

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

On the High Energy Product of Fe-Pt Permanent Magnet Alloys

K. WATANABE and H. MASUMOTO, *Trans. Jpn. Inst. Met.*, 1983, **24**, (9), 627-632

The relationship between permanent magnetic properties and the microstructures of Fe-34-67.5 at.%Pt binary alloys was investigated by a recording fluxmeter, X-ray diffraction and electron microscopy. Excellent permanent magnetic properties were obtained by water quenching from a temperature in the γ phase range and subsequent reheating at a lower temperature in the γ phase range. Typically Fe-38.5at.%Pt exhibits the highest value of maximum energy producing 159kJ/m^3 , with a coercive force of 340 kA/m and a residual flux density 1.08T.

Study of Pt-Re Alloy Systems

L. I. VORONOVA, V. P. POLYAKOVA and E. M. SAVITSKI, *Izv. Akad. Nauk. SSSR, Met.*, 1984, (1), 185-187

Studies were made of the behaviour of Pt-Re alloys containing up to 50at.%Re at high temperatures. Some properties of the alloys in Pt based solid solutions are presented.

Effect of Palladium Additions to AISI 4130 Steel on Its Sulfide Cracking Susceptibility

J. B. LUMSDEN, B. E. WILDE and P. J. STOCKER, *Scr. Metall.*, 1983, **17**, (8), 971-974

Pd metal additions were made to AISI 4130 steel to determine its effects on sulphide stress cracking (SSC) susceptibility and to correlate these effects with changes in the composition and morphology of sulphide inclusions. Pd additions up to 0.1w/o had no effect on SSC resistance; however, cracks did not initiate in specimens with 0.6 and 1.0w/o Pd. The morphology of the sulphide inclusions was not altered by Pd. It is suggested that a segregated layer of Pd prevents the build up of high internal H pressures at sulphide inclusions.

Effect of Palladium and Oxygen Layers on the Hydrogen Absorption Rate of Tantalum Films at 300K

H. UCHIDA and E. FROMM, *J. Less-Common Met.*, 1983, **95**, (1), 153-155

The H₂ absorption rates of Ta films with Pd overlayers and O₂ contamination were compared with curves for pure Ta and Pd films. The Pd overlayers have no effect on the absorption of H₂ by Ta, whereas the absorption of 3.5×10^{15} O₂ molecules/cm² between the Ta and Pd layers reduces the H₂ absorption rate to that of the Pd overlayer.

Hydrogen Embrittlement of Pd-Ag Binary Alloys

T. MARUNO, H. TSUJI and R. OTSUKA, *J. Jpn. Inst. Met.*, 1983, **47**, (9), 768-775

Pd-Ag binary alloys were investigated by electrolytic H charging and X-ray diffraction for H embrittlement. Hydride formation was controlled by varying the Ag content and temperature. H embrittlement occurred only when the hydride was formed. Depending on the Ag content, Pd-Ag alloys were hardened or softened by H charging, but these were not responsible for the direct H embrittlement.

Magnetic Double Transitions in Amorphous Pd_{77.5-x}Cu₆Si_{16.5}Fe_x Alloys

D. M. HERLACH, J. KÄSTNER, A. HELLER and E. F. WASSERMANN, *J. Magn. & Magn. Mater.*, 1983, **40**, (1 & 2), 98-106

Static magnetisation and a.c. susceptibility measurements are reported on sputter cooled amorphous Pd_{77.5-x}Cu₆Si_{16.5}Fe_x with $x = 1-15\text{at.}\% \text{Fe}$. Alloys with $x \leq 5\text{at.}\% \text{Fe}$ exhibit short-range ferromagnetic order with the transition at low temperatures. Alloys with 10-15at.%Fe show double transitions with long-range ferromagnetic order prior to a second transition into a spin-glass like state whereas the ferromagnetic transition is sharp and the critical temperature well defined.

The Young's Moduli of Glassy Pd-Si-H Alloys

R. S. FINOCCHIARO, C. L. TSAI and B. C. GIessen, *J. Non-Cryst. Solids*, 1984, **61 & 62**, (1), 661-666

Young's moduli E, of hydrogenated Pd_{100-x}Si_x metallic glasses with $14 \leq x \leq 22$ were measured as a function of H content at room temperature and at H pressures up to 1000torr. At small H concentrations, n_H, E is almost constant up to a limiting concentration n_{H,c} which depends on the alloy composition, x_{Si}. Above n_{H,c} all hydrogenated Pd-Si glasses show a clear decrease in E with increasing n_H.

Crystallization Process of Amorphous Pd-Si Alloys and the Effect of Atmosphere

K. TOKUMITSU, A. TANAKA and H. INO, *J. Jpn. Inst. Met.*, 1983, **47**, (10), 814-817

The effect of atmosphere on the crystallisation process of amorphous Pd₈₀Si₂₀ was investigated by X-ray diffraction, the Mössbauer effect and AES. The bulk of the specimen was stable during ageing at 473 K both in vacuo and in Si oil. Crystallisation to the f.c.c. solid solution phase occurred only in the surface region ($< 1\mu\text{m}$) even when ageing in Si oil. A Si poor and Pd rich region was formed between the surface and the bulk of the amorphous specimen as a result of the formation of Si oxide at the surface.

Magnetic Properties of RPd_2Si Ternary Compounds with (R = Gd, Tb, Dy, Ho and Er)

D. GIGNOUX, J. C. GOMEZ-SAL and D. PACCARD, *Solid State Commun.*, 1984, **49**, (1), 75-77

Magnetic properties of polycrystalline samples of RPd_2Si compounds are presented. The Gd and Tb based compounds are antiferromagnetic with Néel temperatures of 13.5 and 21K, respectively. In TbPd_2Si a transition between two different antiferromagnetic phases is observed at 8.5K, and for both compounds a metamagnetic transition is observed in low field. The Dy, Ho and Er based compounds are ferromagnetic with Curie temperatures of 9, 3.5 and 2.8K, respectively.

Adsorption of Oxygen on Polycrystalline Rhodium at Low Temperatures

T. MATSUSHIMA, *J. Catal.*, 1984, **85**, (1), 98-104

The adsorption and desorption of O_2 was studied on well-polished polycrystalline Rh surfaces at 120-1350K by thermal desorption, isotope tracer and Auger electron spectroscopy. Isotope-exchange experiments showed that the low temperature desorption peak ($\sim 160\text{K}$) results from molecular adsorption, while the high temperature peak (600-1200K) results from atomic adsorption. At 120K O_2 molecules are dissociated to adatoms.

Phase Study and Magnetic Behaviour of a New Series of Ternary Borides ($\text{RE}_{1-x}\text{Rh}_x$) Rh_3B_2 (RE = Y, La, Nd, Sm, Gd, Tb, Dy, Ho, Er)

T. OHTANI, B. CHEVALIER, P. LEJAY, J. ETourneau, M. VLASSE and P. HAGENMULLER, *J. Appl. Phys.*, 1983, **54**, (10), 5928-5934

A new series of ternary borides with formula ($\text{RE}_{1-x}\text{Rh}_x$) Rh_3B_2 (RE = Y, La, Nd, Sm, Gd, Tb, Dy, Ho, Er) has been prepared. Their crystal structure is hexagonal with $\text{P6}_2\text{m}$ space group. A large homogeneity range is observed, $0.29 \leq x \leq 0.52$, for the Nd compounds. The compounds with magnetic rare earth ions are ferromagnetic with T_c growing up to 15K and show a large increase in μ_{eff} effective moment.

Transition from Antiferromagnetism to Ferromagnetism in the Superconducting Mixed Ternary System ($\text{Sm}_{1-x}\text{Er}_x$) Rh_4B_4

S. E. LAMBERT, L. D. WOOLF and M. B. MAPLE, *J. Low Temp. Phys.*, 1984, **54**, (1/2), 177-190

The mixed ternary system ($\text{Sm}_{1-x}\text{Er}_x$) Rh_4B_4 has been investigated by measuring a.c. electrical resistance in various applied magnetic fields, a.c. magnetic susceptibility and specific heat. Measurements have revealed single transition to long-range magnetic order for all concentrations, changing from antiferromagnetism for SmRh_4B_4 to ferromagnetism for ErRh_4B_4 at $x \approx 0.2$. The upper critical magnetic field versus temperature curves for various Er concentrations have combined features characteristic of both SmRh_4B_4 and ErRh_4B_4 .

The Hf-Os Constitution Diagram

R. M. WATERSTRAT, *J. Less-Common Met.*, 1983, **95**, (2), 335-344

The Hf-Os constitution diagram was determined by metallography, X-ray diffraction and electron microprobe studies. Three new compounds were discovered; η -phase with cubic Ti_2Ni -type structure, the other two ζ and θ phases have not been identified. A glassy phase was produced by ultrarapid quenching of the liquid alloy containing about 25at.% Os.

The (Fe-Os) Iron-Osmium System

L. J. SWARTZENDRUBER and B. SUNDMAN, *Bull. Alloy Phase Diagrams*, 1983, **4**, (4), 396-399

A provisional phase diagram for Fe-Os at 400-3200°C and its comparison with adjusted data is presented, as is a comparison of the calculated equilibrium phase boundaries with data on the transformation temperatures.

Growth and Physical Properties of RuS_2 Single Crystals

R. BICHSEL, F. LÉVY and H. BERGER, *J. Phys. C.*, 1984, **17**, (1), L19-L21

RuS_2 single crystals have been grown by chemical transportation reaction using ICl_3 as transport agent. The specimens crystallise with the correct pyrite structure. The electrical resistivity and Hall effect studies showed n-type semiconducting behaviour. At room temperature the electrical resistivity was $6.2 \times 10^{-2} \Omega \text{ cm}$, the carrier concentration was $3.2 \times 10^{17}/\text{cm}^3$ and the Hall mobility was $310 \text{ cm}^2/\text{Vs}$. The optical gap was $\sim 1.3 \text{ eV}$. Crystals with dimensions up to $4 \times 4 \times 4 \text{ mm}^3$ were produced.

CHEMICAL COMPOUNDS

Stable Olefin Complexes of Pt(II) Containing Trichlorostannate (II) Ligands: Fivefold Coordinated Platinum (II) Structure of $[\text{Ph}_4\text{As}][\text{Pt}(\text{SnCl}_3)_3 (1,5\text{-cod})]$

A. ALBINATI, P. S. PREGOSIN and H. RÜEGGER, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, (1), 78-79

A five fold co-ordinated Pt(II) is contained in the novel title complex. It is the first square-pyramidal Pt-Sn complex, and one of the three Sn atoms adopts the axial position.

Organonickel-Palladium and -Platinum Complexes. Their Chemical Properties and Roles in Organic Synthesis

A. YAMAMOTO, T. YAMAMOTO and F. OZAKA, *J. Synth. Org. Chem., Jpn.*, 1983, **41**, (9), 827-838

An overview of the preparation of organometallic complexes of Pt, Pd and Ni is presented, together with a detailed account of the thermolysis mechanisms of these complexes and their reactions with CO. (71 Refs.)

Sulfide Bronzes: Preparation and Characterization of (RE)Pd₃S₄ (RE = Rare Earth)

D. A. KESZLER and J. A. IBERS, *Inorg. Chem.*, 1983, **22**, (23), 3366-3367

The first chalcogenide analogue of the platinum group bronzes is reported. LaPd₃S₄ was prepared and characterised. Similar materials are formed for most of the rare earth elements. The bronze is conductive and is the first example of a metallic Pd bronze.

Cobalt, Rhodium and Iridium. Annual Survey Covering the Year 1982

J. T. MAGUE, *J. Organomet. Chem.*, 1984, **261**, (1-3), 103-282

Various Rh and Ir complexes are covered in this review. Among the complexes mentioned are those of metal-carbon σ -bonded, metal carbenes, metal isocyanides, metal carbonyls and related compounds, nitrosyls and aryldiazos, alkenes, alkynes, π -allyls, carbocyclics and carboboranes. Dissertations are also noted. (805 Refs.)

Synthesis and X-Ray Crystal Structure of the Mixed-Metal Cluster H₂Ru₂Rh₂(CO)₁₂

J. PURSIANEN and T. A. PAKKANEN, *J. Chem. Soc., Chem. Commun.*, 1984, (4), 252-253

The X-ray analysis of H₂Ru₂Rh₂(CO)₁₂, the first example of an unsubstituted Ru-Rh cluster, reveals a Rh₄(CO)₁₂-like cluster core in which the H atoms bridge a Ru-Ru and a Ru-Rh bond.

BaRu_{1-x}Co_xO_{3-y} System

H.-U. SCHALLER and S. KEMMLER-SACK, *J. Less-Common Met.*, 1984, **96**, (1), 11-22

Studies of the BaRu_{1-x}Co_xO_{3-y} system at 600-1300°C (Ru rich) or 900°C (Co-rich side), showed the presence of different perovskite stacking polytypes in air. These were, among others, the pure Ru compound BaRuO₃ with the rhombohedral 9R structure, a Ru-rich ($x = 0.1$) and a Co-rich ($x = 0.667-0.75$) hexagonal 4H phase. The phase relations and properties are reported.

ELECTROCHEMISTRY

Study of Hydrogenation of Ethylene and Acetylene Adsorbed on Platinum Foil by Diffused Hydrogen

YU. A. ZUBAREV, E. A. ZELYAEVA, R. MORENO FUKEN, V. D. YAGODOVSKII and V. M. GRYAZNOV, *Kinet. Katal.*, 1983, **24**, (5), 1162-1166

Photoelectric and spectroscopic studies of the interaction of acetylene and ethylene with diffused H₂ on Pt foil showed the formation of positively and negatively charged particles at 90-150°C. Adsorbed, negatively charged associative and dissociative complexes formed by interaction with H₂ were firmly fixed on the surface.

Catalytic Properties of Mercury Ad-Atoms in the Electrochemical Oxidation of Formic Acid on Platinum

F. MARAN, A. GENNARO and E. VIANELLO, *Z. Phys. Chem. (Frankfurt am Main)*, 1983, **134**, (1/2), 115-119

Studies were made of the electrochemical oxidation of HCOOH on a polycrystalline Pt electrode, modified by a submonolayer of Hg adatoms. The results suggest the hypothesis that under suitable conditions Hg adatoms catalyse the oxidation in particular on Pt sites with (100) and (111) orientations.

The Influence of Pt-Activation on the Corrosion of Carbon in Gas Diffusion Electrodes - A DEMS Study

J. WILLSAU and J. HEITBAUM, *J. Electroanal. Chem. Interfacial Electrochem.*, 1984, **161**, (1), 91-101

Differential electrochemical mass spectroscopy studies of the dependence on the potential of the anodic oxidation of C electrodes showed that pure C is oxidised only at potentials of >0.9V(R.H.E.), and that Pt activation catalyses the oxidation of a CO_{surf} surface layer to CO₂ at potentials of 0.6-0.8mV (R.H.E.), with the CO_{surf} being formed on the C at E >0.3V (R.H.E.). It is assumed that the Pt-induced C corrosion occurs in the neighbourhood of the Pt sites, thus damaging the Pt to C contact. This results in a surface segregation of Pt-clusters and a loss of catalytic activity.

Hydrogen Chemical Potentials and Diffusion Coefficients in Hydrogen Diffusion Membranes

F. A. LEWIS, J. P. MAGENNIS, S. G. MCKEE and P. J. M. SSEBUWUFU, *Nature*, 1983, **306**, (5944), 673-675

Hydrogen diffusion measurements through Pd₈₁Pt₁₉ alloy are reported. Pd₈₁Pt₁₉ alloy tubes, Pd black coated inside of wall thickness 0.2 mm were filled with aqueous H₂SO₄ saturated with H₂ at atmospheric pressure, with a platinised Pt reference electrode immersed in the solution. The outer electrolyte was H₂ saturated. A second experiment involved the tubes being evacuated and H₂ pressures being measured inside the tubes. The results are consistent with Gorskii's hypothesis.

The Hydrogen Adsorption on Skeletal Catalysts of the Palladium-Rhodium System

J. M. GRISHINA, L. I. LAZAREVA and G. D. VOVCHEKNO, *Vestn. Mosk. Univ., Ser. Khim.*, 1983, **24**, (5), 477-480

Adsorption of H₂ on skeletal 5, 10, 35, 50 and 60% Pd-Rh catalysts was studied in 1N H₂SO₄ and HCl at 20°C by the galvanostatic loading curve method. The effect of specific adsorption of Cl⁻ ions on the form of loading curves is established. Comparison is made of values of specific surfaces obtained electrochemically and by a volumetric method at constant pressure in electrocatalytic Pd-Rh systems.

Amorphous Pd-Zr Alloys for Water Electrolysis Cathode Materials

M. ENYO, T. YAMAZAKI, K. KAI and K. SUZUKI, *Electrochim. Acta*, 1983, **28**, (11), 1573-1579

Studies of amorphous Pd_{0.35}Zr_{0.65} alloys prepared by a melt-quench technique showed that the electrocatalytic activity for cathodic H₂ evolution on the as-obtained electrode was 100 times lower than on Pd foil electrodes, but was improved after a treatment in HF acid. The activity in the highest state exceeds that of Pd by one order of magnitude. The improvement in activity was found to be due to increased Pd concentration on the surface after removal of a Zr-enriched surface layer, which had been produced during fabrication.

The Acidic Behaviour of Osmium (VIII) and Osmium (VI)

S. M. GALBÁCS, Á. ZSEDNAI and L. J. CSÁNYI, *Transition Met. Chem.*, 1983, **8**, (6), 328-332

The acidities of Os(VIII) and Os(VI) were found by various methods. For Os(VIII) acid at 298K the apparent $K_1 \sim 6.3 \times 10^{-3}$ and $K_2 \sim 4 \times 10^{-15}$. For Os(VI) acid $K_1 \sim 3.2 \times 10^{-9}$ and $K_2 \sim 4.0 \times 10^{-11}$. The dependence of the pH of solution on the K osmate(VI) concentration can be interpreted in terms of the base inclusions in the preparation, rather than in terms of the dimerisation of the Os(VI).

Oxygen Gas Evolution at, and Deterioration of, RuO₂/ZrO₂-Coated Titanium Anodes at Elevated Temperature in Strong Base

L. D. BURKE and M. McCARTHY, *Electrochim. Acta*, 1984, **29**, (2), 211-216

The addition of a second, more inert ZrO₂ oxide to the active RuO₂ layer on a Ti substrate was found to substantially increase the service life of DSA-type anodes with respect to O₂ gas evolution in 6.0mol/dm³ NaOH at 80°C. The optimum service life (~200h) was observed with an 80/20 (RuO₂/ZrO₂) mol% oxide mixture. The increased stability of the mixed oxide-coated system is attributed to better protection of the base metal. Attack on this leading to shedding of the active layer, is a major route for deterioration of this type of anode.

PHOTOCONVERSION

Photoelectrochemical Characteristics of Semiconductor-Metal/SPE/Metal Cells

K. UOSAKI and H. KITA, *J. Electrochem. Soc.*, 1983, **130**, (11), 2179-2184

A solid polymer electrolyte (SPE) photoelectrochemical cell, semiconductor-metal/SPE/Pt, is proposed as a new device to convert solar energy to electrical and/or chemical energy. The photoelectrochemical characteristics of TiO₂-Pt/SPE and TiO₂-Au/SPE were studied as well as those of the whole cell systems TiO₂-Pt/SPE/Pt and TiO₂-Au/SPE/Pt.

Photocatalytic and Photoelectrochemical Reactions of Aqueous Solutions of Formic Acid, Formaldehyde and Methanol on Platinized CdS Powder and at a CdS Electrode

M. MATSUMURA, M. HIRAMOTO, T. IEHARA and H. T. SUBOMURA, *J. Phys. Chem.*, 1984, **88**, (2), 248-250

H₂ evolves by illumination of suspensions of platinized CdS powder in aqueous solutions of formic acid, formaldehyde and methanol. The organic compounds are oxidised. The reaction rate is high at low pH for formic acid, and at high pH for methanol. The reactivities of these compounds on platinized CdS powder at various pH have good correlation with their photoanodic reactions on a CdS electrode.

Photoelectrochemical Hydrogen Evolution and Water-Photolyzing Semiconductor Suspensions: Properties of Platinum Group Metal Catalyst-Semiconductor Contacts in Air and in Hydrogen

D. E. ASPNES and A. HELLER, *J. Phys. Chem.*, 1983, **87**, (24), 4919-4929

The properties of electrical contacts between Pt, Rh and Ru and semiconductors n-TiO₂, n-SrTiO₃, n-CdS and p-InP, as air exposed contacts forming Schottky junctions were measured. The effect of the dry H₂ atmosphere is examined, resulting in reversibly converting the n-TiO₂ contacts to true Ohmic behaviour and near Ohmic behaviour for n-SrTiO₃, and reducing barrier heights for n-CdS contacts. Barrier heights for the p-InP contacts increase upon hydrogenation.

Reaction Mechanism of Photocatalysis for the Liquid-Phase Dehydrogenation of 2-Propanol with Rhodium Porphyrin Complex

R. IRIE, X. LI and Y. SAITO, *J. Mol. Catal.*, 1984, **23**, (1), 17-22

Liquid-phase dehydrogenation of 2-propanol was studied under visible light irradiation with a Rh porphyrin complex catalyst. Kinetic studies showed that a bimolecular process between hydrido-Rh porphyrin complexes in the photoexcited and ground states is involved in the photocatalytic cycle.

The Incorporation of Ruthenium Oxide in Polypyrrole Films and the Subsequent Photooxidation of Water at n-GaP Photoelectrode

R. NOUFI, *J. Electrochem. Soc.*, 1983, **130**, (10), 2126-2127

A scheme is presented incorporating RuO₂ in polypyrrole (PP) film deposited on Pt and n-GaP electrodes. Photodissociation of H₂O from 1M HClO₄ occurred at the surface of n-GaP when modified with a film of RuO₂-catalysed PP. Here the RuO₄²⁻ ion is incorporated electrochemically and then reduced in the matrix of the film to yield RuO₂.

Photoresponsive Electrode Coated with Bilayer Membranes of Polymer Pendant Ru(bpy)₃²⁺ Complex and Viologen

M. KANEKO, S. MORIYA and A. YAMADA, *Electrochim. Acta*, 1984, **29**, (1), 115–118

A new type of photodiode was proposed based on photochemical electron transfer occurring between bilayer membranes of polymer pendant Ru(bpy)₃²⁺ complex and pendant viologen. A bilayer system – composed of a graphite electrode coated with polymer pendant Ru(bpy)₃²⁺ as inner layer in contact with the electrode, and with the polymer pendant viologen as outer layer – induced a photocurrent.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodeposition of Ruthenium from Sulphamate Electrolyte

A. V. GORODYSKII, N. E. NECHAEVA and L. B. KHARKOVA, *Ukr. Khim. Zh. (Russ. Ed.)*, 1983, **50**, (1), 53–58

Studies of the cathodic kinetics of Ru electrodeposition from sulphamate showed that electroactive Ru complexes were formed at the ratio C_{Ru(IV)}:C_{NH₂SO₃} = 1 : 1. The stability constant of the electroactive complex [Ru(H₂O)₅.NH₂SO₃]³⁺ was calculated as $\beta = 1.33 \times 10^3$.

HETEROGENEOUS CATALYSIS

Selectivities of Some Hydrogenations on Metal-Modified Platinum Catalysts

L. ČERVENÝ, K. SURMA, V. RŮŽICKA and I. PASEKA, *Collect. Czech. Chem. Commun.*, 1983, **48**, (12), 3532–3538

Studies of the effect of the modification of Pt catalysts by Cu, Th, Pb or Bi monolayers on the rates and selectivity of hydrogenation were made at 20°C during competitive hydrogenation of 1-hexene and 1-undecene in cyclohexane, and for the consecutive hydrogenation of 1,5-cyclooctadiene in cyclohexane or ethanol.

Effects of Metal-Support Interaction and Temperature on the Sintering of Pt and Ag Particles Supported on Inorganic Solids

M. ARAI, T. ISHIKAWA, T. NAKAYAMA and Y. NISHIYAMA, *J. Colloid Interface Sci.*, 1984, **97**, (1), 254–265

Studies of sintering of Pt and Ag on amorphous C, SiO₂ and Al₂O₃ in vacuum showed liquid-like motions for Pt particles on these supports at 600–750°C. The Pt particles grew through abrupt surface movement and subsequent coalescence of adjacent pairs. The order of the strength of the metal-support interaction was estimated to be Pt/Al₂O₃ > Pt/SiO₂ > Pt/C, from the temperature dependence of the mean particle diameter and the particle technology.

Preparation of Supported Platinum-Gold Catalysts and Alkanes Reactions on Selected Platinum and Platinum-Gold Supported “Clusters”

J. K. A. CLARKE, A. C. M. CREAMER and T. BAIRD, *Appl. Catal.*, 1984, **9**, (1), 85–108

Spectroscopic studies of Aerosil-Pt-Au catalysts prepared by various methods showed that at low metal loading (1w/w%) the incipient wetness method gave excellent dispersion (“clusters”), and also with TiO₂ as support. Reaction of n-pentane and of 3,3-dimethylpentane on the cluster catalysts showed the bimetallic clusters to be highly selective hydrogenolysis catalysts. Supporting Pt as clusters on TiO₂ gave catalysts which displayed excellent dehydrocyclisation selectivity.

Depolluting Exhaust Gases from Diesel Engines by Catalytic Mufflers

E. GOLDENBERG, M. PRIGENT and J. CAILLOD, *Rev. Inst. Fr. Pet.*, 1983, **38**, (6), 793–805

The results of a first series of research on the purification of exhaust gases from diesel engines by Pt base Al₂O₃ mufflers is presented. The catalyst effectiveness for oxidation of CO, unburnt hydrocarbons and SO₂ elimination was determined on an engine test bed and on vehicles on the roads. Using active non-noble metal phases reduced the starting oxidation temperature of soot particles from 380 to ~250°C, eliminating 15–20% of the trapped products between 250 and 350°C.

Pt-Mo Bimetallic Catalysts Supported on Y-Zeolite. II. Activity and Selectivity in n-Butane Conversion

T. M. TRI, J. MASSARDIER, P. GALLEZOT and B. IMELIK, *J. Catal.*, 1984, **85**, (1), 244–252

Pt-Mo bimetallic catalysts prepared by adsorption and decomposition of Mo(CO)₆ on 1-nm Pt aggregates supported on Y-zeolite exhibit enhanced hydrogenolysis activity with respect to PtY zeolite in n-butane conversion. The activity curve versus Pt/Mo composition is volcano-shaped with a maximum near equiatomic composition. The rate at maximum is 7 and 34 times larger than on PtNaHY and Pt/SiO₂, respectively.

Catalytic Chemistry of Palladium Surfaces under Ultrahigh Vacuum Conditions

T. M. GENTLE, V. H. G. RASSIAN, D. G. KLARUP and E. L. MUETTERTIES, *J. Am. Chem. Soc.*, 1983, **105**, (22), 6766–6768

Pd surfaces under ultrahigh vacuum conditions have a chemistry demonstrably different from that of Ni and Pt. Specifically, acetylene trimerises to form benzene on the low Miller index planes of Pd. Other reactions compete with the trimerisation but benzene formation is the major reactor, at least on the Pd(III) surface at near saturation coverage, provided acetylene is initially adsorbed at <–100°C when conversion is ~25%. The presence of S on the surface substantially increases the conversion to benzene.

An Improved Method to Prepare Catalysts for the Selective Decarbonylation of Furan-2 Carboxaldehyde into Furan

P. LEJEMBLE, Y. MAIRE, A. GASET and P. KALCK, *Chem. Lett. Jpn.*, 1983, (9), 1403-1406

Pure furan and pure CO were prepared from furan-2 carboxaldehyde using an improved catalyst. The new catalyst, Pd/C-K₂CO₃ is activated by u.v. irradiation at 254nm for 1 hour.

An Active Methanation Catalyst Prepared from Pd-Zr Alloys

A. YOKOYAMA, H. KOMIYAMA, H. INOUE, T. MASUMOTO and H. KIMURA, *J. Non-Cryst. Solids*, 1984, **61 & 62**, (1), 619-624

A highly active methanation catalyst for the reaction of CO and H₂ to produce CH₄ was prepared in situ from an amorphous Pd₃₅Zr₆₅ alloy. Its turnover frequency was greater than that of the most active methanation catalyst known. The activity of the catalyst was compared with those of the crystalline Pd_xZr_{1-x} (x = 0-1) alloys and Pd(Zr, Si) alloys. The results showed that the active species is an unknown complex oxide of Pd and Zr, in which Pd exists in the oxidising state under the highly reducing reaction conditions. But Pd-base catalysts containing Si as additive did not form active species and deactivated.

The Kinetics of Propylene Oxidative Acetoxylation over Palladium-Copper Zeolite Catalyst

KH. M. MINACHEV, O. M. NEFEDOV, V. V. KHARLAMOV, S. YU. PANOV, A. M. SHKITOV and M. I. TROFIMOV, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, (12), 2688-2692

Studies of kinetic mechanism of propylene oxidative acetoxylation over a 1.5%Pd-2.5%Cu/zeolite catalyst showed that the rate of the acetoxylation did not depend on the partial pressure of CH₃COOH or the proportional O₂ pressure but it went through a sloping maximum in dependence on the partial propylene pressure. Heat reduction studies of the reoxidised catalyst samples showed that at 180°C not more than 20-25% Pd in the catalyst was oxidised. The rate of Pd oxidation did not exceed the total rate of formation of allyl acetate.

Kinetics and Products Inhibition Effects in Toluene Steam Dealkylation over Rh/Cr₂O₃/γ-Al₂O₃

P. BELTRAME, G. CASALONE, L. FORNI, I. FERINO, B. MARONGLU and S. TORRAZZA, *Ind. Eng. Chem., Process Des. Dev.*, 1984, **23**, (1), 176-179

Kinetic studies of toluene steam dealkylation over 2.4wt.%Rh-0.5wt.%K/3.3wt.%Cr₂O₃/γ-Al₂O₃ catalysts performed at 460°C showed conversions up to 68%. A kinetic model that includes a competition between the reaction products and toluene for adsorption gives the best explanation. Separate runs with CO or benzene added to the feed showed that both are inhibitors.

Fischer-Tropsch Synthesis over Zeolite-Supported Ruthenium Catalysts Derived from Ru₃(CO)₁₂

Y.-W. CHEN, H.-T. WANG, J. G. GOODWIN and W. K. SHIFFETT, *Appl. Catal.*, 1983, **8**, (3), 303-314

A number of zeolite-supported Ru catalysts prepared from Ru₃(CO)₁₂ using zeolites NaX, NaY, KL and Na mordenite were characterised and studied under Fischer-Tropsch conditions. Ru₃(CO)₁₂ did not appear to be able to diffuse into NaX. The best catalyst in terms of high Ru dispersion, low methane selectivity and high olefin selectivity was Ru/NaY. The type of zeolite used as the support had a strong effect on methane selectivity. Compared to the ion-exchange method, this method of preparation is much superior in producing high yields of olefins and low yields of methane.

HOMOGENEOUS CATALYSIS

Transition Metals in Organic Synthesis: Hydroformylation, Reduction and Oxidation. Annual Survey Covering the Year 1980

L. MARKÓ, *J. Organomet. Chem.*, 1984, **261**, (1-3), 485-590

The above reactions are examined in detail, together with Rh and Pt catalysts for hydroformylations, supported complexes in heterogeneous systems, the water gas shift reaction, reductions with CO and H₂O, and Ru, Os, Pt and Pd catalysts for olefin hydrogenation. Catalysts examined include those for asymmetric hydrogenation of olefins, for diene and acetylene hydrogenations and those in H transfer reactions. Compounds in transition metal complexes, various oxidations, such as of alkenes and olefins, and epoxidation of olefins, oxidation of N-containing organic compounds with O₂, and catalytic oxidation of organic compounds with organic and inorganic oxidants are discussed. (494 Refs.)

Palladium Catalyzed Olefin Arylation: Extending the Scope of the Heck Reaction to Aryl Chlorides

J. B. DAVISON, N. M. SIMON and S. A. SOJKA, *J. Mol. Catal.*, 1984, **22**, (3), 349-352

The studies showed for the first time that an unactivated aryl chloride, chlorobenzene, undergoes olefin arylation in the presence of a homogeneous Pd complex catalyst.

Palladium Catalyzed Synthesis of Heterocycles

K. UTIMOTO, *Pure Appl. Chem.*, 1983, **55**, (11), 1845-1852

Novel procedures for synthesising heterocycles, using a Pd catalysed intramolecular addition of amine or hydroxyl group to an acetylene bond as a key reaction, are described. Pyrroles and furans were prepared. Insect pheromones containing intramolecular acetal linkages were produced.

A Highly Efficient Version of the Palladium-Catalysed Arylation of Alkenes with Aryl Bromides

A. SPENCER, *J. Organomet. Chem.*, 1983, **258**, (1), 101-108

The Pd-catalysed arylation of alkenes with aryl bromides or iodides is shown to proceed in high yields at very low Pd concentrations when carried out in a suitable strongly polar solvent with a carboxylate anion as base. The preferred combination is N,N-dimethylformamide with NaOAc. The reaction is markedly dependent on the substituents in the aryl bromide, being favoured by electron-withdrawing groups. Turnover numbers up to 134,000 have been achieved.

Oxidation of Butadiene-1,3 in 2-Vinyl-1,4-Dioxane in the Solution of Palladium (II) and Copper (II) Chloride in Ethylene Glycol

M. S. SHLAPAK, S. M. BRAILOVSKI and O. N. TEMKIN, *Kinet. Katal.*, 1983, **24**, (6), 1380-1384

Studies of the oxidation of butadiene-1,3 in a solution of PdCl₂-CuCl₂ in ethylene glycol showed the formation of 2-vinyl-1,4-dioxane in 92% yield. The rate of conversion of butadiene-1,3 was proportional to the PdCl₂ concentration and was four times the CuCl₂ concentration.

Selective Production of C₂-Oxygenate Esters from Synthesis Gas Using Mixed Metal Homogeneous Catalysts

R. WHYMAN, *J. Chem. Soc., Chem. Commun.*, 1983, (23), 1439-1441

C₂-oxygenate esters, particularly ethylene glycol diacetate, may be prepared in high selectivity directly from synthesis gas in the presence of composite homogeneous catalysts which contain mixtures of Rh and Ru and major and minor components, respectively, together with a promoter in the form of N-containing bases of alkali metal cations, in acetic acid as solvent.

Asymmetric Catalysis. 12. New Optically Active P,N Ligands and Their Use in Rh-Catalysed Asymmetric Hydrogenation and Hydrosilylation

H. BRUNNER and A. F. M. MOKHLESUR RAHMAN, *Chem. Ber.*, 1984, **117**, (2), 710-724

New P,N-ligands were prepared by Schiff base condensation of (2-formylphenyl)diphenyl- and tris(2-formylphenyl)phosphane with (R)-(+)-1-phenylethylamine and ethylenediamine. The square planar Rh [(R)-(+)-iminphos]₂X was obtained as a *cis/trans* mixture. The isolated Rh complexes and the combinations [Rh(COD)Cl]₂/new P,N ligands were used as catalysts for the homogeneous hydrogenation of (Z)- α -(acetylamino)cinnamic acid. The optical yield of 1-phenylethanol, a product, increased with ligand excess, decreasing catalyst concentration and decreasing temperature.

Organic Oxygenates Directly from Synthesis Gas

Res. Discl., 1984, (237), 10, No. 23711

A process for the direct conversion of a H₂/CO mixture into organic oxygenates is catalysed by bimetallic mixtures of Rh and Ru, and occurs as a homogeneous or one-phase process. The metals are present in a total concentration $\sim 10^{-4}$ to 5 molar and at a Ru:Rh ratio of $\sim 1:2$ to $5:1$. A halide promoter is necessary, the halide:total metal ratio being 3:1 to 3:10. Acetic acid is the solvent and additional promoter, and the reaction occurs at 200-230°C and 4000-6000 psig. Reaction products are esters such as methyl, ethyl, propyl and butyl acetates.

The Ruthenium Catalysed N-Alkylation of Amides with Alcohols

Y. WATANABE, T. OHTA and Y. TSUJI, *Bull. Chem. Soc. Jpn.*, 1983, **56**, (9), 2647-2651

Amides reacted with primary alcohols in the presence of RuCl₂(PPh₃)₃ catalyst at 180°C to give the corresponding N-monoalkyl amides in fairly good yields. Thus, benzamide reacted with 1-octanol to give N-octylbenzamide in 76% yield with excellent product selectivity. RuCl₂(PPh₃)₃ was the most effective catalyst for this reaction and RuHCl(PPh₃)₃ also showed some catalytic activity.

FUEL CELLS

Electrocatalytic Oxidation of Carbon Monoxide in a CO/O₂ Fuel Cell

J. WU and C. P. KUBIAK, *J. Am. Chem. Soc.*, 1983, **105**, (25), 7456-7457

The electrochemical oxidation of CO in a low temperature CO/O₂ fuel cell using a homogeneous Rh-based electrocatalyst is reported. Activation parameters for the electroodic oxidation of [Rh^I(CO)₂Br₂]⁻ were determined, and the electrocatalytic oxidation of CO by [Rh^I(CO)₂Br₂]⁻ was incorporated into the fuel cell design. The cathode compartment was a Pt gauze immersed in 0.1M HBr solution through which a steady stream of air was bubbled. The cell was kept at 80°C for 72h, and 1.21 mmol CO₂ were produced while 2.71 mmol of electrons were passed through the cell.

CORROSION PROTECTION

Performance of Platinum Clad Columbi-um Impressed Current Anodes in Freshwater

R. BABOIAN, *Mater. Perform.*, 1983, **22**, (12), 15-18

The rate of dissolution of Pt from a roll-bonded, Pt clad Nb anode in fresh water at two resistivities at various current densities was investigated in the presence and absence of superimposed a.c. ripple. The rate was highly dependent on current density. At higher current densities, Pt dissolution was rapid, especially when a.c. ripple was present.

ELECTRICAL AND ELECTRONIC ENGINEERING

Origin of Blistering Observed on Forming-Gas-Annealed Ti/Pt Ohmic Contacts

G. HENEIN, *Thin Solid Films*, 1983, **109**, (1), 115-125
The blistering of Ti/Pt ohmic contacts to GaAs/(Al-Ga-As) semiconductor lasers occurring during a forming gas anneal is reported. The simultaneous presence of Ti, Pt, H and O in the annealing furnace was found to be a necessary condition for the formation of blisters. The Pt-catalysed formation of H₂O vapour occurred at an annealing temperature of >450°C which locally delaminates the film from the substrate. It is also shown how the presence of residual H₂O vapour in the blisters can lead to corrosion of laser chip bonds.

Suppression of Platinum Penetration Failure in Ti/Pt/Au Beam Lead Metal Systems Using a TiN Diffusion Barrier

S. KANAMORI and T. MATSUMOTO, *Thin Solid Films*, 1983, **110**, (3), 205-213
The ability of a TiN diffusion barrier to suppress metal penetration, which induces junction-shortening in a Ti/Pt/Au beam lead metal system on polycrystalline Si is reported. Failure analysis, performed by X-ray spectroscopy using an electron microprobe, showed that the junction-shortening was dominated by Pt penetration equivalent to the localised growth of Pt silicide.

NEW PATENTS

METALS AND ALLOYS

Magnetic Alloy

RESEARCH INSTITUTE OF ELECTRIC & MAGNETIC ALLOYS
U.S. Patent 4,396,441
A permanent magnet having an ultra-high coercive force and large maximum energy product is made from an alloy of specified crystal structure consisting of 63.76-75.96% Pt, remainder Fe.

Brazing Alloy

GENERAL ELECTRIC CO.
U.S. Patent 4,396,577
A brazing alloy particularly suitable for use in high temperature gas-turbine engines consists of 25-95% Pd, up to 5% Si, up to 3.5% B, remainder Co.

High Chromium Superalloy

JOHNSON MATTHEY P.L.C.
East German Patent 202,310
Ni alloys containing 23-27wt.% Cr of improved mechanical properties and corrosion resistance contain up to 1.7% C, up to 1.5% Ti and/or up to 1.5% Al, 0.3-4% Pt and/or 0.3-8% Ru. The alloy is especially suited for use in contact with molten glass, for example in a centrifugal spinner.

Effect of HCl and Cl₂ on Pd Inlay Coupons and Pd Connector Contacts

E. S. SPROLES and S. P. SHARMA, *IEEE Trans. Components, Hybrids Manuf. Technol.*, 1983, **CHMT-6**, (3), 343-348
A study of the effects of Cl₂ and HCl vapours in high relative humidities (RH) on connectors and on coupon surfaces was performed. The high contact resistance values measured on the coupons were not representative of the contact resistance changes detected on connection contacts undergoing accelerated ageing in the mated condition. Pd and 60Pd-40Ag against Au are much superior in performance to Pd against Pd when exposed to Cl₂ environments. Extensive exposure in high concentrations of HCl vapours and high RH effectively destroys Pd inlay coupon samples, but does not significantly degrade any of the connector systems tested.

Fermi Energy Pinning Behaviour and Chemical Reactivity of the Pd/GaAs (110) Interface

T. KENDELEWICZ, W. G. PETRO, S. H. PAN, M. D. WILLIAMS, I. LINDAU and W. E. SPICER, *Appl. Phys. Lett.*, 1984, **44**, (1), 113-115
The room temperature growth of the Pd/n-GaAs (110) intimate interface was studied by soft X-ray core level photoemission spectroscopy. The results showed that Pd reacts with the GaAs surface forming an arsenide compound in which phase segregated Ga metal is included. The Schottky barrier height of this system is experimentally determined to be 0.9 ± 0.05 eV.

ELECTROCHEMISTRY

Water Electrolysis

INSTITUTE OF GAS TECHNOLOGY
U.S. Patent 4,395,316
In a process for producing pure H₂ by water electrolysis, the anode is depolarised with a solution of monosaccharides and/or lignins to suppress the evolution of molecular O₂. The anode is preferably of Pt coated with a Pb-rich Ru pyrochlore of general formula Pb₂(Ru_{2-x}Pb_x)O_{7-y} where x is 0-1.2.

Film Photoelectrodes

DIAMOND SHAMROCK CORP.
U.S. Patent 4,396,485
Film photoelectrodes for use particularly in the conversion of solar energy are claimed. They may contain lanthanide and/or platinum group metals.

Cermet Anodes

DIAMOND SHAMROCK CORP.
U.S. Patent 4,397,729
An improved anode for the electrowinning of a metal especially Al, from a molten salt bath consists of a mixture of a cermet material such as Ni ferrite and Pd, Pt, Ir, Rh, Au or one of their alloys.