

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Magnetic Phase Diagram of Ordered ($\text{Fe}_{1-x}\text{Mn}_x$)Pt Alloys

A. Z. MENSNIKOV, V. P. ANTROPOV, G. P. GASNIKOVA, YU. A. DOROFEYEV and V. A. KAZANTSEV, *J. Magn. & Magn. Mater.*, 1987, **65**, (1), 159-166

The magnetic structure and magnetic phase transitions of ordered ($\text{Fe}_{1-x}\text{Mn}_x$)Pt alloys were investigated by neutron diffraction in the temperature range 4.2-900K. A complete magnetic phase diagram is presented, where the regions for different magnetic states and the character of transitions between them are shown.

Pt-Si Contact Metallurgy Formed by Three-Temperature Annealing Sequences and Short Annealing Time

C.-A. CHANG and R. SEGMÜLLER, *J. Appl. Phys.*, 1987, **61**, (1), 201-205

Pt-Si contact metallurgy has been studied via a wide range of annealing sequences using a three-temperature annealing process but with shorter annealing durations than usual. With 200-300-500°C or 200-300-450°C processes, and a total annealing time of 20-40 min in a $\text{N}_2:\text{H}_2$ mixture of ratio 9:1, all the PtSi films formed showed a complete reaction between Pt and Si, which is a necessary condition.

Hydrogen Induced Changes in the Metallurgical Interactions at PtSi-Si Interfaces

T. T. BARDIN, J. G. PRONKO, R. C. BUDHANI and R. F. BUNSHAH, *J. Vac. Sci. Technol. A*, 1986, **4**, (6), 3121-3126

The role of H in the kinetics of interfacial reactions between $\text{Pt}_x\text{Si}_{1-x}$ ($x=0.67, 0.5$) thin films and Si substrates, and consequent changes in the electrical characteristics of PtSi/Si Schottky diodes were studied. The absolute H concentration in the films decreases with increasing temperature of deposition and increasing Pt concentration. For films with $x < 0.5$ the H reduces the kinetics of the PtSi formation at the film/substrate interface. Diode parameters improve with increasing deposition temperature until 400°C; above, the I-V characteristics deviate from ideality.

ESCA Study of the Oxidation of Pt₃Sn. 2. Exposure to Air

G. B. HOFLUND and D. A. ASBURY, *Langmuir*, 1986, **2**, (6), 695-697

Angle-resolved ESCA was used to examine the effects of exposing a clean Pt-rich Pt₃Sn alloy surface to air at room temperature. Sn segregated to the surface and appeared to cover the Pt-rich layer completely. The surface Sn is oxidised, but Pt stays metallic.

Oxygen Generated Platinum, Rhodium and Palladium Volatile Losses from Pure Metals and Their Alloys

M. RUBEL, M. PSZONICKA, M. F. EBEL, A. JABŁOŃSKI and V. PALCZEWSKA, *J. Less-Common Met.*, 1986, **125**, 7-24

Various techniques have been used to determine volatile products generated from Pt, Pd, Rh, Pt-Rh and Pt-Pd-Rh. The materials were oxidised with O_2 or r.f. O plasma. RhO_2 , $\alpha\text{-PtO}_2$, PdO and probably PtO_3 were produced using the O plasma, while RhO_2 , $\alpha\text{-PtO}_2$, PdO and PtO were generated during O_2 interaction. Oxides generated by plasma from Pt-Pd-Rh were enriched with Pd, and Rh to a lesser extent. No enrichment was detected for oxides formed by plasma etching Pt-Rh. Oxides obtained in O_2 were distinctly enriched with Pt, and oxide formation decreased with increased Rh or Pd in the alloys.

Preparation of Amorphous Palladium-Base Surface Alloys on Conventional Metals by Laser Treatment

N. KUMAGAI, K. ASAMI and K. HASHIMOTO, *J. Non-Cryst. Solids*, 1986, **87**, (1-2), 123-136

An attempt was made to prepare an electrocatalytically active amorphous Pd alloy covering a conventional crystalline bulk metal, which would act as an electrical conductor for use in electrodes. Laser surface melting and subsequent self-quenching vitrified the entire surface of a Pd-25Rh-10P-9Si cast alloy when it was transversely by a continuous CO₂ laser. The surface alloy needs to be bonded to the substrate, prior to laser treatment, to ensure rapid heat absorption from surface to substrate.

Effects of Short-Range Order on the Electrical Resistivity of Plastically Deformed Pd-Ag and Pd-Ag-Fe Alloys

A. RAOUFI, S. ARAJS and K. V. RAO, *Phys. Status Solidi*, 1986, **97**, (2), 571-577

The effects of plastic deformation on the electrical resistivity of $\text{Pd}_{100-x}\text{Ag}_x$ ($x=25, 30, 40, 45$ and 50), $\text{Pd}_{50}\text{Ag}_{50}$ with 2 at.% Fe and $\text{Pd}_{67}\text{Ag}_{33}$ with 1 and 2 at.% Fe alloys at liquid N_2 temperatures under various heat treatments have been studied. The initial drop in electrical resistivity, the "K-effect", is interpreted as the effect of plastic strain on the short-range order in these systems. The passage of dislocations through the lattice during plastic deformation reduces short-range order and decreases resistivity initially. The magnitude of the change in resistivity due to deformation depends on the amount of plastic strain, annealing conditions and alloy composition. The "K-effect" studies appear to be a supplementary method of determining short-range order in systems not easily studied conventionally. This could be used in mapping out phase diagrams.

CHEMICAL COMPOUNDS

Iodo-Bridged Complexes of Platinum(II) and Synthesis of cis Mixed-Amine Platinum(II) Compounds

F. D. ROCHON and P. C. KONG, *Can. J. Chem.*, 1986, **64**, (9), 1894-1896

Iodo-bridged Pt(II) dimers [Pt(L)I₂] with ligands L containing N as the donor atom have been synthesised from the reactions of cis-[Pt(L)₂I₂] with perchloric acid. The dimers can be cleaved in aqueous media by a second N ligand to produce isometrically pure cis-[Pt(L)(L')I₂]. These compounds can be converted to the chloro or carboxylato compounds by precipitating the iodo ligands with a Ag salt and adding KCl or a carboxylate salt.

Synthesis and Electrical Conductivity of a New Family of Pt Mixed Valence Complexes: Pt₆(NH₃)₁₄Cl₁₀X₄ (X = ClO₄, BF₄ and PF₆)

M. TANAKA and I. TSUJIKAWA, *Bull. Chem. Soc. Jpn*, 1987, **59**, (9), 2773-2778

A new family of Pt mixed valence complexes was synthesised from Magnus' Green Salt [Pt(NH₃)₄][PtCl₄] by partial oxidation using an oxidant of H₂O₂ or electrochemically. After partial oxidation 1/6 of Cl⁻ ligands from Magnus' Green Salt are randomly replaced by NH₃ ligands and simultaneously counter ions X are introduced. These complexes comprise one-dimensional chains with direct Pt atom contact. The electrical conductivity σ was measured from 80K to room temperature. The σ at room temperature is high which suggests that σ along a chain direction may be as high as that of K₂[Pt(CN)₄]Br_{0.3}·xH₂O if single crystals could be obtained.

Annual Survey of Ruthenium and Osmium for the Year 1984

P. A. SHAPLEY, *J. Organomet. Chem.*, 1987, **318**, (1-3), 409-468

Ru and Os organometallic complexes are presented for the year 1984. Mononuclear, dinuclear and polynuclear complexes are examined, as are Ru₄, Os₄, Ru₅, Os₅, Ru₆, Os₆, and higher nuclearity clusters. Typical reactions of the complexes are discussed and theses and other reviews are mentioned. (387 Refs.)

A General Route for the Synthesis of Tetranuclear Clusters Containing Closed Triruthenium and Triosmium Triangles

G. A. FOULDS, B. F. G. JOHNSON, J. LEWIS and R. M. SORRELL, *J. Chem. Soc., Dalton Trans.*, 1986, (12), 2515-2518

Cluster compounds [N(PPh₃)₂][M₃M'(CO)₁₃] (where M = Ru or Os, and M' = Co) and [N(PPh₃)₂][M₃M'H(CO)₁₃] (M = Ru or Os, M' = Fe, Ru or Os) have been prepared in good yield by the reaction of an appropriate tetracarbonylmetallate with bis(acetonitrile) complexes. The anionic clusters have been protonated to give the corresponding neutral hydride clusters.

Synthesis of a New Family of Water-Soluble Clusters: Ru₃(CO)_{12-x}L_x (x = 1-3), Os₃(CO)₁₀L₂, and Ir₄(CO)₉L₃ (L = Trisodium Salt (Hydrated) of Tris(m-sulfonatophenyl)phosphine)

B. FONTAL, J. ORLEWSKI, C. C. SANTINI and J. M. BASSET, *Inorg. Chem.*, 1986, **25**, (24), 4320-4322

The synthesis of a new family of water-soluble metal clusters, based on the hydrosoluble ligand L = P[C₆H₄-m-SO₃⁻Na⁺(H₂O)]₃, is discussed. The title Ru₃ cluster has been obtained by three routes.

ELECTROCHEMISTRY

Oxygen Evolution at Platinum Electrodes in Alkaline Solutions 1. Dependence on Solution pH and Oxide Film Thickness

V. I. BIRSS and A. DAMJANOVIC, *J. Electrochem. Soc.*, 1987, **134**, (1), 113-117

The O₂ evolution reaction at Pt electrodes in alkaline solution at various pHs is re-examined. Two linear V-log i regions exist, each having a different dependence on Pt oxide film thickness and OH⁻ concentration. The rate of O₂ evolution is strongly dependent on film thickness at high current densities, but independent at low current densities.

High-Temperature Steam Electrolysis Using SrCeO₃-Based Proton Conductive Solid Electrolyte

H. IWAHARA, H. UCHIDA and I. YAMASAKI, *Int. J. Hydrogen Energy*, 1987, **12**, (2), 73-77

High-temperature steam electrolysis was studied using solid proton conductors based on SrCeO₃ at 700-900°C, and using Pt or Ni as the cathode. The current efficiency for H₂ evolution was >95% at a current density of 0.2A/cm² at 800°C, but it decreased with increasing temperature.

Electrochemical Preparation of a Pt-Ru Alloy

M. A. QUIROZ, I. GONZALEZ, Y. MEAS, E. LAMY-PITARA and J. BARBIER, *Electrochim. Acta*, 1987, **32**, (2), 289-291

The electrochemical reduction of Pt(IV) and Ru(III) in separated and mixed solutions on a Pt electrode in 1N HCl solution showed that simultaneous reduction of both occurred and led to alloy formation.

Palladium/Hydrogen Membrane Electrode for High Temperature/High Pressure Aqueous Solutions

Z. NAGY and R. M. YONCO, *J. Electrochem. Soc.*, 1986, **133**, (11), 2232-2235

A Pd-Ag alloy membrane with suitable H₂ partial pressure on the dryside has been utilised as an electrode for high temperature/high pressure aqueous solutions where fast relaxation measurements of the electrode kinetics are made. The Pd-Ag membrane acted as a classical H electrode between 100-300°C.

New Types of Anodes for the Oxygen Evolution Reaction in Acidic Solution $\text{IrO}_2/\text{TiO}_2/\text{Ti}$

Y. MATSUMOTO, T. TAZAWA, N. MUROI and E.-I. SATO, *J. Electrochem. Soc.*, 1986, **133**, (11), 2257-2262

$\text{IrO}_2/\text{TiO}_2/\text{Ti}$ electrodes, where porous TiO_2 films are made by anodic oxidation accompanied by sparking, were tested as the anode for the O_2 evolution reaction in acidic solution. Thermal decomposition of aqueous IrCl_3 solution provided the IrO_2 . The catalytic activities of these electrodes are higher than those of an IrO_2/Ti electrode, and electrodes prepared at 550°C are superior in long-term tests.

An Iridium-Based Mercury-Film Electrode. Part 1. Selection of Substrate and Preparation

S. P. KOUNAVES and J. BUFFLE, *J. Electroanal. Chem. Interfacial Electrochem.*, 1987, **216**, (1 and 2), 53-69

A Hg-film electrode with Ir as substrate was developed. Of several metals tested only Ir had the desired properties for bearing Hg. It is recommended that pretreatment should include polishing with $1\ \mu\text{m}$ diamond, rinsing with chromic acid and cathodising at -2.0V vs. S.C.E.

Oxidation of 4,4'-Dichlorobiphenyl at a Ruthenium Dioxide Anode

S. LAULE, R. HAWK and D. MILLER, *J. Electroanal. Chem. Interfacial Electrochem.*, 1986, **213**, (2), 329-332

The destruction of difficult-to-destroy polychlorinated biphenyls (PCBs) was investigated using a RuO_2 anode. The destruction could be accomplished via electrochemical oxidation at a RuO_2 anode, using a Pt cathode and a Ag/AgCl reference electrode.

Selective Formation of HCOO^- in the Electrochemical CO_2 Reduction Catalysed by $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ (bpy = 2,2'-bipyridine)

H. ISHIDA, H. TANAKA, K. TANAKA and T. TANAKA, *J. Chem. Soc., Chem. Commun.*, 1987, (2), 131-132

The electrochemical reduction of CO_2 catalysed by $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ in MeOH or MeCN in the presence of several proton sources selectively forms HCOO^- at a fast reaction rate. On increasing the pK_a value of the proton source the selectivity for HCOO^- formation increases.

PHOTOCONVERSION

Photocatalytic Decomposition of Formic Acid on Platinized n-Type Silicon Powder in Aqueous Solution

H. YONEYAMA, N. MATSUMOTO and H. TAMURA, *Bull. Chem. Soc. Jpn.*, 1986, (10), 3302-3304

Photocatalytic decomposition of aqueous formic acid was successfully achieved using platinised n-type Si powder as a photocatalyst, which was spread on the bottom of a reaction cell.

Photoassisted Hydrogen Production from a Methanol-Water Mixture on Platinized Cr_2O_3 -Doped TiO_2

A. SOBCZYNSKI, *J. Mol. Catal.*, 1987, **39**, (1), 43-53

Reduction of previously adsorbed Pt^{4+} species on TiO_2 was used to obtain highly active catalysts for H_2 photoevolution from a $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ solution. A quantum yield up to 22% was observed. Optimum Pt coverage and most favourable reaction conditions were found. Although the Cr_2O_3 dopant shifts the anatase spectrum into the visible, it is not possible to obtain H_2 with light of energy smaller than the bandgap of TiO_2 .

Study of Photocatalytic Reaction of Methanol with Water over Rh-, and Pd-Loaded TiO_2 Catalysts. The Role of Added Alkali Metal Cations

S. NAITO, *Can. J. Chem.*, 1986, **64**, (9), 1795-1799

The product selectivity of the photocatalytic reaction of methanol with water is changed drastically by the addition of alkali metal cations (Na) to Rh- and Pd-loaded TiO_2 catalysts. Over catalysts without alkali metal cations the main products are a 1:1 ratio of H_2 and dimethoxymethane, which changes to H_2 , methyl formate and CO_2 when alkali metal cations are added. The added cations stabilise the reaction intermediate as adsorbed formate instead of adsorbed formaldehyde, thus causing the product selectivity to change from dimethoxymethane to methyl formate.

Light-Induced Reduction of Rhodium (III) and Palladium (II) on Titanium Dioxide Dispersions and the Selective Photochemical Separation and Recovery of Gold (III), Platinum (IV), and Rhodium (III) in Chloride Media

E. BORGARELLO, N. SERPONE, G. EMO, R. HARRIS, E. PELIZZETTI and C. MINERO, *Inorg. Chem.*, 1986, **25**, (25), 4499-4503

Irradiation of aqueous TiO_2 dispersions containing Pd(II) or Rh(III) chloride salts with AM1 simulated sunlight caused photoreduction of the metals. O_2 deterred Rh(III) photoreduction, but not Pd(II) photoreduction. Reduction is most efficient in the presence of CH_3OH . The selective photoreduction and recovery of a mixture of Pt(IV), Rh(III) chloride and Au(III) were tested against parameters for pH, O_2 presence, presence of a hole scavenger and semiconductor concentration.

Photoreduction of CO_2 to CH_4 in Aqueous Solutions Using Visible Light

R. MAIDAN and J. WILLNER, *J. Am. Chem. Soc.*, 1986, **108**, (25), 8100-8101

CO_2 can be photocatalytically reduced to CH_4 using tris(bipyridine)Ru(II) as sensitiser, and a Ru metal colloid as catalyst. The system consists of an aqueous solution of pH 9.5 which includes NaHCO_3 , $\text{Ru}(\text{bpy})_3^{2+}$, TEOA as electron donor, and a Ru colloid. When illuminated at $>420\text{nm}$ under a gaseous CO_2 atmosphere, CH_4 formed.

ELECTRODEPOSITION AND SURFACE COATINGS

Structure and 700°C Hot Corrosion Behavior of Chromium Modified Platinum-Aluminide Coatings

M. DUST, P. DEB, D. H. BOONE and S. SHANKAR, *J. Vac. Sci. Technol. A*, 1986, 4, (6), 2571-2576

The 700°C hot corrosion testing of Cr modified Pt aluminides was studied to determine whether combined additions of Cr and Pt were even more beneficial. The substrates used were two commercial Ni-base superalloys. The structure of the Cr modified Pt aluminide coating was dependent on the sequence of modifying element addition. The optimum coating for this resistance was obtained by the Cr-Pt-Al deposition sequence which gave a coating with a continuous PtAl₃ layer on the surface backed up with a fairly high level of Cr and Pt.

Pulsed Current Electrodeposition of Palladium

S. YOSHIMURA, E. CHIDA and E. SATO, *Met. Finish.*, 1986, 84, (10), 39-42

Ethylenediamine-Pd(II) complex solutions as the electrolyte, Pt-coated Ti as anode and O-free Cu sheet as sample electrode were used in an electrolytic cell of volume 250cm³ to examine Pd electrodeposition using DC and pulsed current. The effects of electrolytic parameters on electrodeposition morphology, occluded H content and current efficiency were also measured. Pulsed current electrolysis produced a fine grained smooth electrodeposit with decreased H content. Important factors affecting electrodeposit morphology were the overpotential and the effect of mass transfer. The overpotential for reasonable current efficiency, H content and electrodeposit morphology was ~200-400mV.

Investigation of Laser-Assisted Palladium Deposition

F. FRIEDRICH and CH. J. RAUB, *Galvanotechnik*, 1986, 77, (11), 2658-2664

The effect of laser light was examined for Pd deposition from ammoniacal Pd electrolytes. Other effects on the structure of the deposited layers which were examined included thickness and thermal conductivity of the substrate, pH of the electrolyte and changes in cathodic polarisation voltage. The deposition of Pd-Ag alloy layers was favourably affected by laser radiation.

Palladium Plating Technique

Res. Discl., 1986, (270), 618

Ni-plated piezoelectric ceramic tubes, used for ink jet printing can be given an overplate of Pd which significantly improves resistance to corrosion. Pd plating is added to the Ni coating on the tubes by replacing the Ni/film with a Pd seed layer by a galvanic reaction, and electrolessly depositing a Pd film over the seed layer. This process produces non-porous films with good adhesion. The tubes can be plated first with Ni when they have no coating.

Electrocoated Layer Compound Materials Based on Palladium for Plug Connectors

D. RÜHLICKE, G. BÄR, M. HAGENI and H. HEYNE, *Neue Huette*, 1987, 32, (2), 77-80

Results of work on contact materials for highly reliable plug connectors are presented. It was found that electroplated layers, combinations of the type 2µmPd/0.2µmAu and 4µmNi/2µmPd/0.2µmAu were most suitable. The plating conditions are discussed.

LABORATORY APPARATUS AND TECHNIQUE

Electrochemical Detection for Liquid Chromatography Using the Wall-Jet Cell/Ultramicroelectrode Detector

S. B. KHOO, H. GUNASINGHAM, K. P. ANG and B. T. TAY, *J. Electroanal. Chem. Interfacial Electrochem.*, 1987, 216, (1 and 2), 115-126

A carbon fibre array and a Pt thin ring ultramicroelectrode were constructed and used with a large volume wall-jet cell for amperometric detectors in liquid chromatography. Electrode characterisation was performed. This combination has much reduced flow rate dependence compared to the wall-jet cell/conventional electrode system. Liquid chromatography in the absence of supporting electrolyte was possible and had good sensitivity using the ultramicroelectrode.

Chemically Responsive Microelectrochemical Devices Based on Platinized Poly(3-Methylthiophene): Variation in Conductivity with Variation in Hydrogen, Oxygen, or pH in Aqueous Solution

J. W. THACKERAY and M. S. WRIGHTON, *J. Phys. Chem.*, 1986, 90, (25), 6674-6679

Microelectrochemical transistors were prepared from Au microelectrodes and platinized poly(3-methylthiophene) (P). The change in conductivity of (P) with change in redox potential is the basis for amplification of electrical or chemical signals; conductivity varying 5-6 orders of magnitude upon change in potential from +0.2 to +0.7V vs. S.C.E. in aqueous electrolyte. The Pt equilibrates (P) with the O₂/H₂O or H₂O/H₂, redox couples. The transistors can be used as room temperature sensors for O₂ and H₂ in aqueous solutions.

Blackbody Having a Platinum Heater and Temperature-Sensitive Element

G. K. KHOLOPOV, S. G. GALIEVA, A. S. CHERYUKANOV, N. YU. BEREZKINA, YU. L. VOLKOV, A. G. MATVEEV and P. A. POTEIKO, *Sov. J. Opt. Technol.*, 1986, 53, (3), 143-145

The construction and operation of a small blackbody is described which is to be used as a thermal radiation source and designed for temperatures from 50-250°C. The temperatures are determined by measuring the resistance of a Pt wire which also serves simultaneously as the heater winding.

An Electrochemical Oxygen Separator Using an Ion-Exchange Membrane as the Electrolyte

Y. FUJITA, H. NAKAMURA and T. MUTO, *J. Appl. Electrochem.*, 1986, 16, (6), 935-940

An electrochemical O₂ separator with two electrodes and an ion-exchange membrane has been developed. The anode consists of a Nafion membrane plated at 3.7mg/cm² with Pt; the cathode, bonded to the other side of the membrane, was formed from a slurry of graphitised furnace black loaded with Pt at 0.2mg/cm². Nafion solution and a PTFE dispersion were added to the slurry. The separator could be operated at 200mA/cm² and produced 70.9cm³/min O₂ of 98.4% purity.

Hydride Formation as a Measure of Alloying in Bimetallic Systems Containing Palladium

S. B. ZIEMECKI, J. B. MICHEL and G. A. JONES, *React. Solids*, 1986, 2, (3), 187-202

The measurement of the H:Pd ratio as an indication of alloying has been studied during temperature programmed reduction (TPR). Pd-Re and Pd-Au alloys were formed during TPR from the component metals. The extent of alloying is related to the suppression of β -PdH formation.

Behavior of Hydrogen in Palladium-Aluminium Metal-Oxide-Semiconductor Structures

F. ENQUIST, M. ARMGARTH and I. LUNDSTRÖM, *J. Appl. Phys.*, 1986, 60, (12), 4297-4299

A new way of studying H in composite metal films by using H sensitive Pd gate MOS devices is described. MOS structures with composite films of Pd and Al were made and the behaviour of H atoms in the passive Al and at the metal-metal interface was examined. Although H atoms pass through the non-catalytic Al layer, there are no adsorption sites with polarised H atoms at the Al-SiO₂ interface.

HETEROGENEOUS CATALYSIS

n-Octane Dehydrocyclisation on Monofunctional and Bifunctional Pt/Al₂O₃ Catalyst

C. T. AKO and A. A. SUSU, *J. Chem. Technol. Biotechnol.*, 1986, 36, (11), 519-526

The dehydrocyclisation of n-octane to iso-octane, ethylbenzene and o-, m- and p-xylene was investigated on monofunctional (non-acidic) and bifunctional (acidic) Pt/Al₂O₃ catalyst in a microreactor with H₂ at 563-673K. On bifunctional Pt/Al₂O₃, the total conversion of n-octane decreased from a high value with increasing temperature; the primary product being iso-octane. On monofunctional Pt/Al₂O₃, the total n-octane conversion increased initially and went through a maximum as the temperature increased; the primary products were ethylbenzene and o-xylene.

A Study of Supported Platinum Catalysts for the Production of Hydrogen Cyanide by the Ammoxidation of Methane

G. J. HUTCHINGS, *Appl. Catal.*, 1986, 28, (1-2), 7-11

The ammoxidation of CH₄ to produce HCN has been investigated over Pt/beryl (Be, Al, Si₂O₃). The method of preparing the catalysts significantly affected the yields of HCN. Supported catalysts are less affected by space velocity and poisons, such as Fe, than gauze catalysts for this reaction.

Influence of Sulfiding Method on Properties of Platinized and Platinized-Iridized Alumina Reforming Catalysts

V. L. MEDZHINSKII, B. B. ZHARKOV, L. F. BUTOCHNIKOVA and A. N. KRASIL'NIKOV, *Chem. Technol. Fuels Oils*, 1986, 22, (3/4), 165-168

The effect of methods used to introduce bound S on the activity and stability of monometallic and bimetallic reforming catalysts has been studied. After preparation the catalysts were reduced at 500°C and sulphided at 340°C with a H₂:H₂S=10:1 mixture and then purged of H₂S. Catalyst activity in heptane reforming was then investigated at 475°C and 1MPa pressure. Sulphiding the catalysts after reduction is more effective: the selectivity in cracking reactions is lowered by a factor of >2 and the selectivity in aromatisation is increased by a factor >3. Adding 0.1wt.%Ir to 0.36Pt/Al₂O₃ doubles the cracking selectivity.

Monodisperse Colloidal Metal Particles from Nonaqueous Solutions: Catalytic Behavior in Hydrogenation of But-1-ene of Platinum, Palladium and Rhodium Particles Supported on Pumice

M. BOUTONNET, J. KIZLING, V. MINTSA-EYA, A. CHOPLIN, R. TOUROUDE, G. MAIRE and P. STENIUS, *J. Catal.*, 1987, 103, (1), 95-104

Monodispersed particles of Pt(2-3nm), Rh(2-3nm) or Pd(5nm) were dispersed via reverse micellar solutions on pumice to form catalysts. Catalysts formed using aqueous or alcoholic solutions produced large aggregates. Catalytic reactions for deuteration, isomerisation and H₂-D₂ exchange of but-1-ene were performed and properties compared. The activities per metal surface area were similar. Pt prepared from microemulsions showed unusually high selectivity for isomerisation.

Synthesis of Acetylene-Terminated Monomers Using a Polymer-Supported Palladium Catalyst

D. L. TRUMBO and C. S. MARVEL, *J. Polymer Sci., Polymer Symposium* 74, 1986, 45-53

A single crystal polyethylene bound Pd catalyst was prepared and used instead of a free Pd catalyst for the synthesis of acetylene-terminated monomers. The yields were lower, 57-64% versus 83-86% for the free Pd catalyst, but the advantages of the bound catalyst outweigh the loss of yield; these include recyclability which lowers costs in the long run, and the products are not contaminated with Pd.

Exhaust-Catalyst Development for Methanol-Fueled Vehicles. 2. Synergism between Palladium and Silver in Methanol and Carbon Monoxide Oxidation over an Alumina-Supported Palladium-Silver Catalyst

R. W. McCABE and P. J. MITCHELL, *J. Catal.*, 1987, 103, (2), 419-425

CH₃OH and CO oxidations were examined over 0.01Pd, 5% Ag and 0.01%Pd-5%Ag catalysts supported on γ -Al₂O₃. The bimetallic catalyst showed greater oxidation activity than the single component catalysts, and the Pd and Ag acted synergistically in the bimetallic catalyst to produce greater CO and CH₃OH oxidation rates and lower yields of methanol partial oxidation products than expected.

Selective Decomposition of Isobutylaldehyde to Propene, Carbon Monoxide and Hydrogen

K. FUJIMOTO and T. KUNUGI, *Appl. Catal.*, 1987, 29, (2), 203-210

Supported Pd modified with Na₂S was an excellent catalyst for the selective decomposition of isobutylaldehyde to propene, H₂ and CO. The conversion was ~90% and 99% propene was produced selectively at 35°C under atmospheric pressure. The S ion suppressed the secondary reaction of propene and H₂ and promoted the desorption of CO.

Lanthanum Oxide Promoted Rhodium/Titania and Rhodium-Platinum/Titania Catalysts for Alcohol Formation from Synthesis Gas

G. C. BOND and D. G. RICHARDS, *Appl. Catal.*, 1986, 28, (1-2), 303-319

TiO₂-supported Rh and Rh-Pt catalysts have been studied for the selective formation of oxygenates from synthesis gas. Adding La₂O₃ as a promoter significantly increased the C₂H₅OH selectivities and formation rates. Pt addition increased overall activity and with La₂O₃ gave higher alcohol selectivities of 25%, compared to 6% for unpromoted Rh. The La₂O₃ seems to promote the formation of the C₂H₅OH, while Pt increases hydrogenation.

Modification of Product Distribution through Periodic Operations; Fischer-Tropsch Synthesis over Ru/Al₂O₃

Y. BARSHAD and E. GULARI, *Chem. Eng. Commun.*, 1986, 43, (1-3), 39-51

Forced concentration cycling during Fischer-Tropsch syntheses over Ru/Al₂O₃ changed the rate and selectivity of the reaction. The rate of reaction was improved by as much as 200% compared to the steady state. Selectivity enhancement was quite complex; under certain conditions significant increases were observed in ethane and propane selectivities. Prolonged exposure to CO was necessary for the formation of higher hydrocarbons. When CO pretreated Ru/Al₂O₃ is exposed to H₂, propane and higher hydrocarbons are produced first.

Ammonia Synthesis over Alumina and Magnesia Supported Ruthenium: Comparative Kinetic Study of the Promotive Action of Metallic and Ionic Potassium

H. BARIS, M. GLINSKI, J. KIJENSKI, A. WOKAUN and A. BAIKER, *Appl. Catal.*, 1986, 28, (1-2), 295-301

The effect of K and KNO₃ promoters on NH₃ synthesis over Al₂O₃ and MgO supported Ru was investigated in a fixed-bed reactor at 300-725K at 150kPa. Promotion with K increased the turnover frequency of the Ru/Al₂O₃ 90 times and ~60 times for Ru/MgO at 623K. The KNO₃ had little effect.

HOMOGENEOUS CATALYSIS

Phase-Transfer and Metal-Complex Catalysis with Quaternary Ammonium Chlorometallates

I. G. IOVEL, Y. SH. GOLDBERG, M. V. SHYMANSKA and E. LUKEVICS, *J. Chem. Soc., Chem. Commun.*, 1987, (1), 31-32

Quaternary ammonium chlorometallates prepared with complexes of Pt^{IV}, Ir^{III} and Fe^{III} were produced and their bifunctional catalytic properties were tested in the hydrosilylation reaction of phenylacetylene with triethyl- and (dimethyl)phenyl-silane (metal-complex catalysis), followed by addition of dichlorocarbene (phase-transfer catalysis). Their catalytic activity for both reactions studied was not lower than that of conventional catalysts, thus two reactions can run consecutively in the same vessel.

Coordination Chemistry with Alkanes: Homogeneous Solutions for Reactive sp³ C-H Bonds

M. L. DEEM, *Coord. Chem. Rev.*, 1986, 74, 101-125
Cleavage of alkane C-H bonds, by metals from Groups 3d, 8d, 9d and 10d, including Pt(II), Pd(II), Ir(0), Ir(I), Ir(III), Rh(I), Os(II), Ru(0) and Re, is considered for non-aqueous liquid systems at <150°C. Alkane conversion to H₂ and alkenes is of industrial importance and this method is a different way to the same products as catalytic reforming of hydrocarbons. Driving forces for the homogeneous phase C-H sp³ bond activation are identified, and in a typical reaction several of the driving forces participate to allow regioselective conversion (at low levels) of n-octane to 2-octene by chlorotris-(triphenylphosphine)Rh(I) if triglyme is present. (105 Refs.)

Cyclodextrin-Palladium Chloride. New Catalytic System for Selective Oxidation of Olefins to Ketones

A. HARADA, Y. HU and S. TAKAHASHI, *Chem. Lett. Jpn.*, 1986, (12), 2083-2084

Terminal olefins are oxidised to ketones in high yields under mild conditions using PdCl₂ and cyclodextrins as catalysts in two-phase systems. Separation of products from catalysts or solvents is easy. Cyclodextrins show substrate selectivity.

Rapid Thermal Hydrogen Production from Alcohols Catalysed by [Rh(2,2'-bipyridyl)₂] Cl

D. MORTON and D. J. COLE-HAMILTON, *J. Chem. Soc., Chem. Commun.*, 1987, (4), 248-249

[Rh(bipy)₂] Cl was found to thermally catalyse the production of H₂ via the dehydrogenation of propan-2-ol, butane-2,3-diol, ethanol, and methanol. The rates of H₂ production are dramatically higher than any previously observed system. Turnover numbers of 100/h for H₂ production were seen.

Ruthenium-Catalyzed Amidation of Nitriles with Amines. A Novel, Facile Route to Amides and Polyamides

S.-I. MURAHASHI, T. NAOTA and E. SAITO, *J. Am. Chem. Soc.*, 1986, **108**, (24), 7846-7847

A new method applicable for synthesis of various amides and polyamides is presented. It involves Ru catalysed condensation of nitriles with amines in the presence of water to give the corresponding amides and NH₃. The reaction is clean and highly efficient under neutral conditions, and is performed in a single step, although the reaction temperature is high. RuH₂(PPh₃)₄ was the most effective catalyst.

Some Aspects of the Coordinations and Catalytic Chemistry of Ruthenium

J. HALPERN, *Pure Appl. Chem.*, 1987, **59**, (2), 173-180

Among characteristic features of the co-ordination chemistry of Ru complexes containing a wide range of ligands is the propensity for intra- and intermolecular metallation of arenes and for the formation of polyhydride complexes. The roles of Ru polyhydride complexes in catalytic hydrogenation are discussed. Distinctive features of such complexes include catalytic hydrogenation of arenes and ketones.

FUEL CELLS

Hydrogen Sulfide Poisoning of Platinum Anode in Phosphoric Acid Fuel Cell Electrolyte

D.-T. CHIN and P. D. HOWARD, *J. Electrochem. Soc.*, 1986, **133**, (12), 2447-2450

The effect of H₂S on the anodic oxidation of H₂ on Pt in 94wt.% phosphoric acid fuel cell electrolyte was studied from 25-170°C. Anodic I/V curves of a stationary Pt electrode were measured with a half-cell set up in the presence of H₂S. Adding H₂S to H₂ caused a rapid decrease in the anodic current due to adsorption of H₂S on Pt. The amount of H₂S poisoning decreased with increasing temperature and increased with increasing potential. Adsorbed H₂S species blocked the active sites available for the adsorption/desorption of H and thus retarded the rate of H₂ oxidation on Pt. At sufficiently high anodic potentials a layer of adsorbed S formed on the electrode surface and suppressed the formation of Pt oxide at the O adsorption potentials.

ELECTRICAL AND ELECTRONIC ENGINEERING

The Ammonia Sensitivity of Platinum-Gate MOSFET Devices: Dependence on Gate Electrode Morphology

J. F. ROSS, I. ROBINS and B. C. WEBB, *Sens. Actuators*, 1987, **11**, (1), 73-90

The response to NH₃ of Si-based MOSFET devices with Pt gate electrodes has been studied. Devices with evaporated Pt gate electrodes, which are non-continuous are very NH₃ sensitive, but devices with sputtered Pt gate electrodes which are continuous, are not NH₃ sensitive. Both devices show a similar response to H₂, typically changes in threshold voltage of ~ -420mV and -350mV, respectively, to 500ppm H₂ at 150°C.

Laser Direct-Write Metallization in Thin Palladium Acetate Films

M. E. GROSS, A. APPELBAUM and P. K. GALLAGHER, *J. Appl. Phys.*, 1987, **61**, (4), 1628-1632

Micron-scale Pd lines have been produced by a photothermal laser direct-write process in thin Pd acetate films. The range of observed structures relates to the complex thermal profiles generated by coupling of the incident laser radiation with the exothermic heat of reaction. Deviations of the electrical resistivities of the features from that of pure Pd result from porosity in the lines.

TEMPERATURE MEASUREMENT

Constant-Volume Gas Thermometry between 4K and 100K

P. P. M. STEUR and M. DURIEUX, *Metrologia*, 1986, **23**, (1), 1-18

Gas-thermometer measurements between 4-100K were performed in preparation for a revision of the IPTS. Gas-thermometer temperatures were compared between 13.8 and 100K with Pt resistance thermometers calibrated on IPTS-68, and between 4.2 and 27.1K with Re-Fe resistance thermometers calibrated on NPL scale of 1975.

MEDICAL USES

Synthesis and Antitumour Activity of Organometallic cis-Dichloro(enamine)-(amine)Platinum(II) Complexes

A. R. KHOKHAR, S. L. DORAN, D. B. BROWN and M. P. HACKER, *Inorg. Chim. Acta Bioinorg. Chem.*, 1987, **135**, (b18), (2), 81-83

A series of Pt(II) organometallic complexes have been synthesised and their in vivo anti-tumour activity has been evaluated. Preliminary results indicate that this class of complexes has good in vivo cytotoxicity against L1210 murine leukaemia cells.