(I), a tertiary amine as electron donor and an organic solvent. (64 Refs.)

LABORATORY APPARATUS AND TECHNIQUE

Anodic Detection in Flow-Through Cells

D. C. JOHNSON, J. A. POLTA, T. Z. POLTA, G. G. NEUBERGER, J. JOHNSON, A. P.-C. TANG, I.-H. YEO and J. BAUR, *J. Chem. Soc., Faraday Trans. I*, 1986, **82**, (4), 1081-1098

Progress in electrocatalytic processes for anodic detection in flowing aqueous solutions is discussed. Pulsed amperometric detection at Pt electrodes can sensitively detect the HCOOH groups in all alcohols, polyalcohols and carbohydrates, the N in amino acids and aminoglycosides, etc., and S in most inorganic and organic compounds. Detection at Pt is largely restricted to alkaline media. (85 Refs.)

Solid State Potentiometric Oxygen Gas Sensors

W. C. MASKELL and B. C. H. STEELE, *J. Appl. Electrochem.*, 1986, **16**, (4), 475-489

A review of recent literature on O₂ sensors which are used in industry, internal combustion engines and in domestic appliances is presented. The sensors operate in the zero current mode and are based on O ion conducting solid electrolytes. Among sensors considered are ones with Pt electrodes and platinum group metal reference electrodes. (60 Refs.)

Variable-Temperature ¹⁹⁵Pt NMR Spectroscopy, a New Technique for the Study of Stereodynamics. Sulfur Inversion in a Platinum(II) Complex with Methionine

D. D. GUMMIN, E. M. A. RATILLA and N. M. KOSTIĆ, *Inorg. Chem.*, 1986, **25**, (14), 2429-2433

The use of variable-temperature ¹⁹⁵Pt NMR spectroscopy for studying stereodynamics is discussed. It is uniquely suited to monitoring S inversion in the complex [Pt(N-acetyl-L-methionine)Cl₂]⁻, and to studying dynamic processes involving relatively complex biomolecules and processes causing subtle changes in molecular structure, which are not easily followed by ¹H and ¹³C NMR methods. Since the ¹⁹⁵Pt chemical shifts span a range greater than that of any other nucleus, they are highly sensitive to the nature of ligands and to subtle changes in molecular environment.

A New Method for Protection against Electrical Overheating Using a Sacrificial Coating and a CHEMFET Gas Sensor

J. F. ROSS, C. I. TERRY and B. C. WEBB, *J. Phys. E*, 1986, **19**, (7), 535-540

A method using a urea-containing paint which liberates NH₃ on heating was used to detect overheating in an electronic system. A Pt gate MOSFET was used as the detector. The urea-containing paint/Pt gate MOSFET was evaluated and could detect overheating of a resistor having a 0.025mm thick spray coat of the paint, at 100°C.

An Integrated Hydrogen-Switching Sensor with a Pd-Si Tunnel MIS Structure

M. OGITA, D.-B. YE, K. KAWAMURA and T. YAMAMOTO, *Sens. Actuators*, 1986, **9**, (2), 157-164

An integrated H-switching sensor has been made on a pn⁺ or np⁺ Si wafer by conventional means. The sensor has a MIS junction with a thin Pd film in series with a pn junction on the Si substrate. It can detect H₂ down to 10ppm or less at 100°C and can close or open an electric circuit depending on H₂ concentration. It can thus act as an actuator. The transition time is within 1min at 100ppm and 100°C.

Development of a Laboratory Cycle for a Thermochemical Water-Splitting Process (Me/MeH Cycle)

W. WEIRICH, B. BIALLAS, B. KÜGLER, M. OERTEL, M. PIETSCH and U. WINKELMANN, *Int. J. Hydrogen Energy*, 1986, **11**, (7), 459-462

A metal-metal hydride process for splitting water using heat has been developed with a TiNi membrane separating the H acceptor from the electrolyte. Metals for use as membranes which have high H permeation rates, corrosion resistance to the electrolyte and long service life are discussed. Coated membranes Pd/Cu on Ta or Nb have high H permeation rates and long term stability, suitable for up to 500°C.

Applications of Novel Proton-Conducting Polymers to Hydrogen Sensing

A. J. POLAK, S. PETTY-WEEKS and A. J. BEUHLER, *Sens. Actuators*, 1986, **9**, (1), 1-7

Two types of H₂ sensors based on the PVA/H₃PO₄ proton-conducting polymer electrolyte are examined. One is a solid state Pd hydride reference sensor and the other, which uses a gaseous reference source, has a self-supporting membrane with Pt electrodes on both sides. The ionic conducting polymer supports proton conduction down to -40°C and has a cationic transfer number of 1. The sensor could measure H₂ pressure (concentration) accurately and reproducibly from 10⁻⁴atm to 1atm, only CO and O₂ affected its performance. Both sensors had a response time <6s and could operate over a wide concentration range.

Summary Abstract: A Hydrogen Plasma Diagnostic Based on Pd Metal-Oxide-Semiconductor Diodes

R. BASTASZ and R. C. HUGHES, *J. Vac. Sci. Technol. A*, 1986, **4**, (3), Part 1, 629-630

When a PdMOS diode is used as a detector in H plasma or H ion beam, the energetic H ions striking the surface of the sensor are implanted into the device and bypass surface controlled steps. Energetic ions coming to rest in a thin Pd film at >20°C diffuse quickly to the sensitive junction and are rapidly detected, thus PdMOS diodes should be useful as H selective monitors for monitoring the flux and possibly the energy of plasma ions.

HETEROGENEOUS CATALYSIS

Immobilization of Colloidal Platinum Particles onto Polyacrylamide Gel Having Amino Groups and Their Catalyses in Hydrogenations of Olefins

H. HIRAI, M. OHTAKI and M. KOMIYAMA, *Chem. Lett. Jpn.*, 1986, (3), 269-272

Colloidal Pt dispersions are prepared and treated with polyacrylamide gel having amino groups, resulting in stable immobilisation of the Pt colloid onto the gel. This catalyst then exhibits high activities for olefin hydrogenations at 30°C under 1atm.

Lead Tolerance of Noble Metal Catalysts for CO Oxidation

T. CHANG and Y. S. SOHN, *Bull. Korean Chem. Soc.*, 1986, 7, (1), 12-15

The Pb tolerance of Pt/Al₂O₃ catalysts was evaluated for CO oxidation depending on the properties of the Al₂O₃ supports and base metals added as promoters. Promoters used were MnCl₂·4H₂O, SnCl₄·5H₂O, Fe(NO₃)₃·9H₂O and Cr(NO₃)₃·9H₂O, and base metals selected for incorporation into the Pt were B, Mn, V, Sn, Fe and Cr. Among the four different Al₂O₃ supports those with a large macropore volume (0.45 cm³/g) and 5% Ce showed the best resistance to Pb poisoning. Most of the base metals added to the Pt were ineffective for improving Pb resistance, but B has shown excellent Pb tolerance, although it decreases the initial catalytic activity.

Kinetics of the Reforming of C₇ Hydrocarbons on a Commercial PtRe/Al₂O₃ Catalyst

P. A. VAN TRIMPONT, G. B. MARIN and G. F. FROMENT, *Appl. Catal.*, 1986, 24, (1-2), 53-68

The kinetics of reforming C₇ hydrocarbons on a presulphided Pt-Re/Al₂O₃ catalyst between 627 and 776K and pressures 4.4-16.5 bars, with a H₂ partial pressure of 4-15.5 bars were compared with reforming on a Pt/Al₂O₃ catalyst. At 723K the production rates and selectivities for iso-heptanes and aromatics from a C₇ feedstock are higher on Pt-Re than on Pt. The Re-Pt has a higher affinity for S than Pt, allowing Pt-Re/Al₂O₃ to operate under S-free conditions without pronounced hydrogenolysis.

CO Oxidation on Pd/Al₂O₃. Transient Response and Rate Enhancement through Forced Concentration Cycling

X. ZHOU, Y. BARSHAD and E. GULARI, *Chem. Eng. Sci.*, 1986, 41, (5), 1277-1284

The catalytic oxidation of CO over Pd/Al₂O₃ was studied in a novel monolithic reactor with inside detection. The feed was periodically switched between CO/N₂ and O₂/N₂ giving time-averaged rates >40 times the maximum achievable steady-state rate. Mapping the time-averaged reaction rates gave a unique global maximum at each temperature and flow.

Palladium-Lanthanum Catalysts for Automotive Emission Control

H. MURAKI, H. SHINJOH, H. SOBUKAWA, K. YOKOTA and Y. FUJITANI, *Ind. Eng. Chem., Prod. Res. Dev.*, 1986, 25, (2), 202-208

A Pd/La₂O₃ was examined as a three-way catalyst in engine exhaust gas, simulated exhaust gas and for H₂, NO, H₂-NO-O₂, CO-H₂O and propylene-H₂O reactions. Air:fuel dependence of Pd/La₂O₃ was similar to that of Rh, and the NO conversion during warm-up conditions was much better than that of Pd in engine exhaust control. The La₂O₃ increases the activity and selectivity of Pd for NO reduction by H₂, it increases the activities for CO and propylene reactions with H₂O and also increases the amount of NO chemisorption.

New "Pd/Ultra-Thin Amorphous-Oxide Layer/ZSM-5" Catalysts for Selective Formation of Propane from CO/H₂

A. KASE, K. ASAKURA, C. EGAWA and Y. IWASAWA, *Chem. Lett. Jpn.*, 1986, (6), 855-858

Three new types of the title catalyst, containing La₂O₃, SiO₂ or TiO₂ layers were prepared. The La₂O₃ coated ZSM-5-supported Pd catalyst was selective for propane formation (68%) from CO and H₂ at 543K and 1.01MPa.

Silica-Supported Cationic Rhodium(I) Complexes as Hydrogenation Catalysts

V. ZBIROVSKÝ and M. ČAPKA, *Collect. Czech. Chem. Commun.*, 1986, 51, (4), 836-841

Cationic SiO₂ supported Rh(I) complexes prepared from Rh(COD)(acac) and phosphines of the type (C₂H₅O)₃Si(CH₃)_nP(C₄H₉)₂ (n=1-3), in the presence of p-toluene sulphonic acid were found to be efficient catalysts for the hydrogenation of alkenes, alkydienes and Z-α-acetamidocinnamic acid at 40°C and normal H pressure. The most efficient catalysts had a P:Rh ration = 2. With this ratio for each molecule of the immobilised complex, the catalysts were 3-4 times more active than their homogeneous analogues.

The Effect of Chlorine in the Hydrogenation of Carbon Monoxide to Oxygenated Products at Elevated Pressures on Rh and Ir on SiO₂ and Al₂O₃

B. J. KIP, F. W. A. DIRNE, J. VAN GRONDELLE and R. PRINS, *Appl. Catal.*, 1986, 25, (1-2), 43-50

The activities of Rh and Ir supported on SiO₂ and Al₂O₃ during the syngas reaction at elevated pressures were investigated. Rh was found to be more active than Ir and had a greater selectivity to higher hydrocarbons and C₂-oxygenates. For Rh/SiO₂ high oxo-selectivities were obtained (40%), while on Cl containing Al₂O₃ this selectivity was rather low. When a Cl-free metal precursor was used or when the RhCl₃/Al₂O₃ catalyst had special treatment, the oxo-selectivities were rather high (30%).

Anionic Homo and Heterometallic Clusters Associated with Polymer-Supported Cations Catalysts for Alkene Hydroformylation: Evidence for a Bimetallic Synergistic Effect

H. MARRAKCH, M. HAIMEUR, P. ESCALANT, J. LIETO and J.-P. AUNE, *Nouv. J. Chim.*, 1986, **10**, (3), 159-163

Polymer supported M_3 , M_4 ($M = Os, Ru$) and RuO_5 anionic clusters were catalysts for simultaneous hex-1-ene hydroformylation and isomerisation. The supported clusters were more active and selective than their soluble analogs. Os clusters were more active than Ru clusters, but Ru clusters were more selective. The mixed metal cluster was more active than corresponding single metal clusters.

HOMOGENEOUS CATALYSIS

The High Activation of $(Ph_2P)_2C=CH_2$ by Palladium Acetate or Palladium Chloride towards Additions

A. M. HERRING, S. J. HIGGINS, G. B. JACOBSEN and B. L. SHAW, *J. Chem. Soc., Chem. Commun.*, 1986, (11), 882-883

Pd acetate very highly activates co-ordinated $(Ph_2P)_2C=CH_2$ towards additions to amines, hydrazines, amino acid esters, alcohols, phenols, thiols, acetylacetone and acetoacetic ester. $PdCl_2$ also activates, but less strongly. $Pd(OAc)_2$ catalyses additions to the free ligand $(Ph_2P)_2C=CH_2$.

New Synthetic Reactions Catalyzed by Palladium Complexes

J. TSUJI, *Pure Appl. Chem.*, 1986, **58**, (6), 869-878

Pd-phosphine complexes catalyse four reactions of allylic β -keto carboxylates. Decarboxylation-allylation gives α -allyl ketones, and decarboxylation-dehydrogenation in boiling acetonitrile gives α , β -unsaturated ketones. The latter has been used as an industrial process for methyl jasmonate. Decarboxylation-deacetoxylation of α -acetoxy-methyl- β -keto carboxylates gives α -methylene ketones. Decarboxylation-hydrogenolysis occurs. (43 Refs.)

A Novel Rhodium-Tri-N-Alkylphosphine Catalyst System for the Hydrogenation of Carbon Monoxide, Formaldehyde and Glycolaldehyde

E. WATANABE, Y. HARA, K. WADA and T. ONODA, *Chem. Lett. Jpn.*, 1986, (3), 285-288

Syngas treatment of a mixture of a Rh compound of a large equimolar tri-n-alkylphosphine or tri(α -nonsubstituted alkyl)phosphine, and a solvent gives an orange yellow solution which is a highly active catalyst for CO hydrogenation to ethylene glycol and CH_3OH . Similarly, formaldehyde and glycolaldehyde are hydrogenated to CH_3OH and ethylene glycol, respectively, by the same catalyst.

Partial Hydrogenation of Benzene with Ruthenium Catalysts Prepared by a Chemical Mixing Procedure: Preparation and Properties of the Catalysts

S.-I. NIWA, F. MIZUKAMI, S. ISOYAMA, T. TSUCHIYA, K. SHIMIZU, S. IMAI and J. IMAMURA, *J. Chem. Technol. Biotechnol.*, 1986, **36**, (5), 236-246

Ru catalysts were prepared in different alcohols by a chemical mixing technique and characterised by preparation of a homogeneous solution containing the catalyst components and then uniform coagulation of the solution through hydrolysis. This technique has potential for controlling the surface area of the catalysts and for making them porous. The catalysts prepared by this method were much more effective for the partial hydrogenation of benzene to cyclohexene in the absence of poisons, such as alkali metal hydroxide or transition metal sulphates.

The Chemistry and Catalytic Properties of Ruthenium and Osmium Complexes. Part 4. A Comparative Study of the Reduction of Nitro Compounds under Hydrogen, Syngas and Water Gas

R. A. SANCHEZ-DELGADO and B. A. ORAMAS, *J. Mol. Catal.*, 1986, **36**, (3), 283-291

The reduction of nitrobenzenes to the corresponding anilines is efficiently achieved by using a series of Ru and Os complexes under H_2 , H_2/CO and CO/H_2O at moderate conditions. The reaction is best performed under water gas shift conditions in basic medium, in polar solvents. For monohydride catalysts, substitution of the aromatic ring by electron withdrawing groups results in lower rates and substitution by electron-releasing groups results in higher rates than the unsubstituted substrate, while the reverse is observed for dihydride species.

FUEL CELLS

Combined Electrochemical/Surface Science Investigations of Pt/Cr Alloy Electrodes

K. A. DAUBE, M. T. PAFFETT, S. GOTTESFELD and C. T. CAMPBELL, *J. Vac. Sci. Technol. A*, 1986, **4**, (3), Part II, 1617-1620

The role of Cr and its nature at the electrode surface was examined for C-supported PtCr electrodes for O_2 reduction in phosphoric acid fuel cells. Cyclic voltammetry in 85% phosphoric acid and XPS measurements are given. Electrodes with up to 40% Cr were stable up to +1.6V vs. dynamic-H electrode. Intermediate Cr levels had Cr leached from the surface by +1.5V, leaving a porous Pt electrode with increased electrochemical H adsorption capacity. $Pt_{0.7}Cr_{0.3}$ at >1.4V had Pt^{+4} and Cr^{+6} species stabilised in a porous phosphate overlayer up to 50Å thick. The Pt electrochemical H adsorption capacity simultaneously increased by a factor of 15.

Platinum-Vanadium Carbon Supported Catalysts for Fuel Cell Applications

G. CAMBANIS and D. CHADWICK, *Appl. Catal.*, 1986, **25**, (1-2), 191-198

Pt-V/C catalysts with various Pt:V ratios were prepared and reduced at several temperatures in N_2 , followed by characterisation which indicated Pt-V alloying. Activities for O_2 electroreduction were measured at 180°C in 100% orthophosphoric acid.

Methanol Electro-Oxidation and Surface Characteristics of Amorphous Pt-Zr Alloys Doped with Tin or Ruthenium

K. MACHIDA, M. ENYO, I. TOYOSHIMA, Y. TODA and T. MASUMOTO, *Surf. Coatings Technol.*, 1986, **27**, (4), 359-369

CH₃OH electrooxidation on amorphous Pt-Zr alloy electrodes doped with Sn or Ru were studied in 0.5 M H₂SO₄ by potentiostatic polarisation and compared with surface characteristics. The electrocatalytic activity was considerably enhanced by brief treatment with aqueous HF, which yielded a porous surface layer on the electrodes. The layer was in a higher state of dispersion than ordinary Pt black.

Improvement of Palladium-Carbon Electrodes for Hydrogen-Oxygen Fuel Cell. III. Preparing Methods of Hydrogen Electrode Catalysts Using Organic Palladium Complex

M. UEHARA and T. SUZUKI, *Denki Kagaku*, 1986, **54**, (4), 347-351

A method of preparing highly active catalysts from bis-2-phenyl- π -allyl Pd chloride was examined. The catalysts prepared were examined for anodic activity at 30°C in a half cell, and among other things it was concluded that to improve the dispersed adsorption an improvement in wetting the carrier surface was needed and for mild reduction of the complex the Pd complex should be added to almost freezing solvent. The catalysts obtained had 8 times the reactivity of usual Pd/C catalysts.

ELECTRICAL AND ELECTRONIC ENGINEERING

Pt-Si Contact Metallurgy Using Sputtered Pt and Different Annealing Processes

C.-A. CHANG, A. SEGMÜLLER, H.-C. W. HUANG, B. CUNNINGHAM, F. E. TURENE, A. SUGERMAN and P. A. TOTTA, *J. Electrochem. Soc.*, 1986, **133**, (6), 1256-1260

PtSi contacts were formed by different annealing processes using sputtered Pt. Two annealing sequences and three annealing ambients for each annealing sequence are compared. A three-temperature sequence allows a complete reaction between Pt and Si, leaving a thin passivating oxide layer with excellent protection against etching in aqua regia.

UHV-AES Investigation of Sulfur Surface Segregation in Precious Metal Wear Tracks

J. N. LLOYD, R. W. VOOK and L. E. POPE, *IEEE Trans. Components, Hybrids, Manuf. Technol.*, 1986, **CHMT-9**, (1), 92-96

Oscillatory sliding experiments in an UHV clean environment with 1atm He were performed on a Pd-base alloy pin on a Au-base alloy plate. The elements present in the wear tracks were measured by AES before and after several thousand cycles, and S was found which increased as the number of sliding cycles increased. The S partial pressure present in the He was $< \sim 1 \times 10^{-4}$ torr, and it is concluded that S originates from the bulk of the alloys.

TEMPERATURE MEASUREMENT

A Cryogenic Temperature Controller with a Stability of ± 0.03 K over Several Days

K. SRINIVASAN and H. W. HECK, *J. Phys. E*, 1986, **19**, (8), 594-597

The construction and operation of a temperature controller which has been used in the range 85-105K is described. A stability of ± 0.03 K in space and time can be ensured for a continuous operation over several days. Calibrated Pt resistance thermometers were used together with suitable bridges for measurement and control. No vacuum is used in the set-up.

Amorphous $Zr_{0.7}Pd_{0.3}$ as a Temperature Reference Near 2.5K

N. MAENE, F. BIERMANS, J. CORNELIS, A. VAN DEN BOSCH and J. VAN SUMMEREN, *Thermochim. Acta*, 1986, **103**, (1), 63-65

The superconducting transition temperature of high solidification rate material $Zr_{0.7}Pd_{0.3}$ was used as a temperature reference to estimate the temperature deviation between the thermometer and the sample in the pan of a vacuum microbalance with 10^{-9} N sensitivity. The latter equipment belongs to a system for measuring magnetic susceptibilities at low temperatures down to 2.2K.

Temperature Measurement in High Pressure Cells Using a Rhodium + 0.5%Iron-Chromel Thermocouple Pair

D. R. P. GUY and R. H. FRIEND, *J. Phys. E*, 1986, **19**, (6), 430-433

A thermocouple pair of Rh and 0.5at.%Fe-chromel provides usable sensitivity down to liquid He temperatures, for temperature measurement inside high pressure cells. The device has lowest sensitivity of $\sim 4\mu$ V/K at 15K, together with sufficient mechanical strength to withstand the handling necessary to assemble it inside the pressure cell.