

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

A Scanning Auger Microscopy Study of the Influence of Platinum on the High-Temperature Oxidation of a Nickel-Silicon-Magnesium Alloy

G. R. JOHNSTON, J. L. COCKING and W. C. JOHNSON, *Oxid. Met.*, 1985, 23, (5/6), 237-249

The oxide scale on Ni-4.4Si-0.1Mg alloy samples heated in air at 1100°C were analysed by high resolution scanning Auger microscopy. Concentration profiles through the oxide were taken. The presence of Pt, either in contact with the alloy or in the hot zone of the furnace increased the oxidation rate by an order of magnitude in comparison with the Pt-free rate. In the absence of Pt the multi-layered oxide scale was an outer layer of Mg-doped Ni oxide, overlying a silicate layer $(\text{Mg,Ni})_2\text{SiO}_4$, on top of a thin interfacial layer of SiO_2 . With Pt present the concentration of Mg in the oxide scale was below the detection limit.

Compositional Variations in the Near Surface Layers, an Atom-Probe Study of Cosegregation of Sulfur in Pt-Rh and Pt-Ir Alloys

M. AHMAD and T. T. TSONG, *J. Chem. Phys.*, 1985, 83, (1), 388-396

Equilibrium composition depth profiles with true single atomic layer depth resolution were obtained for the (001) plane of a Pt-Ir and five Pt-Rh alloys using the atom-probe field ion microscope. Pt segregates to the top two layers in Pt-Ir, and Rh segregates to the top layer in Pt-Rh alloys after annealing for 5 minutes at 700°C. An S overlayer segregates to the surface of these alloys, even though the bulk impurity content <100ppm. The coverage of S overlayers for Pt-Rh alloys varies between 0.22 and 0.52 of a monolayer, and increases with increasing surface Rh.

Ion-Induced Phase Formation in Metal-Silicon Systems

L. S. HUNG and J. W. MAYER, *Thin Solid Films*, 1985, 123, (2), 135-144

⁴He ion backscattering techniques and TEM were used to investigate the interaction of ion beams with thin film structures in a number of silicide forming systems. The mixed layer was an equilibrium compound of Pd and Pt metals and an amorphous phase for refractory metals. For Pd, the Pd_2Si phase grew with ion dose and remained crystalline up to high dose. Pd-Si and Pt-Si were the only systems where silicides formed and remained crystalline during ion irradiation at room temperature. Differences at liquid N_2 temperatures with doses were observed.

Study on the Electrical Conductivity of Pt/ZnO Catalysts

H. ZU-PEI, G. XIU-YING and L. WEN-ZHAO, *J. Catal. (Dalian, China)*, 1985, 6, (1), 87-90

An in situ examination of the electrical conductivity of Pt/ZnO catalysts during or after H treatment at room temperature and $\geq 300^\circ\text{C}$ has been performed. The electrical conductivity increased instantaneously by six orders of magnitude when Pt/ZnO catalyst pellets were exposed to H at room temperature. But it returned to its original value if the pellet was purged with N_2 or evacuated at room temperature to remove H_2 .

Perpendicular Magnetic Anisotropy in Pd/Co Thin Film Layered Structures

P. F. GARCIA, A. D. MEINHALDT and A. SUNA, *Appl. Phys. Lett.*, 1985, 47, (2), 178-180

Magnetic studies have been made of thin film periodic Pd/Co layered structures with ultrathin Co (4-13Å). Films with Co of thicknesses <8Å were easy to magnetise along a direction normal to the film surface. The best films had saturation magnetisation of $\sim 500\text{emu/cm}^3$ and a coercivity of 550 Oe, and could be used for vertical magnetic recording.

The Mg-Pd (Magnesium-Palladium) System

A. A. NAYEB-HASHEMI and J. B. CLARK, *Bull. Alloy Phase Diagrams*, 1985, 6, (2), 164-167

An assessed Mg-Pd phase diagram from 0-1600°C based on several cited references is reported. A discussion of intermediate phases, crystal structure data and lattice parameter data is also presented.

The $\text{H}_2\text{-O}_2$ Reaction on Palladium Studied over a Large Pressure Range: Independence of the Microscopic Sticking Coefficients on Surface Condition

H. M. DANNETUN, D. SÖDERBERG, I. LUNDSTRÖM and L. H. G. PETERSSON, *Surf. Sci.*, 1985, 152/153, (1), 559-568

The $\text{H}_2\text{-O}_2$ reaction was studied on the Pd gate of a Pd-MOS structure over a large pressure range. By measuring shifts in the C vs. V curve the changes in free H atom concentrations can be monitored. These results and others indicate a critical $\text{P}_{\text{H}_2}:\text{P}_{\text{O}_2}$ ratio of 0.4 where the surface turns from being O dominated to being H dominated. The critical ratio is independent of the absolute pressures and of surface conditions and shows no temperature dependence from 50-200°C. This implies H and O have similar sticking coefficients at the Pd surface. This device can be used as an H sensor in a catalytic reaction over a large pressure range.

XPS Studies on the Surface of Amorphous Pd₈₀Si₂₀ Alloys

Y. TAKAGI, C.-H. HWANG, H. SEKIZAWA and K. KAWAMURA, *Jpn. J. Appl. Phys.*, 1985, **24**, (4), 390-396

The depth profiles of the chemical states and composition of Pd and Si near the surface region of amorphous Pd₈₀Si₂₀ alloys have been studied by XPS. The depth profile can be divided into three characteristic regions: bulk, transient and skin. On passing through the transient region from the bulk to the skin, the amount of SiO₂ increases while that of Pd decreases. In the skin, amorphous SiO coexists with metallic Pd. The chemical state of Si in this region depends on the preparation conditions.

Hydrogen Adsorption States at the External and Internal Palladium Surfaces of a Palladium-Silicon Dioxide-Silicon Structure

L.-G. PETERSSON, H. M. DANNETUN, J. FOGELBERG and I. LUNDSTRÖM, *J. Appl. Phys.*, 1985, **58**, (1), 404-413

The H₂ adsorption states at the external and internal Pd surfaces of a H sensitive Pd-SiO₂-Si (Pd-MOS) structure have been studied in high and ultra high vacuum. The steady state response of the Pd-MOS shows a logarithmic dependence on H₂ pressure. The heat of adsorption of the internal surface is coverage dependent. There are always H adsorption states available at the internal surface, independent of the applied pressure, which explains how the Pd-MOS structure acts as an H sensor over wide pressures.

Electrical Conductivity of (Bi,Pb)₂MO₄ (M=Pd,Pt) Linear Chain Compounds

N. BETTAHAR, P. CONFLANT, J. C. BOVIN, F. ABRAHAM and D. THOMAS, *J. Phys. Chem. Solids*, 1985, **46**, (3), 297-299

Partial oxidation of Pd in Bi₂PdO₄ was achieved by substituting Pb²⁺ for Bi³⁺ up to Bi_{1.91}Pb_{0.09}PdO₄. Partial oxidation is necessary to stabilise the isostructural Pt compound Bi_{1-x}Pb_xPtO₄ in the range 0.33 ≤ x ≤ 0.52. Pt compounds had relatively high conductivities (σ ≈ 10/Ωcm) and low activation energies (≈ 0.02eV) with small variations in x. Pd compounds had lower conductivities which increased linearly with mean oxidation degree.

Oxygen Potential and the Chemical State of the Fission Products Ruthenium, Rhodium and Palladium in Irradiated Oxide Fuels

M. S. CHANDRASEKHARIAH, *J. Nucl. Mater.*, 1985, **130**, 366-374

Thermodynamic properties of intermetallic compounds of the type M₃U and M₃Pu where M = Pd, Rh or Ru are examined. These intermetallics have unusual thermodynamic stability. The presence of these intermetallics in nuclear fuel uranium-plutonia is unexplained. The critical O potential of the oxide fuel matrix for their formation is suggested.

CHEMICAL COMPOUNDS

Redox, Ligand-Exchange, Oligomerization, and Hydrosilation Chemistry of trans-Dichloro(ethylene) (phenazine) platinum

A. R. SIEDLE, K. R. MANN, D. A. BOHLING, G. FILIPOVICH, P. E. TOREN, F. J. PALENSKY, R. A. NEWMARK, R. W. DUERST, W. L. STEBBINGS, H. E. MISHMASH and K. MELANCON, *Inorg. Chem.*, 1985, **24**, (14), 2216-2223

A series of compounds of the type trans-(amine)PtCl₂(C₂H₄) (where amine = phenazine, quinoxaline, pyrazine, phenazine N-oxide, 2,6-dimethylpyrazine, tetramethylpyrazine, acridine) was prepared by displacement of chloride from PtCl₃(C₂H₄)⁻. (phenazine)PtCl₂(C₂H₄) is an effective hydrosilation catalyst and is the source of a series of novel bimetallic Pt-phenazine complexes and of polymetallic reduction products which are accessible by a number of routes.

η³-Allylpalladium Compounds

P. W. JOLLY, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, (4), 283-295

An in-depth study of the chemistry of the Pd-C bond is presented concentrating on η³-allylpalladium complexes. Their preparations, structures and reactions are examined. These complexes are frequently involved as intermediates in the Pd catalysed transformations of dienes. (76 Refs.)

A Novel Giant Palladium Cluster

M. N. VARGAFTIK, V. P. ZAGORODNIKOV, I. P. STOLYAROV, I. I. MOISEEV, V. A. LIKHOLOBOV, D. I. KOCHUBEY, A. L. CHUVILIN, V. I. ZAIKOVSKY, K. I. ZAMARAEV and G. I. TIMOFEEVA, *J. Chem. Soc., Chem. Commun.*, 1985, (14), 937-939

Various analytical techniques have been used to examine a new catalytically active cluster prepared by reduction of Pd(OAc)₂ by H₂ in the presence of L = 1,10-phenanthroline, or 2,2'-bipyridine, followed by O₂ treatment. The cluster produced contains a closely packed metal nucleus (570 ± 30 Pd atoms), bearing 60 ± 3 co-ordinated L and 180 ± 10 OAc⁻ in the outer sphere of the cluster. It is soluble in H₂O and polar organic solvents, and catalytically active in the oxidative acetoxylation of ethylene by O₂ to form vinyl acetate.

Synthesis of Novel Chiral Ruthenium Complexes of 2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl and Their Use as Asymmetric Catalysts

T. IKARIYA, Y. ISHII, H. KAWANO, T. ARAI, M. SABURI, S. YOSHIKAWA and S. AKUTAGAWA, *J. Chem. Soc., Chem. Commun.*, 1985, (13), 922-924

Reactions of [RuCl₂(COD)]_n (COD = cyclo-octa-1,5-diene) with the chiral bidentate phosphine ligands give new chiral Ru(II) complexes Ru₂Cl₄(BINAP)₂(NEt₃) and Ru₂Cl₄(p-tolyl-BINAP)₂(NEt₃). These act as excellent catalysts.

PHOTOCONVERSION

The Au/GaPc-Cl/Ferri, Ferrocyanide/GaPc-Cl/Pt Photoelectrochemical Cell

W. J. BUTTNER, P. C. RIEKE and N. R. ARMSTRONG, *J. Am. Chem. Soc.*, 1985, **107**, (12), 3738-3739

A photoelectrochemical cell has been constructed based upon vacuum-deposited (chlorogallium phthalocyanine, GaPc-Cl) thin films in contact with a Au/GaPc-Cl anode and a Pt/GaPc-Cl cathode, and a ferri/ferrocyanide redox electrolyte which acts as contacting phase between photoanode and photocathode. The work function difference between the two metals gives the driving force for the photoelectrochemical response. The resulting cell gave a photopotential response ~20% of the theoretical maximum dictated by the sum of the apparent band gaps.

Energy- and Electron-Transfer Processes for the Lowest Triplet Excited State of Tetrakis(diphosphito)diplatinat(II)

J. R. PETERSON and K. KALYANASUNDARAM, *J. Phys. Chem.*, 1985, **89**, (12), 2486-2492

Efficient transfer of excitation energy from ${}^3\text{Pt}_2(\text{POP})_4^{4-}$ was found to occur to various acceptors including naphthalene and $\text{Ru}(\text{bpy})_3^{3+}$. Efficient formation of redox products occurs both in reductive and oxidative quenching. Intense room temperature phosphorescence, high solubility in aqueous and non-aqueous media and long triplet lifetimes make $\text{Pt}_2(\text{POP})_4^{4-}$ useful as an energy sensitiser.

Hydrogen Photoproduction in a Continuous Flow System with u.v.-Light and Aqueous Suspensions of $\text{RuO}_x/\text{Pt}/\text{TiO}_2$

R. SIMARRO, S. CERVERA-MARCH and S. ESPLUGAS, *Int. J. Hydrogen Energy*, 1985, **10**, (4), 221-226

H_2 generation rates of up to $110\mu\text{mol/h}$ have been obtained in a continuous gas flow apparatus for the liquid phase photolysis of water using neutral aqueous suspensions of $\text{RuO}_x/\text{Pt}/\text{TiO}_2$.

Radiation Reduced Ir Sols: A Study of Their Catalytic Efficiency for Reduction of H_2O to H_2 by $\text{MV}^{+\bullet}$ Compared with Pt Catalysts

M.-O. DELCOURT and N. KEGHOUCHE, *Nouv. J. Chim.*, 1985, **9**, (4), 235-240

Ir colloids were prepared and used as catalysts to convert H_2O to H_2 via electron transfer from $\text{MV}^{+\bullet}$. Kinetic parameters using pulse radiolysis indicated that a fast process involves the fresh metal particles, while a slow one corresponds to a H-covered surface state. H_2 production with Pt or Ir was investigated and a catalytic mechanism is proposed. The Pt and Ir metal surfaces are almost totally covered by adsorbed H atoms, the desorption of which controls the overall process. H_2 desorption competes with MV^{2+} hydrogenation, the latter being favoured at high metal concentrations.

An Iridium-Bipyridine Complex as a Photosensitizer for the Bromide Oxidation to Bromine by Oxygen

A. SLAMA-SCHWOK, S. GERSHUNI, J. RABANI, H. COHEN and D. MEYERSTEIN, *J. Phys. Chem.*, 1985, **89**, (12), 2460-2464

An Ir(III)-bipyridine complex, $[\text{Ir}(\text{C}^3\text{-N}^1\text{-bpy})(\text{bpy})_2]^{2+}$, was used as a photosensitiser in aqueous bromide solutions. Steady-state photolysis of oxygenated solutions by near-u.v. and visible light produces equal concentrations of Br_3^- and H_2O_2 . The quantum yield of Br_3^- equivalents depends on pH, illumination dose and bromide concentration.

Hydrogen from Hydrogen Sulfide Cleavage. Improved Efficiencies via Modification of Semiconductor Particulates

M. BARBEN, E. PELIZZETTI, G. BORGARELLO, N. SERPONE, M. GRÄTZEL, L. BALDUCCI and M. VISCA, *Int. J. Hydrogen Energy*, 1985, **10**, (4), 249-253

Visible light irradiation of CdS dispersions containing H_2S in alkaline aqueous media gives efficient H_2 evolution; however, an improvement is observed when the CdS particles are loaded with RuO_2 . A combination of TiO_2 and CdS both loaded with RuO_2 gives increased efficiency. The H_2 evolution rate depends on the preparation conditions of CdS and TiO_2 . For the best catalyst combination and under direct sunlight irradiation the overall conversion efficiency of solar energy is 2%.

The Effect of the Substitution of Ru for Ti on the Electro- and Photoelectrochemical Properties of TiO_2 Crystals

C. GUTIÉRREZ and P. SALVADOR, *J. Electroanal. Chem. Interfacial Electrochem.*, 1985, **187**, (1), 139-150

The photoelectrochemical behaviour of a Ru doped TiO_2 crystal electrode of composition $\text{Ti}_{0.97}\text{Ru}_{0.03}\text{O}_2$ in contact with aqueous electrolyte was investigated. The substitution of Ru^{4+} for Ti^{4+} in the TiO_2 has two main effects, namely sensitisation to visible light and reduction of the overpotential for O_2 evolution.

ELECTRODEPOSITION AND SURFACE COATINGS

Experience with Platinum Aluminide Coatings in Land-Based Gas Turbines

R. BAUER, K. SCHNEIDER and H. W. GRÜNLING, *High Temp. Technol.*, 1985, **3**, (2), 59-64

Two Pt aluminide coatings were applied by a two-stage process to industrial gas turbines. Hot-corrosion crucible tests with salt mixtures to simulate actual blade deposits were then performed. Significant improvement to resistance against hot corrosion at intermediate temperatures $750-850^\circ\text{C}$ and against high temperature oxidising conditions of $\sim 950^\circ\text{C}$ were found. Coating life exceeded that of conventional NiCrSi coatings.

Electroplated Palladium-Silver (60/40wt%) Alloy as a Contact Material

F. I. NOBEL, *IEEE Trans. Components, Hybrids Manuf. Technol.*, 1985, **CHMT-8**, (1), 163-172

The use of electroplated 60Pd-40Ag in electronic and electrical applications is discussed. The properties of the deposits, including wearability, contact resistance, hardness and density of deposits, corrosion resistance, corrosion and preparations before use are examined. Comparisons with 80:20 Pd-Ni, Ag, Pd and hard Au are made. It is concluded the Pd-Ag electrodeposit is comparable to hard Au.

LABORATORY APPARATUS AND TECHNIQUE

New High Temperature Palladium Detectors for Oxygen Determination. Part I. Principles and General Signal Formula of a Semi-Continuous Detector

E. KOZŁOWSKI, M. BOWNIK and T. GÓRECKI, *Fresenius' Z. Anal. Chem.*, 1985, **320**, (7), 757-761

A new high temperature O₂ detector which operates in repeatable cycles is described. The detector has a 1.5g thin Pd foil bed in a stainless steel chamber in which, during the first part of the cycle, H₂ is made to dissolve. In the second part the sample gas flows through the bed. An instantaneous temperature rise due to the heat evolved in the reaction of the O₂ contained in the sample gas with H₂ dissolved in the bed gives a measure of the O₂ content. An equation for the output signal has been theoretically derived and experimentally confirmed in the range 205-450°C.

HETEROGENEOUS CATALYSIS

On the Chemical Oscillations in Differential Reactors: A Case Study of Ammonia Oxidation on Platinum

P. NOWOBILSKI and C. G. TAKOUDIS, *Chem. Eng. Commun.*, 1985, **33**, (1-4), 211-217

A review of the theories of the isothermal reaction mechanisms of NH₃ oxidation on a heterogeneous Pt catalyst is presented. It is shown that even in a differential catalytic reactor with conversions much less than 5%, the changes of the bulk concentrations of the reacting species may drastically affect the dynamic behaviour of the reaction system; it is suggested that they may drive the oscillations.

Free Radical Formation in the Catalytic Oxidation of NH₃ over a Polycrystalline Pt Surface at High Temperatures

G. S. SELWYN and M. C. LIN, *Langmuir*, 1985, **1**, (2), 212-219

The catalytic oxidation of NH₃ over a polycrystalline Pt surface at 800-1400K was investigated. Free radicals and transient species produced included NH, NH₂, OH, HNO, NO₂ and diatomic NH and OH. NH produced was diminished drastically by O₂ and yielded a desorption energy of 66kcal/mol.

Mathematical Modeling of Catalytic Converter Lightoff. Part II: Model Verification by Engine-Dynamometer Experiments; Part III: Predictions of Vehicle Exhaust Emissions and Parametric Analysis

S. H. OH and J. C. CAVENDISH, *AIChE J.*, 1985, **31**, (6), 935-942; 943-949

A transient mathematical model was developed to describe the behaviour of packed-bed catalytic converters during warmup. The predictions of the model agree very well with the results of engine-dynamometer experiments for three Pt/Al₂O₃ catalysts of widely different properties. Two catalysts were surface impregnated with 0.09wt.% and 0.56wt.%Pt and one was subsurface-impregnated. The model was also used to simulate the performance of a packed-bed converter during the cold-start period of vehicle emission tests. Effects of poisons on catalysts, and converter designs are examined.

Production of Hydroxylamine from Nitrogen Oxide: A Short Review

G. R. TAUSZIK and P. CROCETTA, *Appl. Catal.*, 1985, **17**, (1), 1-21

The industrial production of hydroxylamine by hydrogenation of NO in dilute H₂SO₄ using a Pt/C catalyst was studied. Various aspects of this process, including catalyst composition, reaction kinetics and mechanisms, role of mass transport phenomena and the electrochemical reduction of NO, are discussed. It is concluded that more experimental work is needed to clarify the reaction mechanism and that attention to catalyst poisoning is needed. (40 Refs.)

Dynamic Behavior of Automotive Catalysts. III. Transient Enhancement of Water-Gas Shift over Rhodium

R. K. HERZ and J. A. SELL, *J. Catal.*, 1985, **94**, (1), 166-174

The responses of catalysts Rh/Pt/Ce/Al₂O₃, Pt/Ce/Al₂O₃ and Pt/Rh/Al₂O₃ were examined for the water-gas shift reaction in engine exhaust gases. A transient reduction in CO emission was observed over all three catalysts when they were stabilised under rich exhaust and then given a 1s exposure to lean exhaust. Explanations of part of the responses were made, but lean-to-rich step response experiments gave evidence for the water-gas shift reaction.

Characteristics and Surface Morphology Change of Modified PtRh10 Gauze of HCN Synthesis

T. BACZYŃSKA, M. SEWERYNIAK and J. WRZYSZCZ, *React. Kinet. Catal. Lett.*, 1985, **17**, (1), 21-25

The modification of Pt-Rh10 gauze catalysts, used for HCN synthesis, by coating their surfaces with a thin film of Pt-Rh/Al₂O₃ is reported. Comparisons in activity, selectivity and morphological changes in the catalyst surface for standard gauzes and those covered with a thin film are reported.

The Deuterium-Exchange Reaction between Water and Hydrogen with the Thin-Film Hydrophobic Catalyst

H. YAMASHITA, M. MIZOMOTO and S. MATSUDA, *Nippon Kagaku Kaishi*, 1985, (4), 669-673

The D₂ exchange reaction between H₂O and H₂ with a hydrophobic Pt/porous PTFE catalyst as support was studied. Catalyst reactivity was measured in a trickle bed reactor at atmospheric pressure and temperature 20-70°C. Pt particles on thin film PTFE work efficiently as catalysts because the reactants were easily diffused to the active sites. The isotopic exchange rate with the thin film catalyst increased with the increase in the liquid: gas ratio and with the rise of the reaction temperature.

Colloidal Noble Metal Catalysts Supported on Ion-Exchange Resins

Y. NAKAO and K. KAERIYAMA, *Kobunshi Ronbunshu*, 1985, 42, (4), 223-229

Hydrosols of Pt, Rh, Pd and Ru were prepared from aqueous solutions of the corresponding noble metal salts by NaBH₄ reduction. Anion exchange resins adsorbed the colloidal particle to give noble metal catalysts for hydrogenation, while for cation exchange resins only a H-form resin adsorbed colloidal Rh and Ru to give supported catalysts. Electron micrographs indicate that Rh on the cation exchange resins has more "coagulated" states than on the anion exchange resins. Two mechanisms for the adsorption are presented. Catalytic activity is higher for cation exchange resin.

Some Catalytic Properties of Palladium and Rhodium Supported Catalysts

G. A. DEL ANGEL, B. COQ, G. FERRAT, F. FIGUERAS and S. FUENTES, *Surf. Sci.*, 1985, 156, (2), 943-951

Some reactions involving C-H, C-C, C-Cl and C-O bonds were investigated on Rh and Pd supported catalysts in relation to the metallic structure. Generally there is a structure insensitivity for Pd, but not for Rh. For Rh, small particles are more active than large particles when SiO₂ is the support.

Synthesis Gas Conversion Utilizing Mixed Catalyst Composed of CO Reducing Catalyst and Solid Acid. IV. Selective Synthesis of C₂, C₃, and C₄ Paraffins from Synthesis Gas

K. FUJIMOTO, H. SAIMA and H. TOMINAGA, *J. Catal.*, 1985, 94, (1), 16-23

Synthesis gas could be converted selectively to C₂-C₄ paraffins with hybrid catalysts of Pd/SiO₂ (methanol synthesis catalyst) and Y-type zeolite. Best conditions were 300-350°C and 1.0-5.1 MPa. A hybrid catalyst containing a steam-treated high SiO₂ Y-zeolite gave C₂-C₄ paraffins with a selectivity >85%, with almost no aromatic hydrocarbons and coke with CH₄ selectivity of 2% or less, while CH₃OH conversion on the zeolite gave aromatic hydrocarbons and coke with selectivities of 30% and 11%, respectively.

Palladium/Polyethylenimine Catalysts

G. P. ROYER, W.-S. CHOW and K. S. HATTON, *J. Mol. Catal.*, 1985, 31, (1), 1-13

The preparation and evaluation of Pd catalysts made from polyethylenimine(PEI)/SiO₂ composites are discussed. PEI was adsorbed on either porous SiO₂ beads or SiO₂ gel. After crosslinking, the material was loaded with base to increase surface area and availability of the polymer. Pd/PEI/SiO₂ beads are used effectively in suspension with HCOOH acid as the H donor; deprotonation of carbobenzoxy-Glycine-O-t-butyl is very rapid compared to Pd/C.

Preparations of TiO₂-Attached Rh Catalysts and Their Catalysis

Y. IWASAWA and H. SATO, *Chem. Lett. Jpn.*, 1985, (4), 507-510

The preparation of new TiO₂-attached Rh catalysts is described. The catalysts were prepared by the reaction between Rh(η^3 -C₃H₅)₃ and surface OH groups on TiO₂ followed by chemical treatment with H₂. The catalysts had higher activities for ethane hydrogenolysis and ethene hydrogenation than a conventional impregnated Rh catalyst. The most active catalyst was the mononuclear Rh hydride species. The surface structures of these catalysts have no analogues with homogeneous and conventional heterogeneous catalysts, and may be typical examples of a new class of catalysts.

Preparation and Catalytic Activity for Ammonia Synthesis of Several Ruthenium Supported Catalysts

P. RAMIREZ DE LA PISCINA, N. HOUS and J. E. SUEIRAS, *Z. Anorg. Allg. Chem.*, 1985, 522, 235-240

Supported Ru catalysts were prepared from RuCl₃.3H₂O and K₄[Ru(CN)₆].3H₂O solutions, upon several acid/base pretreated γ -Al₂O₃ samples, using water and acetone as solvents. An increasing Ru content of the catalysts with increasing acid site content of the support is observed, when K₄[Ru(CN)₆].3H₂O is used as a precursor. Catalysts prepared from K₄[Ru(CN)₆].3H₂O were about 10 fold more active than those prepared from RuCl₃.3H₂O. The more active catalyst was sensitive to acid pretreatment of γ -Al₂O₃, while those prepared from RuCl₃.3H₂O were not.

HOMOGENEOUS CATALYSIS

Carbonylative Cross-Coupling Reaction of Aryl Iodides with Alkylaluminums by Palladium Complex Catalysis

Y. WAKITA, T. YASUNAGA and M. KOJIMA, *J. Organomet. Chem.*, 1985, 288, (3), 261-268

Secondary and/or tertiary alcohols and unsymmetrical ketones have been obtained in moderate to good yields by Pd catalysed carbonylative coupling of aryl iodides with alkylaluminium compounds under very mild conditions. The type of reaction product depended on the kind of Al reagent used.

Homogeneous Catalytic Hydrogenation of Soybean Oil: Palladium Acetylacetonate

S. KORITALA, *J. Am. Oil Chem. Soc.*, 1985, **62**, (3), 517-520

Soybean oil was hydrogenated with Pd acetylacetonate at 60-170°C, 150psi H₂ pressure and 1-60ppm Pd. The best linolenate selectivity was found at 80-120°C. At 120°C Pd acetylacetonate hydrogenated faster than the Pd/C catalyst. Trans isomerisation with the homogeneous catalyst was much higher than with Pd/C.

Homogeneous Catalysis of the Water Gas Shift Reaction by (Polypyridine) Rhodium Complexes

D. MAHAJAN, C. CREUTZ and N. SÜTIN, *Inorg. Chem.*, 1985, **24**, (13), 2063-2067

Homogeneous catalysis in the water gas shift reaction under mild conditions (<100°C and 1atm CO) was achieved with several (polypyridine)Rh(I) complexes as catalyst precursors in alcohol-water mixtures. Complex Rh(bpy)₂⁺ was the most active catalyst precursor (~3 turnovers/h at 90°C).

Rhodium Complexes as Catalysts for Hydrosilylation Crosslinking of Silicone Rubber

M. HEIDINGSFELDOVA, *J. Appl. Polym. Sci.*, 1985, **30**, (5), 1837-1846

The vulcanisation of a Si rubber compound, based on polysiloxane-containing vinyl and Si-H groups catalysed by [RhCl(CO)₂]₂, [RhCl(C₂H₄)₂]₂, [RhCl(1,5-COD)]₂, [RhCl(NBD)]₂, RhClP(C₆H₅)₃]₃, and Rh(acac)₃ (1,5-COD = 1,5-cyclooctadiene, NBD = norbornadiene, acac = acetylacetonate) was studied. Effect of solvent, the cross-linking density of the rubber, sol content, vulcanisation times and catalysts were examined.

FUEL CELLS

Electrode Designs and Concepts for Bipolar Alkaline Fuel Cells

K. KORDESCH, J. GSELLMANN and R. D. FINDLAY, *Int. J. Hydrogen Energy*, 1985, **10**, (5), 317-324

The construction and production of mass produced alkaline fuel cells are described. The multiple layer electrodes used in alkaline electrolytes, and alkaline and acidic electrolytes are discussed. All use Pt/C with various amounts of Pt in their construction.

A Chemically Regenerative Redox Fuel Cell. II

J. T. KUMMER and D.-G. OEI, *J. Appl. Electrochem.*, 1985, **15**, (4), 619-629

Redox fuel cells with V²⁺/V³⁺ and Mo³⁺/Mo⁴⁺ redox couples as the anolyte and a NO₂⁻/NO catalyst system for VO²⁺ oxidation were examined. Highly acidic (~3M H₂SO₄) molybdate solutions were readily reduced by H₂ using Pt or Pd as catalyst.

ELECTRICAL AND ELECTRONIC ENGINEERING

Tungsten-Platinum Alloy Schottky Barriers on n-Type GaAs

T. OKUMURA and K. N. TU, *Appl. Phys. Lett.*, 1985, **47**, (1), 42-44

Alloys of W and Pt were studied as Schottky contact materials in n-type GaAs. Schottky barrier heights for W₅₀Pt₅₀ and W₈₀Pt₂₀ were measured, and were found to be 0.90 ± 0.02eV by C-V and photoresponse techniques, and did not change with annealing at 350°C for 20h. However the value from the I-V technique changed from ~0.6 to 0.7 eV upon annealing. W₅₀Pt₅₀ was the more stable on GaAs.

Platinum Intermetallic Resistors for GaAs-Based Circuits

S. TIWARI and W. H. PRICE, *Electron. Lett.*, 1985, **21**, (10), 429-430

A simple technique for making GaAs/Pt intermetallic resistors of sheet resistance ~25Ω/□ is described. The resistors were made by reacting a 300Å Pt film with GaAs and then sintering. X-ray diffraction identified PtGa and PtAs₂ in all samples, and PtGa₂ in samples annealed at 450°C. The TCR was ~9.2 × 10⁻⁴/°C at 25°C, and the resistors were stable up to current densities of 10⁵A/cm².

Properties of Electroplated Noble Metal Layers as Contact Materials for Switching Contacts

H. GROSSMANN, M. HUCK, G. SCHAUDT and F. J. WAGNER, *Metall.*, 1985, **39**, (7), 619-623

Various electrodeposits of 5μm and 10μm thicknesses on non-precious metals were tested on a model device as materials in switching contacts in relays and keys. The resistance of the electroplated contact layers was related to their hardness. Electrodeposits were tested at various electric load conditions: 28-550mA DC at 12V and 24V. For loads of 12V/12mA and on a layer thickness of 5μm the following number of operations were possible: AuCo 5 × 10⁴, AuPd6Cu₂ 5 × 10⁶, Pd, PdNi₂₀ ~ 10⁷, Rh > 10⁷.

Electron Emission and Surface Composition of Osmium and Osmium-Tungsten Coated Dispenser Cathodes

D. BRION, J.-C. TONNERRE and A. SHROFF, *Appl. Surf. Sci.*, 1985, **20**, (4), 429-456

The surface composition of impregnated cathodes with coatings of pure Os 50-30,000Å thick or mixed Os-W coatings (10-70% Os) were measured by AES, during activation and short duration ageing at 1000°C_B (degrees Celsius brightness). During activation of cathodes with pure Os coatings (>3000Å) the W diffuses into the Os until saturation of the θ phase occurs throughout the coating depth. Electron emission from cathodes coated with pure Os is three times greater than that of "type S" cathodes, whatever the coating thickness. Electron emission from mixed-coated cathodes is slightly less than that of pure Os.