ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Positive Ion Emission from a Platinum Hot Wire Gas Sensor


A clean Pt wire when heated to 500°C produces a steady positive ionic current in the presence of organic vapours. Higher responses were obtained for vapours with more C atoms per molecule and greater ease of oxidation by the wire. Oxidisable gases with little or no C produced little or no ionic response. Ionisation potentials of ~ 6 eV were calculated. Wires at 500-1000°C in contact with organic vapours or contaminated by surface C also emitted positive ions in air. Both clean and C-contaminated wire responses can be used to design selective gas sensors.

Electrical Resistivity of Ordered Fe_{1−x}Pt_{x} Alloys between 4 and 1200K


The electrical resistivity of ordered Fe_{1−x}Pt_{x} alloys containing 20, 22, 24, 26, 28 and 30 at.% Pt was investigated from 4 to 1200K. A new phase was found at low temperatures (T<240K) for alloys with 26, 28 and 30 at.% Pt. Both the α-γ transition and the transition to the new phase exhibit hysteresis in the electrical resistivity curves.

Formation of PtSi in the Presence of Al


The formation of Pt silicides in the presence of Al using Al/Pt/Si structures with different Al thicknesses was studied. The Pt-Si and Pt-Al reactions occur simultaneously at ~ 200°C and PtSi and PtAl formation is completed by 400°C. With three equal layer thicknesses the two alloys formed stay in contact and are stable up to ~ 500°C. With twice or more Al thickness to Pt and Si, the PtSi layer is completely converted to PtAl, at 450°C.

Superconductivity and Antiferromagnetic Order in the U(Pt, Pd) System


A phase diagram for the superconducting and antiferromagnetic states in U(Pt_{1−x}Pd_{x}), x≤0.10 is presented. Superconductivity is depressed for x>0.005, whereas antiferromagnetism is observed for 0.01⩽x<0.1. Specific heat experiments show a sharp transition at the Néel temperature of 6.1K for x=0.05, in contrast to x=0.02 and 0.07 where rather broad anomalies are observed at ~ 3.6 and 5.5K.

Synthesis and Electrocatalytic Properties of Rare Earth Platinum and Palladium Bronzes


DyPt and DyPd bronzes Dy_{M}X_{3} (M=Pt, Pd; X=O, S, Se or Te) were synthesised by a solid state technique, except for DyPt. They all had high electrical conductivity, with Q=0.3-2.6×10^{-7} S/cm, and the oxide bronzes crystallised with a Na_{2}Pt_{2}O_{5} type structure. The Pt oxide bronzes in particular had high activity for the methanol electro-oxidation, as compared to ordinary Pt electrodes.

The High-Temperature Elastic Properties of Palladium Single Crystals


A thin-line acoustic method was used to measure the single crystal elastic moduli of Pd between 30-1200K. The single crystal constants behave, at high temperatures, in a classical manner, in contrast to a large modulus defect observed in polycrystalline Pd. The latter effect may be due to grain boundary relaxation.

Magnetic Interface Anisotropy in Pd/Co and Pd/Fe Multilayers


Pd/Co and Pd/Fe multilayer thin films containing ultrathin, 2-12Å Co and Fe layers were prepared by vapour deposition in UHV. Their magnetisations were measured at room temperature in fields parallel and perpendicular to the film plane. The Pd/Co multilayers show a transition of the preferred direction from lying in the film plane towards lying along the film normal when the thickness of the Co layer is decreased below 8Å. The Pd/Fe multilayers are preferably magnetised in the film plane, although the anisotropy decreases with lower Fe layer thickness.

Structural and Electronic Properties of Implanted Metal Hydrides


A review of Pd and Ni low temperature H implanted hydrides is presented, and comparisons between the properties of both are discussed and related to various methods of preparation. Similarities include superconducting transition temperatures and photon energies, while differences include the phase diagrams. Metastable hydrides can thus be prepared with properties very similar to those of classically charged hydrides. (33 Refs.)
Preparation of Amorphous Ni-Pd-P Particles by Melt Ejection into Stirred Water and Their Hardness and Thermal Stability

The preparation of amorphous spherical particles with diameters 0.5–1.4mm by melt ejecting Ni-rich Ni-Pd-P alloys into stirred cold water with 1 vol.% surfactive agent is described. The sphericity of the particles was better than 98%. Particles with diameters <1.0mm have hardness, crystallisation temperatures and heat of crystallisation similar to those of amorphous ribbon of the same composition and ~40µm in thickness, but the onset temperature and heat of relaxation are different. Thus the particles have the same thermal stability as that of the amorphous ribbon but their structure is in a more disordered state than the ribbon.

Effect of Ambient Gases on Emission Properties of Pd-Ni-Si-Be-B LM Ion Source

The effects of ambient gases on the emission properties of a Pd,Ni,Sn,Si,Be,B liquid metal ion source were studied. O₂ and water vapour had a significant effect on the ion emission stability. A very stable and reliable ion emission with a lifetime >100 hours was obtained by operating the source at 8×10⁻⁸ torr.

Absorption of Hydrogen in Pd-Co and Pd-U Alloys

The absorption of H₂ in structurally disordered Pd₉₆Co₁₄, Pd₉₆Co₁₈, Pd, U, and Pd, U was studied experimentally between 300–600K and up to 50bar H₂ pressure. Pure U readily absorbs H₂, while Co does not; however absorption of H₂ is reduced more in the Pd-U alloys than in the Pd-Co alloys. In Pd, U no appreciable absorption could be detected.

Electrical Resistance and Hydrogen Solubility Anomalies in a Pd-8at.%Y Solid Solution Alloy

The H₁ (protium and deuterium) solubility and electrical resistance measurements have been made on a Pd-8at.%Y solid solution alloy over a range of temperatures and pressures. A solubility enhancement effect occurs for the Pd-8at.%Y-H₁ system, and enhanced resistance values at low temperatures occur for Pd-8at.%Y-H₂ and Pd-8at.%Y-D₁. Both effects disappear at a critical value of H:metal atom ratio of 0.32, which may correspond to a diamagnetic to paramagnetic transition. The effects disappear on sample cooling but can be recreated by removing the H and reannealing the sample.
Crystal Structure and Superconductivity of New Ternary MTGe Germanides (M = Ti, Zr, Hf and T = Ru, Os, Rh, Ir)


ZrIrGe and HfIrGe crystallise with a TiNiSi-type structure and exhibit a superconducting transition at 2.75 and 4.98 K, respectively. TiIrGe and HfRhGe have two allotropic varieties and their superconducting properties are strongly influenced by their crystal structure. No superconducting transition above 1.6 K was observed for TiTGe (where T = Ru, Os, Rh), ZrIrGe and HfIrGe crystallise with a TiNiSi-type structure and exhibit a superconducting transition at 4.98 K.

Equilibria Description for the System BaO-RuO$_2$-Fe$_2$O$_3$ with Less than 55 mol.% BaO at 1300°C in Platinum Capsules: A Crystallographic and Leaching Study


The system BaO-RuO$_2$-Fe$_2$O$_3$ with <55 mol.% BaO was investigated after heating at 1300°C in Pt capsules. The Ru valence was not constant and was therefore considered as an extra variable. Thus the system is considered as a description of the equilibria and not as a ternary phase system. Three quaternary compounds were determined and a new ternary compound was found.

CHEMICAL COMPOUNDS

Cobalt, Rhodium and Iridium. Annual Survey Covering the Year 1985


A review covering continuing studies in Rh, Ir and Co organometallics covering literature, including dissertations, published in 1985 is presented. The range of complexes covered include metal-C bonded, metal carbones, metal isocyanides, metal carbynyls and related compounds, nitrosyls and aryldiazos, alkynes, alkynes, α-allyls, carbocyclics, metallaboranes and -carboranes and other miscellaneous complexes. (822 Refs.)

Reactivity of Pentaammineosmium(II) with Benzene


The reduction of Os(NH$_3$)$_5$(CF$_3$SO$_3$)$_2$, with Mg in the presence of excess benzene gives a deep orange coloured solution containing [Os(NH$_3$)$_5$(η$^5$-benzene)][TFMS]$_2$(1). NMR and i.r. spectroscopies were performed, and compound (1) in acetone liberates benzene and forms complex [Os(NH$_3$)$_5$(η$^3$-acetone)]$^+$$. Compound (1) will react with a variety of ligands, and especially amides and esters.

Some Reactions of Ruthenium Cluster Carbonyls under Mild Conditions


Substitution reactions of Ru cluster carbonyls with t-buty1 isocyanide, and of Ru(CO)$_5$, with a range of isocyanides, tertiary phosphines, phosphites, arsines and SbPh$_3$, resulted in a range of easily made new complexes which were then characterised and the facile reaction routes described. (174 Refs.)

A Double Cluster of Ruthenium and Boron: [1-η$^7$-(η$^6$-C$_5$M$_6$)$_3$Ru$_2$H$_4$]-isocloso-1-RuB$_{10}$H$_{23}$-2,3-(OE)$_2$]


The novel double cluster title compound, obtained in 31% yield as an unexpected product from the reaction between the mononuclear Ru complex arachno-[1-(η$^6$-C$_5$M$_6$)$_3$Ru]- and closo-[B$_{10}$H$_{14}$] in ethanol, has a unique non-carbonyl containing triangular {Ru$_3$} cluster and a closo-type eleven-vertex {RuB$_{10}$} cluster joined at a common Ru atom.

ELECTROCHEMISTRY

Electrochemical and Surface Science Investigations of PtCr Alloy Electrodes


Electrodes of supported Pt, modified with Cr, have an increase in electrochemical activity for O$_2$ reduction in phosphoric acid fuel cells, compared to Pt supported electrodes. A series of Pt$_x$Cr$_{1-x}$ bulk alloys (x = 0.9, 0.65, 0.5, 0.2) were tested to clarify the role of the Cr. Surface characterisation of the electrode surfaces were performed by various techniques, and the H$_2$SO$_4$ electrolyte was also analysed. The surface Cr was oxidised to Cr$^{2+}$ oxide for various potentials, and to soluble Cr species. For potentials > +1.3 V. Alloys with Cr content 30.5 produce very porous Pt-rich surfaces. Loss of Cr was also observed for Cr content 30.5. Pt$_x$Cr$_{1-x}$ gave Pt$^{2+}$ and Cr$^{2+}$ species.

"Transparent" Metallic Electro catalysts


Highly transparent films of thickness 30–60 nm, of Pd, Rh, Pb, Re on InP have been prepared. The films contain 30–60% metal, yet transmit most of the light of wavelengths between 210 and 750 nm. The films contain three microstructural levels, and because the particles and their aggregates are smaller than the u.v. wavelength, and because they are not well connected, the film appears specular and transparent. The films are prepared by photoloduction on to P-InP-photocathodes and exhibit normal catalytic behaviour and have normal crystal structures.
Iridium-Based Small Mercury Electrodes
The preparation of Ir-based small Hg electrodes, for use in electroanalytical chemistry is described. Ir was used as a base because of its very low solubility in Hg, and because Hg can be electroplated onto Ir so that it wets the surface. The prepared electrodes were hemispherical and had the chemical properties of a hanging Hg drop electrode. The amount of Hg used was 50% of that needed to form a regular hemisphere with the radius of the Ir base. The most stable electrode was prepared by electrolysis of Hg in 0.1 M HClO₄ at 0.4 V for 11–13 minutes using a 127 μm diameter Ir disk as substrate.

Electrooxidation of Methanol on Iridium in Acidic Solutions: Electrocatalysis and Surface Characterization by Infrared Spectroscopy
The electro-oxidation of methanol was studied on Ir in H₂SO₄ and HClO₄ to examine the catalytic activities of the electrode in various oxidation states, and of the adsorbed CO, examined by i.r. spectroscopy. Ir had a higher catalytic activity than Pt at low positive potential regions, but its catalytic activity decreased with time at a constant-potential polarisation, and was inhibited by CO gas. Adding CO shifted the maxima in the i.r. spectra to higher wave numbers.

Mechanism of Oxygen Reactions at Porous Oxide Electrodes. Part I. Oxygen Evolution at RuO₂ and RuSn₁₋ₓO₂ Electrodes in Alkaline Solution under Vigorous Electrolysis Conditions
The electrocatalytic performance and long-term stability of thermally prepared RuO₂ and RuSn₁₋ₓO₂ coated Ti anodes with respect to O₂ evolution in strongly alkaline solution at elevated temperatures under vigorous electrolysis conditions has been studied. Adding a controlled amount of an inactive oxide improves the long-term stability and electrocatalytic activity of RuO₂ electrodes. RuO₂ electrodes could possibly be used in large-scale water electrolysis cells.

Cathodic Metal Oxide Electrocatalysts vs. Metals in Chlor-Alkali Membrane Cell Technology
A cathode for use in chlor-alkali membrane cells is described. It consists of a Ni substrate with a roughened surface, coated with RuO₂ for the H₂ evolution reaction, ZrO₂, as an electrochemical stabilising agent and La sesquioxide as a mechanical stabilising agent.

Electrochemical Properties and Corrosion Behaviour of Ruthenium-Titanium Oxide Anodes
Kinetic reactions of by-processes on RuO₂-based anodes in chlor-alkali electrolytes have been studied. The investigation of parallel electrode processes allows the kinetics of the by-process to be established by studying the dependence of its partial rate on the overall current density. With the increase of the overall current density, the rates of O₂ evolution and Ru dissolution increase much more slowly than the rate for the anodic Cl₂ evolution process, and thus the specific Ru consumption and the current efficiency for O₂ evolution are decreased.

PHOTOCONVERSION
A New Photosynthesis-Like System for the Light-Induced Reduction of Water to Molecular Hydrogen
Two Zn porphyrinate-modified Pt electrodes, one acting as a n-type semiconductor, the other as a p-type semiconductor (cathode) were used in a photosynthesis-like system for solar energy conversion to H₂ upon visible light irradiation. The cathode compartment contains the ZnTPyP electrode surrounded by aqueous electrolyte of KCl, N,N-dimethylpyridinium dichloride and highly dispersed platinnised TiO₂.

Photo-Oxidation of Water Sensitised by Cadmium Sulphide Dispersions
A dispersion of CdS in alkali, of pH 12, was used to sensitise the photo-oxidation of water to O₂ by a sacrificial electron acceptor, PtCl₆³⁻. Heat treatment and platinisation of the CdS particles prior to irradiation markedly improved (20–40 times) their sensitising power. Below pH 12 no O₂ evolution was observed. After prolonged use at pH 13 the Pt/CdS loses the capacity for water photo-oxidation.

Photocatalytic Hydrogenation of Ethylene on the Bimetal-Deposited Semiconductor Powders
The photocatalytic hydrogenation of ethylene was studied on bimetal loaded/TiO₂ powders and on monometal loaded samples, using Pt, Pd, Cu and Ni. Pt and Cu co-catalysts produced ethane selectively. When the selectivity of C₂H₄ production over CH₄ was optimised by the Pt/Cu catalyst, the volume of H₂ concurrently evolved diminished. This suggested that the Pt surface was suitable for the photohydrogenation of C₂H₄.
Photoelectrochemical Properties of p-RuS


RuS₂ crystals were grown and doped to produce p-type conductivity. An impedance study of the p-RuS₂/aqueous electrolyte interface confirmed the existence of a Fermi level pinning of the semiconductor. The photocurrent is limited by the moderate quality of the barrier which allows forward currents flowing through the interface.

LABORATORY APPARATUS AND TECHNIQUE

Optimization of Ammonia-Sensitive Metal-Oxide-Semiconductor Structures with Platinum Gates


NH₃ gas sensitive MOS capacitors with Pt as a thin active metal gate were studied. Pt thicknesses of 10-30nm were favourable for a large response to a small NH₃ concentration.

Optical-Fibre Flammable Gas Sensor


The sensing element of a flammable gas sensor is a 100nm monomode fibre coated with Pt. The rate of the exothermic reaction of the hydrocarbon gases with O₂ is increased in the presence of Pt, and the resultant heat is transduced to a phase retardance by a fibre-guided light beam, which is recovered interferometrically.

A Solid-State Proton Conductor Sensor with an Ammonia Sensitivity at Room Temperature


A new type of solid-state gas sensor using an antimonious acid proton conductor has been used to detect small amounts of NH₃ in air at room temperature. The sensor has a four-probe type structure with two outer Pt electrodes and two inner Ag probes. The sensor response varied with NH₃ concentration from 50 ppm to 5030 ppm in air.

Ion Beam Mixing of Pt with René N₄ Alloy


I on mixing was studied in the Pt-René N₄ alloy system. The substrate, René N₄, is a Ni-base superalloy with about 66% of ordered γ' precipitates by volume. The average precipitate size is ~0.42μm. Mixing was performed by 1MeV Pt⁺ ions at two different doses and followed by Rutherford back scattering and Auger sputter profiling.

Gas Sensors Based on Catalytic Metal-Gate Field-Effect Devices


A review of the properties of gas-sensitive semiconductor devices with catalytic metal gates (Pt, Ir, Pd). A mostly of structure metal-SiO₂-Si, is presented. Emphasis is on field effect structures sensitive to H₂ containing molecules, such as H₂, NH₃, H₂S, alcohols, ethylene, etc. The principles of H sensors with Pd gates are described and NH₃ sensitive field effect devices with thin catalytic metal gates are discussed. (66 Refs.)

Interferometric Fibre-Optic Hydrogen Sensor


A H₂ sensor has been developed, where the sensing element is a Pd wire mechanically attached to a monomode optical fibre. In the presence of H₂, the Pd is converted to Pd hydride with resulting changes in the physical dimensions of the wire. These dimensional changes produce a longitudinal strain in the optical fibre, which is transduced to a phase retardance in a light beam guided by the fibre, and which is recovered interferometrically.

The Effect of Os Addition on Sputtered Iron Oxide Films

O. ISHIH, F. YOSHIMURA and A. TERADA, J. Appl. Phys., 1987, 61, (8), Part II B, 3825-3827

The average grain size of sputter deposited γ-Fe₂O₃ films is markedly decreased by Os addition. The grains grow during the reduction process from α-Fe₂O₃ to Fe₂O₃ and maintain the same size in subsequent oxidation from Fe₂O₃ to γ-Fe₂O₃. The reduction temperature decreases by 100°C at >0.88at.%Os addition. Thus the grain size of γ-Fe₂O₃ films decreases from 84 to 35nm as the Os content increases from 0 to over 0.88at%. An accelerating effect on the reducing reaction increases the saturation magnetisation and the squareness ratio of γ-Fe₂O₃ films. Thus an Os-added γ-Fe₂O₃ thin-film disk has higher output voltage and signal-to-noise ratio than other disks.

JOINING

Enhanced Dry Solder Wetting Using Au/Pt Coating Layer

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A thin Pt film can be incorporated between an antioxidant layer and a conducting layer to achieve dry solder wetting, which overcomes the problems of outdiffusion through the overcoating layer to the surface where they are oxidised and thus prevent subsequent wetting and joining by solder. A Au/Pt/Cu interface can be formed with only interdiffusion between the Cu and Pt and no outdiffusion of Cu to the Au surface. The Au/Pt/Cu layers can be deposited by any technique and the layers are 1000-2000Å thick.
HETEROGENEOUS CATALYSIS

Is There a Single Mechanism of Catalytic Rate Oscillations on Pt?

Experiments are summarised which show that the NO+CO reaction on clean Pt(100) or on clean polycrystalline Pt can exhibit oscillations at all pressures between 10⁻¹⁰ and 1 torr and that this is caused by the hexagonal --I×I-- surface phase transition. Many of the rate oscillations on Pt surfaces may arise from the adsorbate induced I phase transition of Pt(100).

Synthesis and Characterization of Small Platinum Particles Formed by the Chemical Reduction of Chloroplatinic Acid

Pt spheres of diameter ~20–30Å, Pt strands of ~60Å diameter and Pt composites of ~100–200Å size could be synthesised from the chemical reduction of chloroplatinic acid, where careful control of the nature of the reducing agent, the presence and type of protective agent and the reduction conditions were undertaken. The optimum protective agent was polyvinylpyrrolidone. The distribution of particle diameters for the spherical Pt can be described by a log-normal distribution function. It may be possible to incorporate unprotected Pt or other metal alloy particles in the hydrosol state into biological systems, such as vesicles, to give high catalytic activity.

Catalytic Dehydration of Acetic Acid on a Graphitized Platinum Surface

A continuous flow microreactor was used for the steady-state catalytic dehydration of acetic acid to ketene and water at 8×10⁻¹⁰ and 7×10⁻⁷ torr pressure and 500–800K. A polycrystalline Pt wire with a monolayer of graphite acted as catalyst.

Selective Aromatization of Light Paraffins on Platinum-Ion-Exchanged Gallium-Silicate Bifunctional Catalysts

The direct conversion of propane to aromatics was investigated on Ga-ion exchanged H-ZSM-5, Pt-ion-exchanged H-ZSM-5, Ga silicate and Pt-ion-exchanged Ga silicate. Pt/Ga silicate had the best performance; the conversion of propane and selectivity to aromatics was 92.3% and 60.7%, respectively at 600°C. Pt/H-ZSM-5 was much more active than Ga silicate, but was not selective for aromatisation. Pt/Ga silicate was also effective for the aromatisation of light paraffins. The Pt in Pt/Ga silicate reduces catalyst decay and regenerates the decayed catalyst with air.

Development of a Wetproofed Catalyst Recombiner for Removal of Airborne Tritium

A catalyst system capable of removing airborne tritium from nuclear fusion experiments, converting it in a recombiner to water vapour, which is then adsorbed, has been developed for use at ambient temperatures. Wetproofed Pt/C and Pt/SiO₂ catalysts were prepared and their activities measured with H₂. Pt/C was comparable to conventional Pt/Al₂O₃ under similar conditions. The Pt/SiO₂ was similar to the Pt/C but its activity could be increased by a factor of 5 by exposure to air at 150°C containing 50–200 ppm H₂. The activities of the catalysts when exposed to liquid water or air at 100% humidity were maintained. The wetproofer catalyst recombiner enables the operation to be performed at room temperatures.

Silica-Supported Alloy Catalysts for Triglyceride Hydrogenation: The Preparation and Properties of Pd-Ag and Pd-Ni Systems

The binary metal systems Pd-Ag and Pd-Ni were prepared on a Si support with a total metal loading of 2.5%. Twelve catalysts of each were prepared covering the range 0–100at.%Pd. The catalysts were characterised by various techniques, and their activity and selectivity were measured for the hydrogenation of soya bean oil in stirred and shaken batch reactors at 1 atm H₂ pressure and 100–160°C. The Pd-Ag system had an activity maximum in the 90–100at.%Pd range, while the Pd-Ni system had constant activity for alloys containing 0–60at.%Ni.

Effect of Hydrogenation Catalyst Activity on Adsorption and Surface Reaction Rates

Dynamic studies of the hydrogenation of α-methyl styrene over a Pd/Al₂O₃ catalyst prepared from PdCl₂ and Fischer-Tropsch syntheses were performed. Measurements were taken at 22, 38 and 50°C. Increasing the reduction temperature of PdCl₂ to Pd in H₂ from 250–420–510°C decreased Pd dispersion and reduced the equilibrium adsorption, etc.

Hydrogenation Activity and Acidity of Bifunctional Catalysts

The hydrogenating and acidity characteristics of two Pd/LaY zeolite catalysts containing 0.27 and 1.30wt.%Pd were investigated by a simple method for ethylbenzene conversion. Ethylbenzene acted as a probe molecule in H₂ and in an inert gas atmosphere, where it was hydrogenated to ethylcyclohexane and disproportionated to benzene/diethylbenzenes.
Sulfur Poisoning of Supported Palladium Methanol Synthesis Catalysts
The deactivation of Pd dispersed on SiO₂, η-Al₂O₃, SiO₂-Al₂O₃, TiO₂ and Nd₂O₃ was studied in the presence of 2ppm H₂S during CO hydrogenation at 523K, 1.5MPa and a H₂:CO ratio of 3. Activities and selectivities without S were first established. Pd/SiO₂ and Pd/Nd₂O₃ were most selective to methanol, while Pd/TiO₂ was the most active CO hydrogenation catalyst, giving CH₃OH, CH₂ and CH₂OH. Addition of H₂S reduced methanation activity by ~50%, but all oxygenate activity was lost, giving a marked selectivity shift to CH₂, Pd/SiO₂ was more S tolerant and stabilised at ~40% of its initial methanol activity. The Pd catalysts are more active than other metals when H₂S is present. There may be at least two different types of active sites for CO hydrogenation.

Dehydrogenation of Cyclohexane on Alumina-Supported Rhodium Catalysts. Effect of Oxidation-Reduction Treatment on the Catalytic Activity
The cyclohexane dehydrogenation and H₂ chemisorption on Rh/Al₂O₃ catalysts was studied as a function of reduction temperature (373–773K) preceded by O₂ treatment at 673K. The catalytic activity increased by a factor of 5 after reduction at 773K, while there was almost no change in the H₂ chemisorption on varying the reduction temperature.

Preparation of Highly Active Hydrogenation Catalysts by Immobilization of Polymer-Protector Colloidal Rhodium Particles
Colloidal Rh particles were firmly immobilised onto a polyacrylamide gel having amino groups at pH 4–9. The resultant catalysts had high activities for olefin hydrogenation, 2–22 fold larger than a Ru/C catalyst at 30°C under 1atm, and could be used repeatedly without measurable decrease in the activity.

Hydrogenation of Carbon Dioxide into Light Hydrocarbons at Atmospheric Pressure over Rh/Nb₂O₅ or Cu/SiO₂-Rh/Nb₂O₅ Catalyst
The two title catalysts give C₂ hydrocarbons, mainly C₂H₄ and C₂H₆ with 30–50% selectivity at 250–350°C and atmospheric pressure. The activity and selectivity of the Cu/SiO₂ containing catalyst are significantly greater than of the Rh/Nb₂O₅ alone. The Cu/SiO₂-Rh/Nb₂O₅ catalyst is composed of two layers and the Cu/SiO₂ is at the inlet of the catalyst when it converts CO₂ into CO.

Evidence for the Role of a “Hydridic” Hydrogen on the Selective Hydrogenation of Ethyl Acetate to Ethanol with the Bimetallic System Rh-Sn Supported on Silica
Catalyst Rh-Sn/SiO₂, resulting from the interaction of Sn(n-C₃H₇), and Rh/SiO₂, is more active and selective than Rh/SiO₂ for the hydrogenation of ethyl acetate to ethanol. Conversions of 100% and 98% selectivities are attainable, depending upon conditions. There is an inverse relationship between the amount of Sn fixed and the amount of H “weakly” adsorbed on Rh, and a linear relationship between the amount of Sn fixed and the amount of “strongly” adsorbed H. The selectivity for ester hydrogenation to alcohol may be due to the “strongly” adsorbed H resulting from the presence of Sn.

Selective Synthesis of Acetic Acid in High Pressure Carbon Monoxide Hydrogenation over a Rh-Mn-Ir-Li/SiO₂ Catalyst
A highly efficient Rh-Mn-Ir-Li/SiO₂ catalyst for the direct synthesis of acetic acid from syngas has been developed. Acetic acid was produced with a >65% selectivity in C₂H₄ and with high space time yield, a typical value being 130g/dm³cat/h at 280°C and 100kg/cm² pressure, a space velocity of 10/h and a H₂:CO ratio of 1:1. The Mn, Ir and Li act synergistically towards the Rh/SiO₂.

Electronic Effects on CO Hydrogenation over Ru-Metal Oxide Catalysts
The electronic structure of supported Ru catalysts is shown to be markedly affected by the nature of the metal oxide support, and the specific activity of CO hydrogenation increases as the electron density of the metal oxide support decreases. Seven supports were investigated, including TiO₂, MgO, SiO₂, etc.

The Catalytic Hydrogenation of Benzene over Supported Metal Catalysts. III. Gas-Phase Hydrogenation of Benzene over Silica-Supported Ru-Cu Catalysts
The gas phase hydrogenation of benzene over Ru/Cu/SiO₂ was studied from 300–400K and total pressure 130kPa. Two catalysts, one with ~10% Ru surface covered by Cu, the other with ~70% Cu coverage were prepared. With ~11% Cu coverage the lifetimes of the catalysts are considerably increased without seriously affecting the activity/Ru surface atom. A shift in the Cu electron binding energy is observed, indicating a small electron transfer from Ru to Cu; at ~68%Cu coverage this shift disappears.
Chemisorption and Catalysis by Metal Clusters. Hydrogenation of Carbon Monoxide and Carbon Dioxide Catalysed by Supported Ruthenium Clusters Derived from Ru, (CO)12 and H2Ru, (CO)12. S. D. JACKSON, R. B. MOYES, P. B. WELLS

The properties of catalysts containing active clusters derived from Ru, (CO)12 and H2Ru, (CO)12, are thus protected from sintering which, with ligand-COY ligand-C and support-ported on SO, is described. The clusters, with ligand-COY ligand-C and support-cluster interaction, are thus protected from sintering and are stable under a range of reaction conditions, giving highly reproducible activity for CO and CO2 hydrogenations. After preparation the catalysts have an initial none-steady state when C is progressively retained and activity rises to a maximum, then declines to a steady-state value.

HOMOGENEOUS CATALYSIS

Reduction of Nitroaromatics with Poly-(Vinylpyridine). Complexes of Palladium(II) and Platinum(II)


Pd(II) and Pt(II) anchored to 2- and 4-vinylpyridine polymers of different molecular weights were used for the H2 reduction of various nitroaromatics and benzaldehyde in ethanol at 50°C. Pd(II) complexes were far more effective than their Pt(II) analogues and the activity decreased with increasing polymer molecular weight. The nitroaromatics were selectively and almost completely reduced to anilines.

Aldehydes via Palladium Catalysed Reductive Carbonylation of Esters


A route to produce acetaldehyde from synthesis gas at low pressures is presented. The aldehydes and acetic acid are obtained in high selectivity from the Pd(OAc)2 catalysed reaction of esters and syngas. Results suggest that HRh(CO)(PMe3)2 under irradiation with the H2 reduction of various nitroaromatics and benzaldehyde in ethanol at 50°C. Pd(II) complexes were far more effective than their Pt(II) analogues and the activity decreased with increasing polymer molecular weight. The nitroaromatics were selectively and almost completely reduced to anilines.

Asymmetric Hydrogenation Catalyzed by Aminophosphine-Phosphinite Rhodium Complexes Derived from Natural Amino Alcohols


The asymmetric catalytic reduction with Rh aminophosphine-phosphinite complexes was studied to find the best conditions for complete conversion with the highest enantiomeric excess. A new aminophosphine-phosphinite ligand was synthesised, and the Rh complex, Rh((SS)-biprophosphos)1 was prepared. The stereodifferentiating ability of (1) in asymmetric hydrogenation was dramatically affected by the solvent. Cu(1) complexes of aminophosphine-phosphinite were used as a source of chiral ligands in asymmetric hydrogenation with Rh complexes.

Alcohol Electrooxidation Catalysts from Degraded Polyamionic Chelating Ligand Complexes. The Uncertainty for Catalyst Identification that Accompanies a Decomposing Catalytic System


The electro-oxidation of trans-Os(9'-CHBA-Et)-(py)2, where HxCHBA-Et = 1,2-bis(3,5-dichloro-2-hydroxybenzamido)ethane, in the presence of alcohols produced several catalytic systems for the electro-oxidation of alcohols. The Os complex underwent a multistep ligand oxidation/hydrolysis sequence. The degradation sequence and catalytic reactions were studied. Primary alcohols were condensed to aldehydes at high alcohol concentrations. Cyclohexanol was oxidised to cyclohexanone.
Synthesis of Ketones and Esters from Olefins, Carbon Monoxide and Alcohols by Using Ruthenium-Iodide Catalysts


Ru-iodide systems catalyse the reaction of olefins, CO and alcohols to give esters and ketones. Using PhI and CH₃I for the carbonylation of ethylene with methanol gives a mixture of methyl propionate and diethyl ketone, the ratio of which depends upon I:Ru ratio. Using ionic iodides, such as NaI, gives methyl diethyl ketone, the ratio of which depends upon I:Ru and CH₃I for the carbonylation of ethylene with methanol gives a mixture of methyl propionate and ketones. Using PhI and alcohols to give esters and ketones. Using PhI and alcohols to give esters and ketones.

Ruthenium Catalyzed Oxidation of Alkanes


A Ru catalyzed oxidation of alkanes in CCl₃-CH₂CN-water is described. The products are a mixture of tertiary alcohols and ketones. Norbornane and bicyclo[2.2.2.]octane are oxidised to the corresponding ketones, while adamantane is transformed to 1-adamantanol.

FUEL CELLS

Carbon-Based Electrodes Carrying Platinum-Group Bimetal Catalysts for Oxygen Reduction in Fuel Cells with Acidic or Alkaline Electrolytes


The electrochemical activity for O reduction in acid and alkaline electrolyte at C electrodes with Pt-Ru and Pt-Pd bimetal catalysts was measured as a function of electrode composition. Electrodes containing 4wt.%Pt+6wt.%Pd exhibit the maximum catalytic activity, which is also higher than that of the individual metal catalysts.

ELECTRICAL AND ELECTRONIC ENGINEERING

Platinum-Tungsten Electrodes for the Alkali Metal Thermoelectric Converter


High power, co-sputtered W-Pt electrodes for the alkali metal thermoelectric converter (AMTEC) are reported. The electrodes provide stable power densities of 0.35W/cm² over 90h. The electrodes have trilayer construction, consisting of an inner layer 0.1–0.2µm thick of W, an intermediate co-sputtered Pt-W layer 1–4µm thick and an outer Pt layer 0.1–0.2µm thick. Pt-Na interactions were studied.

Stable Silicon Solar Cells with High Temperature Survivability


By incorporating a thin layer of reactively sputtered TiN in the cell structure, stable solar cells could be produced which had no degradation in their electrical performance after heat treatments up to 600°C for 15 mins. The TiN is initially sputtered on the entire wafer area. The Ti, Pd and Ag were then applied, and cells were fabricated onto 100 Si. A junction ~0.34µm deep was formed on p-Si wafer by P-diffusion. The back metallisation was 1200Å Ti, 350Å Pd and 35kÅ Ag. The Pd acts as a barrier to O₂ to prevent TiN oxidation.

Long-Life High-Reliability Iridium-Coated M-Type Dispenser Cathode


A long-life Ir-coated M-type cathode has been developed for use in various electron tubes such as space travelling wave tubes. The Ir coating is 0.1–0.5µm thick and is produced by sputtering. The cathode, operating at a current density of 0.8A/cm² and 1000°C or below has a 150,000h life before the emission decreases by 4%, which far surpasses that of conventional Os-Ru-coated M-type cathodes. The long-life of this type of cathode is attributable to the Ir-W alloy layer (the ε₁₂ phase) formed by alloying the Ir coating with the W substrate.

Reactively Sputtered RuO₂ Diffusion Barriers


The thermal stability of reactively sputtered RuO₂ films was investigated as diffusion barriers in Si contact metallisations with an Al overlayer. Backscattering spectra of Si/RuO₂/Al samples and electrical measurements on shallow junction diodes with <Si>/TiSi₃/RuO₂/Al contacts show that RuO₂ films are effective diffusion barriers between Al and Si for 30 minutes annealing at 600°C. Thus RuO₂ is interesting for application as diffusion barriers in VLSI technology.

TEMPERATURE MEASUREMENT

Stability of Industrial Grade Platinum Resistance Thermometers in the Range 13–273K

J. VEPRÉK, Cryogenics, 1987, 27, (4), 202–204

A comparison is made between the stabilities of five two-lead industrial grade 100Ω Pt resistance thermometers used from 13-273K. The static stability was tested by storage over 3 months, and the dynamic stability was tested by cycling the thermometers over 5 and 50 cycles in the range between room temperature and liquid He temperatures.