of current literature on the platinum metals and their alloys

PROPERTIES

Interaction of O₂ with Pt(100). I. Equilibrium Measurements. II. Kinetics and Energetics

Two newly discovered phases on the Pt(100) surface produced by the adsorption of O have been investigated. One phase is associated with the O-saturated surface, where a very complex LEED pattern is seen; the other is observed at an average coverage of 0.44 ± 0.05 monolayers and gives rise to a (3 x 1) LEED pattern. Rutherford backscattering experiments indicate large Pt atom displacements. (19 Refs; 20 Refs.)

Inhibition of Acid Etching of Pt by Pre-exposure to Oxygen Plasma

The characteristics of Pt etching in aqua regia have been studied. Prior exposure to an O₂ plasma inhibited the dissolution of the Pt O₂, which is more abundant in the exposed than the unexposed Pt helps to form an inhibition layer, such as PtO₂, which prevents Cl⁻ attack. This inhibition layer appears to retard Pt etching effectively in Cl⁻ based etch solutions.

Isothermal Section of Phase Diagram of the Gold-Platinum-Rhodium System at 1000°C

Microstructural and spectroscopic studies were made of the character of phase equilibrium in the Au-Pt-Rh system at 1000°C. Boundaries for reciprocal solubility of components at 1000°C and for permeation of separation in liquid state in ternary systems are obtained.

Phase Diagrams of Platinum-Ruthenium-Rhodium, Platinum-Ruthenium-Palladium and Platinum-Ruthenium-Iridium Systems at 1400°C

Physico-chemical studies of ternary systems Pt-Ru-Rh, Pt-Ru-Pd and Pt-Ru-Ir were made and a region of phase equilibrium was established at 1400°C.

Thermal Diffusion of Pt in Silicon from Pt₅Si

Pt diffusion in n-type Si was measured using various spectroscopic techniques for deep energy levels. Pt acts as an acceptor which captures electrons. An energy level of 0.23 ± 0.02 eV was found for the trap.

In Situ Study of Film Stress and Kinetics of Platinum Silicide Formation on Silicon

In situ studies of the film stress and film reflectivity were performed when samples of Pt film on Si were sintered in an inert gas ambient. The reflectivity of the film dropped in two stages when the reaction between Pt and Si transformed the Pt film to a Pt₅Si film and then to a Pt₅Si film.

Pt-Ni Bilayers on n-Type Silicon. Metallurgical and Electrical Behaviour

Silicide formation in PtNi/Si and Ni/Pt/Si structures has been investigated. Pt and Ni films were deposited on <100> n-type Si. The reaction starts by formation of Ni₂Si or Pt₂Si where metal meets Si and proceeds until all the inner metal film is silicide. When held at ~300°C for 30 mins the outer metal diffuses through this silicide and builds up at the Si surface. When heated at 400°C for 30 mins NiSi forms and pushes out the Pt from the Si surface. Ni₂Si changes to NiSi and the structures become non-uniform. The Pt₂Si to Pt₅Si transformation at 500°C is accompanied by Pt transport through the NiSi.

The Investigation of Hydrogen Diffusion in Palladium by the Chemichromic Effect

The chemichromic effect in WO₃ was used to investigate H₂ diffusion in Pd by the differential cell method enabling visual control of the H₂ in, for instance, the walls of metallic pipelines for chemical transport to be checked for corrosion. Half of a thin Pd foil was covered with a 1μm film of WO₃ and the sample was fixed into a differential cell, with a laser beam and photoelectron multiplier. H₂ was generated and the change in potential recorded by Ag/AgCl electrodes. The reflected laser light recorded changes in optical density. The appearance of H₂ at the Pd/WO₃ interface causes a colourless → blue transition.
SAXS Study on Crystallisation of an Amorphous Pd$_{76}$Au$_6$Si$_{18}$ Alloy


The crystallisation behaviour of a Pd$_{76}$Au$_6$Si$_{18}$ alloy was studied by means of small angle X-ray scattering technique. The amorphous alloy crystallised to form MS-I phase with composition Pd$_{78}$Au$_{22}$ in the amorphous matrix, which later crystallised as MS-II. The remarkable increase of the scattering intensity corresponded to the growth of MS-I phase, the kinetics of which were found to be controlled by the diffusion mechanism. The interdiffusion constant was obtained from $D = 6.0 \times 10^{-13}$ exp$(-420$kJ/mol/RT)$\text{m}^2\text{s}^{-1}$.

Superconductivity and Atomic Ordering of Pd-Cu-H Solid Solutions


The superconducting transition temperature $T_C(n)$ dependences on the H: metal atomic ratio, n, for ordered and disordered Pd-Cu-H solutions containing 10–40 at.% Cu were studied. Pd-Cu samples were hydrogenated for 24h at $100 \leq T < 300^\circ\text{C}$ and $H_2$ pressures $\leq 8$ GPa. X-ray analyses of the alloys under various $H_2$ pressures were performed and the structural results are discussed. Replacing Pd by Cu resulted in no essential changes in the $T_C(n)$ dependence of the Pd-H $\gamma$-solutions for hydrogenation under conditions close to thermodynamic equilibrium.

Change of Electrical and Magnetic Properties of Pd-W Alloys during Hydrogenation


Studies were made of magnetic susceptibility and electroresistivity of hydrogenated solid solutions in Pd$_{100-x}$W$_x$ systems ($x = 0$, 1, 7 and 8) with $H < Pd \leq 0.5)$. Both the temperature coefficients of resistance and the susceptibility of Pd-W alloys decreased with the increase of W concentration. Magnetic susceptibility of the alloys decreases linearly with the increase of H concentration during hydrogenation.

High-Pressure Magnetic Susceptibility of the Intermediate Valence System EuPd$_2$Si$_2$


Studies of the pressure dependence of the magnetic susceptibility of the intermediate valence system EuPd$_2$Si$_2$ at 77–300K and 0–7kbar showed that the thermally induced valence transition became more gradual on application of pressure. The characteristic fluctuation temperature was pressure dependent.

Activation Volume for Hydrogen Diffusion in Palladium Hydride


A method for measuring activation volume for $H_2$ diffusion in Pd hydride, which consists of parallel measurements of Fick's diffusion for pure gaseous $H_2$ and for a mixture of $H_2$ and $H_2$ is reported. $H_2$ occupies the octahedral interstitial sites in the Pd lattice. The number of sites available is independent of the pressure and therefore the volume of activation measured relates to the kinetic part only. It involves the dilatation of the lattice during the intermediate step and the numerical value indicates that this dilatation is comparable with the partial molar volume of $H_2$. The activation volume in the system may be a function of the composition and the pressure (at a given temperature).

SQUID—Magnetometer Combined with Ion Implantation


A magnetron is presented which allows the in situ determination of the magnetic susceptibility of PdFe and InMn samples produced by low temperature ($T < 10K$) ion implantation into corresponding Pd and In foils. The superconducting transition temperature of InMn and the ferromagnetic transition temperature of PdFe samples are used in studies of the performance of the instrument. The operating principle is based on a superconducting quantum interference device (SQUID) detecting changes in the magnetisation as a function of the temperature of a sample positioned within a static magnetic field.

Thermal Stability of Crystalline and Amorphous Zr$_2$PdH$_3$


Differential scanning calorimetry and powder X-ray diffraction have been used to study the phase transitions and decompositions of the a-Zr$_2$Pd alloy, a-Zr$_2$PdH$_{1.9}$ and several crystalline c-Zr$_2$PdH$_{1.94}$ compositions. The H-free alloy undergoes low energy exothermic transitions that are very similar to crystallisation behaviour in other metallic glasses, however the lower exothermic peak may be due to the formation of a metastable phase. A strongly endothermic peak is observed for a-Zr$_2$PdH$_{1.9}$.

The Structure of [Er(1)$_{1-x}$Sn(1)$_x$] Er(2)$_4$Rh$_8$Sn(2)$_3$Sn(3)$_{12}$Sn(4)$_{2}$ A Ternary Reentrant Superconductor


The crystal structure of phase II of the above compound, which has re-entrant superconductivity ($T_C = 0.97$ and $T_M = 0.57K$) has been solved, and refined from single crystal X-ray diffraction data. The space group is $I4_1/acd$, with eight formulae per unit cell of dimensions $a = 13.73$ and $c = 27.42\text{A}$. 

*Platinum Metals Rev.*, 1984, 28, (3) 133
Phase Diagram and High-Resolution Photoemission Study of the Superconducting and Magnetic Pseudo-ternary Body-Centered-Tetragonal Ho(Rh$_{1-x}$Ru$_x$)$_3$B$_4$ System


The phase diagram for b.c.t. superconducting pseudoternary system Ho(Rh$_{1-x}$Ru$_x$)$_3$B$_4$ (0.07 $\leq x \leq 1$) is reported for temperatures above 1.3K, showing an abrupt drop in $T_c$ near the critical concentration $x_c \approx 0.40$, characteristic for this class of compound. To clarify the origin of this phenomenon, high resolution photoemission spectra have been taken of samples with $x = 0.07, 0.37$ and 0.90. The analysis of the valence band data near $x$ relative to the transition metal d-electron structure.

CRYSTAL STRUCTURE OF NEW SUPERCONDUCTING MATERIALS LAIrSi$_3$ AND LARhSi$_3$. STRUCTURAL RELATION BETWEEN LARh$_2$Si$_2$, LA$_2$Rh$_3$Si$_5$ AND LARhSi$_3$


Two new superconducting silicides LARhSi$_3$ and LAIrSi$_3$ have been prepared by arc melting the elements and annealing for ten days at 900°C. A single crystal study shows these materials to have tetragonal symmetry and to be isostructural with BaPtSi$_3$. Their $T_c = 1.9-2.7\,K$ depends strongly on stoichiometry and thermal treatment. The structures are compared to those of superconducting LAIr$_2$Si$_2$, La$_2$Rh$_3$Si$_5$, and LARh$_3$Si$_5$. The superconductivity seems to be related to the presence of similar co-ordination polyhedra for Rh or Ir and Si atoms.

THICK OSMIUM TARGETS


Os targets 20-40 mg/cm$^2$ sandwiched in graphite by centrifuging and hot-pressing in Ar have been prepared for electron scattering experiments. The elastic and inelastic electron scattering cross sections could then be targeted. The target needs to endure temperatures up to 500°C for ~100h without showing chemical or mechanical change.

MOSSBAUER EVIDENCE FOR RU(IV) AND RU(II) IN TiO$_2$


The Mössbauer absorption of the 89.4 keV line of $^{95}$Ru has been measured at 4.2K for samples of Ru in TiO$_2$ and in TiO$_2$ doped with Ta. It is deduced that Ru replaces Ti substitutionally in TiO$_2$ as Ru(IV) and that no delocalisation of the four Ru(IV) 4d electrons occurs. If the donor Ta is added to the system, the Ru(II) ion is formed, showing that Ru behaves as an acceptor in TiO$_2$.

CHEMICAL COMPOUNDS

INTERACTION OF RHODIUM (III) WITH ANTHRANILIC ACID


Chemical, thermogravimetric and spectroscopic studies of the interaction of Rh(III) with anthranilic acid showed, for the first time, formation of complex compounds $[\text{Rh(C}_2\text{H}_5\text{O}_2\text{N}_2]\text{Cl}_2\text{H}_2\text{O}]$ and $[\text{Rh(C}_2\text{H}_3\text{O}_2\text{N}_2]\text{H}_2\text{O}]$. The prepared compounds are not soluble in H$_2$O, ethanol, acetone, etc., but $[\text{Rh(C}_2\text{H}_3\text{O}_2\text{N}_2]\text{H}]\text{O}$ dissolved in HNO$_3$.

ELECTROCHEMISTRY

ELECTROCATALYSIS BY ELECTRODEPOSITED SPHERICAL Pt MICROPARTICLES DISPERSED IN A POLYMERIC FILM ELECTRODE


Electrochemical methods for the dispersion of Pt microparticles at microgram levels in polymeric matrices of poly(vinylacetic acid) glassy C electrodes, Pt-PVAA/GC are described. Cyclic voltammetry and single and double potential step electrolysis were applied to form Pt$^0$ particles on PVAA/GC from an acidic hexachloroplatinate solution. The Pt particles were randomly dispersed in the polymer and were spherically shaped. This electrode had high activity toward the electrochemical generation of H$_2$ and reduction of O$_2$. The electrodes have a large surface area at low loading levels, high catalytic efficiency and excellent stability.

METHANOL ELECTROOXIDATION ON PLATINUM DIRECTLY BONDED TO A SOLID POLYMER ELECTROLYTE MEMBRANE


Methanol electrooxidation was performed in perchloric acid solution on Pt directly bonded to a solid polymer electrolyte (SPE) membrane. After an initial sharp deactivation in a short time at the polarisation, the Pt-SPE was found to retain high activity for a long duration, whereas the platinised Pt showed a considerable decrease in activity during the polarisation. A surface mediator action of Pt$^+$ and Pt$^{2+}$ was essential for the durability of a high catalytic activity.

ADSORPTION AND OXIDATION OF PHENOL ON PLATINUM AND GRAPHITE ANODES


Studies were made of the anodic behaviour of phenol on Pt and graphite anodes under potentiodynamic and galvanostatic regimes and the dependence of the values of phenol adsorption on the potential in acid, neutral and alkali media was established. The reaction order for the oxidation of phenol was $1$ for phenol concentration of $1.10^{-3}$-$1.10^{-4}$M at pH $\leq 7$. 

Platinum Metals Rev., 1984, 28, (3) 134
Cyclic Voltammetric Investigation of Platinum-Rhodium Alloys


Cyclic voltammetric studies were performed on Pt-Rh alloys in a wide range of pH value solutions. The potential of the O desorption peak on the voltammogram was found to vary linearly with alloy composition. At lower or higher pH values, preferential dissolution of Rh results in Pt concentration at the alloy surface. At pH 13.0, a hydrated Rh oxide layer develops on the electrode, and changes in the stoichiometry of this oxide give rise to anodic and cathodic current peaks.

Study of the Composition of the Surface of Platinum, Rhodium and Their Alloys after Anodic Polarisation at High Potentials by X-Ray Electron and Auger Spectroscopy


X-ray electron and Auger spectroscopy studies of the surface of Pt, Rh and 10–20wt.% Rh-Pt alloys after anodic polarisation at high potentials showed a PtO$_2$-H$_2$O oxide, depending on the polarisation and concentration of solution on the surface.

Thermochromatographic Behaviour of Oxygen-Containing Iridium and Platinum Compounds in Ultra Small Quantities

V. P. DOMANOVI, B. AIKHLEV and I. ZVARA Radiokhimiya, 1984, 26, (1), 66–76

Radioactive Ir and Pt compounds were prepared in air at 725 ± 25°C by isolation in a SiO$_2$ thermochromatographic column. Both elements formed two adsorption zones and adsorption zone centres were at 265 ± 20°C and 175 ± 20°C for Ir and at 280 ± 20°C and 55 ± 15°C for Pt. It is suggested that MeO$_3$ oxides are adsorbed at the higher temperature zones and compounds are fixed to oxides at the lower temperature zone.

Structure and Electrical Properties of Pd-Ag-H Alloys Synthesised at High Hydrogen Pressures


Studies of the behaviour of electrical resistivity, composition and crystal structure of solid hydrogen solutions Pd-Ag-H were performed on Pd-Ag alloys containing 0, 20, 50, 78 and 100 at.% Ag prepared under a H$_2$ pressure of 67 kbar at up to 350°C. New phase conversions in the systems Pd$_{10}$Ag$_{90}$-H and Pd$_{2}$Ag$_{78}$-H were obtained. The results showed that the conversion in the Pd$_{10}$Ag$_{90}$-H system occurred by atomic ordering in the metallic matrix of its solution.

Electrochemistry in Liquid Sulfur Dioxide. 5. Oxidation of Bipyrindine and Phenanthroline Complexes of Osmium, Ruthenium, and Iron


The electrochemical oxidation of bipyrindine and phenanthroline complexes of Ru, Os and Fe in liquid SO$_2$ was investigated by cyclic voltammetry and coulometry. Os(bpy)$_2$' and Os(phen)$_2$' undergo two successive one-electron oxidations to form stable 3+ and 4+ species. Fe(phen)$_2$' and Ru(phen)$_2$' when oxidised to the 4+ form, produce an electroactive layer on the electrode surface.

Hydrogenation of Acetylene and Ethylene Alcohols in the Liquid Phase on Palladium with Nickel and Ruthenium


Studies of the hydrogenation of a number of unsaturated aliphatic alcohols in the liquid phase over H$_2$ permeable Ru-Ni membrane catalyst showed that most active and selective were membrane catalysts made of 6wt.% Ru-Ni alloy. Capacity of the surface of the membrane catalyst during hydrogenation of acetylene alcohol was almost 100 times higher than those of supported and skeletal catalysts.

Novel Effect of Neighboring Groups on the Quenching of the Excited State of a Polymer-Pendant Ru(bpy)$_2$' by Methylviologen


A polymer-pendant tri(2,2'-bipyridine)Ru(II) complex was prepared from the copolymer of 4-methyl-4'-vinyl-2,2'-bipyridine and acrylic acid, and the quenching of its excited state by methylviologen was studied. The quenching rate showed a great pH dependence and was an order of magnitude larger than that of the monomeric Ru[bpy]$_2$' in alkaline medium.

PHOTOCONVERSION

Photolysis of Water over Pt/TiO$_2$ Catalysts


The quantum efficiency was measured for the photolysis of gaseous H$_2$O over NaOH-coated Pt/TiO$_2$ catalysts and was maximised by selection of crystal structure and source of TiO$_2$. The catalysts could be activated by illuminating them in a wet state and then in a dry state in the presence of gaseous water. A maximum quantum efficiency of 17% occurred when MCB anatase was used.
Resin-Immobilized Photocatalyst for Visible Light-Induced Hydrogen Evolution


Resin-immobilised colloidal Pt catalysts were prepared by refluxing an anion-exchange resin and chelate resin hexachloroplatinate complexes in ethanol-water. The catalysts were active for visible light-induced H₂ evolution in an EDTA/Ru(bpy)³⁺/MV²⁻ aqueous solution. Ternary photocatalysts were prepared by further immobilisation of Ru(bpy)³⁺ and MV²⁻ on the chelate resin-immobilised Pt catalyst by electrostatic means. Irradiation of this ternary photocatalyst in an aqueous solution of disodium EDTA resulted in H₂ evolution.

Photocatalyzed Hydroxylation of Benzene in the Presence of Semiconductors


TiO₂ was loaded with Pt, Pd, Cu, RuO₂, PdO₂, IrO₂, RhO₂, and PtO₂ to try to enhance the yield of phenol during the photocatalytic hydroxylation of benzene and other aromatic compounds. Benzene hydroxylation was conducted at 30°C under 1 atm O₂ by irradiation with a 500W Xe lamp. The above catalysts had quite high relative activities ranging from 3.0 to 4.3 when used in H₂SO₄-added solution. The highest relative activity (4.8) was obtained with the RuO₂/TiO₂ catalyst in the H₂SO₄-acidified solution containing 4-methyl-2-pentanone.

Hydrogen-Evolving Solar Cells

A. HELLER, Science, 1984, 223, (4641), 1141–1148

A review is given of H₂-evolving photochemical cells with semiconductor electrodes where sunlight is directly converted to chemical energy. In H₂-evolving photoelectrodes, electron-hole pairs photogenerated in the semiconductor are separated at electrical microcontacts between the semiconductor and group VIII metal, including Pt group metal, catalyst islands. Their Gibbs free energy efficiency solar-to-hydrogen conversion of 13.3% approaches the solar-to-electrical conversion efficiency of the best p-n function cells. (123 Refs.)

Luminescence and Triplet-Triplet Absorption Spectra of Rhodium (III) Porphyrins


Photophysical studies of four Rh(III) porphyrins RhTPPS(H₂O)³⁺, RhTPP(C)(L), RhOEP(C)(L), and RhMesoPME(C)(L) showed them to be characterised by a moderate phosphorescence (µ > 10⁻²) and a very weak fluorescence (µ < 5 x 10⁻⁶) in solution at room temperature. TPP derivatives also have moderately intense triplet-triplet absorption.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrochemical Deposition of Conducting Ruthenium Oxide Films from Solution


A new method of electrodeposition conducting hydrated Ru oxide films from stable aqueous solutions containing a Ru(II) complex is described. The films slowly dissolve in aqueous electrolyte upon potential cycling, yet appear to be catalytic during water oxidation.

LABORATORY APPARATUS AND TECHNIQUE

Sputtered Platinum Films on Colloidal Gold Particles: A Calibration Specimen for Quartz Film Thickness Monitors


A method for calibrating quartz crystal monitors is described, which makes use of 20nm Pt sputtered colloidal Au particles. The actual thickness is measured on TEMs of Au particles protruding from the edge of fractured, rolled up, C films.

Use of Arsenic Resonance Line of 197.2nm and Matrix Modification for Determination of Arsenic in Environmental Samples by Graphite Furnace Atomic Absorption Spectrometry Using Palladium as a Matrix Modifier


An atomic absorption spectrometer with a graphite furnace was used to measure As absorbance at 197.2nm. The As-containing river sediment solutions were injected into the heated graphite furnace along with the same volume of aqueous Pd solution. When a L’vov platform with matrix modification by Pd was used the tolerable charring temperature for As was raised to 1500°C, and the peak absorbance sensitivity increased. This can be used with biological samples to determine As levels.

Impregnation of Biological Material by ZnI₂-OsO₄, KI-OsO₄, and NaI-OsO₄ Mixtures for Electron Microscopic Observations: Chemical Interpretation of the Reaction


Alkaline iodide-OsO₄ mixtures were used in the electron microscopic study of plant cells and gave better results in the preservation of the cell structure, in contrast to the cell structure observed when ZnI₂-OsO₄ mixtures are used.
Osmium Tetroxide: A New Probe for Site-Specific Distortions in Supercoiled DNAs


OsO₄ has been shown by gel electrophoresis to bind to supercoiled DNA, to induce its relaxation without nicking, and to form single-stranded regions at specific sites which are recognisable by nuclease S1 and visualised as a denaturation “bubble” in the electron microscope. The amount of Os bound to the DNA increases with the extent of DNA relaxation. The “bubble” remains stable, yielding the possibility of site mapping. Thus Os may represent another probe for local distortions in the DNA structure.

Spectrophotometric Determination of Carbon Monoxide with Ruthenium (II) Octaethylporphyrin


A novel spectrophotometric method for estimating CO at levels from 2–250 ppm is presented. It is based on the formation of a carbonyl complex of Ru(II) octaethylporphyrin and measurement of the difference in absorbance at 393.5nm between this complex and the porphyrin reagent. O₂ and N₂ do not interfere and up to 500 ppm of SO₂ and ~1500 ppm CO₂ can be tolerated and determine CO at the 4–10 ppm levels. H₂S interferes and must be eliminated before determination.

HETEROGENEOUS CATALYSIS

Studies of the Deactivation Processes of Platinum Catalysts during Burning up of Exhaust Gases in the Internal Combustion Engine


Studies of the deactivation processes were performed on 1 wt.% Pt/Al₂O₃ catalyst prepared by saturation with H₂PtCl₆ followed by drying and reduction in H₂ at 850–900°C. The results showed that continuous exposure of Pt catalyst to exhaust gases in the combustion engine leads both to the sintering of the active Pt particles and to sulphating of the support, causing change in its phase state.

Optimization of an n-Pentane Isomerisation Reactor


The optimisation of the operating variables in a pentane isomerisation reactor was studied during isomerisation on Pt/Al₂O₃ reforming catalyst where there is the problem of catalyst decay due to the carbonaceous deposits. The improvement obtained with optimal operation ranges from an increase of 7% to an increase of 36% in the production rates.

I. Kinetics of Catalytic Hydrocracking of n-Decane, n-Undecane and n-Dodecane on Platinum/Alumina Catalyst. II. Composition of the Products of Hydrocracking of n-Decane, n-Undecane and n-Dodecane on Platinum/Alumina Catalyst


Studies of the kinetics of catalytic hydrocracking and the composition of hydrocracking products were performed during hydrocracking of n-decane, n-undecane and n-dodecane over Pt/Al₂O₃ catalyst at 450°C. Relative constants of the rate of isomerisation and cracking reactions of the initial organic compounds are reported.

Radial Profiles in Pt/Al₂O₃, Re/Al₂O₃ and Pt-Re/Al₂O₃


The competitive effect of HCI on H₂PtCl₆ and/or HReO₄ deposition on γ-Al₂O₃ was studied by determining HCl, H₂PtCl₆ and HReO₄ adsorption isotherms and by obtaining their radial distribution profiles. The results show that the three components compete for the same surface sites and the number of occupied surface sites per adsorbed molecule of HCl, H₂PtCl₆, and H₂PtCl₆ is 1, 2 and 4, respectively. The adsorbate-support interactions were strong and the shape of the radial profiles indicated that the H₂PtCl₆, HCl and HReO₄ adsorption was more rapid than the interparticle diffusion.

Aromatisation of n-Heptane on Platinum Catalysts


Studies of the effect of thermal treatment on the activity and selectivity of Pt containing zeolite, PtKL and PtNaX type catalysts were performed during dehydrocyclisation of n-heptane. The most active and selective were catalysts thermally treated in air, then in an Ar atmosphere and then reduced in H₂. It is suggested that the inert gas removes adsorbed oxygen in zeolites thus inhibiting the local thermal effects.

Valence State Platinum and Catalytic Activity of Palladium/Support Catalysts


Studies were made of Pt supported catalysts prepared by impregnation of γ-Al₂O₃, MgO and SiO₂ with anionic and cationic Pt complexes, (NH₄)₂PtCl₆, (NH₄)₂PtCl₆ and Pt(NH₄)₂Cl₂. The nature of the initial Pt complex determines the catalytic properties of the catalysts.
Kinetics of Isomerisation of n-Pentane on Aluminum-Platinum-Lead Catalyst

Studies of the kinetics of isomerisation of n-pentane were made on Pt-Pb/Al2O3 catalysts prepared by saturation of a 0.55% Pt–3.5% F/Al2O3 catalyst with Pb acetate, dried in air at 120°C for 4 h and reduced in H2 at 450°C for 6 h. The Pt-Pb/Al2O3 catalyst contained 2.5% Pb and studies were performed at 400–480°C.

Selectivity of Hydrogenation in an Alkyne-Alkene System on Palladium Catalysts Modified with Inorganic Salts

Studies were made of the competitive catalytic hydrogenation of 2-octyne and 1-heptene in methanol over 3% Pd/activated C and Pt black catalysts modified with NH4Cl, KCl, K23CO3 and CaCO3. The rates of hydrogenation of the two substrates and the rate of isomerisation of 1-heptene were measured. The effect of inorganic salts on the activity and selectivity of the catalysts is discussed.

Adsorption and Catalytic Behaviour of Palladium Dispersed on Rare Earth Oxides

Studies of adsorption of H2, CO and O2 and of catalytic activity of Pd dispersed on La2O3, CeO2, Pr6O11, Nd2O3, Sm2O3 and Eu2O3 showed that large fractions of the Pd surface were blocked by the oxide support. Turnover frequencies for both CH4 and CO2 formation varied by an order of magnitude and for both reactions activity maxima at Pr or Nd occurred when plotted vs. atomic number. Mainly oxygenate formations occurred in these catalysts.

Enhanced Activity of Pd/TiO2 Catalysts for the CO/H2 Reaction in the Absence of Metal-Support Interactions (SMSI)

The dispersion of the Pd in Pd/TiO2 and Pd/SiO2 catalysts was studied during H2 and CO adsorption, and catalytic activity was determined for the hydrogenolysis of ethane and for the CO/H2 reaction. It is found that the Pd/SiO2 and Pd/TiO2 catalysts reduced at low temperature, show normal chemisorption and catalytic properties. For the CO/H2 reaction it is found that all the Pd/TiO2 catalysts have enhanced activity, irrespective of whether or not SMSIs are operative. It is concluded that the high activity of TiO2-supported catalysis in the CO/H2 reaction is not due to SMSI. It is proposed that the role of the support is to create new active sites at the interface between metal and support.

Catalytic Chemistry of Oxide Bound Transition Metal Complexes

New electrocatalytic oxide-bound catalysts were investigated using high oxidation state organometallic compounds on high surface area oxides. Systems investigated were tris(allyl)Ru on Al2O3 or zeolite X and bis(allyl) Pd on zeolite X, zeolite Y and SiO2. Treatment of the supported allyl Pd species with H2 resulted in Pd metal formation. Methanol carbylation, methane chlorination and heteroatom oxide reduction using CO as reducing agent were tested. Pd complexes were better than Rh complexes for the last reaction. All the Pd complexes reacted quickly with Cl2 to give similar species. The selectivity in product formation suggested that electrophilic attack by the Pd complex on an alkane was the key activating interaction.

Spectroscopic Studies on Adsorbed Metal Carbonyls. Part 1. Interaction of [Rh1(CO)12] and [Rh6(CO)16] with Alumina, Silica and Titania

Spectroscopic studies of the interaction of [Rh6(CO)16] (1) and [Rh4(CO)18] (2) with Al2O3, TiO2, TiO2 and SiO2 using isotopic substitution and spectrum simulation techniques showed conversion of (1) into (2) on Al2O3 and TiO2. Isolated Rh(CO)2 sites were considered to exist on all three oxides after oxidative fragmentation of (1) or (2).

Rhodium(I) and Ruthenium(II) Complexes of Sulphonated Triphenylphosphine Immobilised on Ion-Exchange Materials

Complexes of sulphonated triphenylphosphine with Ru(II) and Rh(I) were immobilised on strongly basic anion exchanges. The heterogenised complexes were successfully applied to the hydrogenation of various olefins in solution and in the gas phase at 60°C and 120°C, respectively, and at 0.1 MPa total pressure. The results suggest that the anchored RuCl3(m-SP3)2 exerts its catalytic effect via the same molecular pathway as in homogeneous solutions.

Stoichiometric and Catalytic Homologation of Olefins on the Fischer-Tropsch Catalysts Fe/SiO2, Ru/SiO2, Os/SiO2 and Rh/SiO2. Mechanistic Implication in the Mode of C-C Bond Formation

With the above catalysts CnH2n olefins can be stoichiometrically or catalytically (under H2) homologated to higher and lower olefins, and there is evidence that the mode of the C-C bond formation is the same in Fischer-Tropsch and in homologation.

Platinum Metals Rev., 1984, 28, (3) 138
Chemisorption and Catalysis. I. Chemisorption of Carbon Monoxide and of Oxygen Supported Osmium Clusters Derived from Os₆(CO)₁₈ and from Os₈(CO)₁₈


Studies of CO and O₂ chemisorption on the high-catalysts as the Si₃ chemisorption was found for the ion-exchanged O₃(CO)₁₈ impregnated on SiO₂, Al₂O₃ and TiO₂ were performed at 293K. It is suggested that CO and O₂ each adsorb molecularly in both the primary and the secondary regions. In the primary region CO adsorption occurs at Os sites on the cluster whereas in the secondary region it occurs at ligand-carbon bonded to Os.

Hydrogen Chemisorption Suppression in Ru-Zeolite Catalysts


Ru catalysts prepared using Na-X, Na-Y, K-L and Na-mordenite as supports were characterised by H₂ and CO chemisorption. Significant suppression of H₂ chemisorption was found for the ion-exchanged catalysts as the Si : Al ratio increased. Chemical interactions between the metal and support are the main cause of the H chemisorption suppression.

Catalytic Oxidation of Carbon Monoxide over Ru/SiO₂. An In Situ Infrared and Kinetic Study


A spectroscopic study of the partial deactivation of a series of Ru/SiO₂ catalysts during the CO oxidation reaction showed that partial deactivation occurs as the result of the formation of a more tightly bound O₂ species, perhaps lattice O₂ which reacts more slowly with adsorbed CO than O₂ in the reactant gas mixture. The results of a temperature-programmed reduction study showed that the CO species responsible for the CO adsorption band at 2910/cm react preferentially with H₂ to form CH₄.

Quantitative Studies on the Paramagnetic Behavior of RuO₂–TiO₂ (Anatase) Powders Catalytically Active in Water Oxidation


The paramagnetic behaviour of RuO₂ islands on TiO₂ was studied since the paramagnetic properties of surfaces have a profound effect on chemical reactions. In the reaction 4Ce⁴⁺ + H₂O = 4Ce³⁺ + 4H⁺ + O₂, catalysed by RuO₂, the paramagnetic species are responsible for the catalysis since the observed reaction goes through isolated RuO₂ islands on the catalyst surface. A 6% RuO₂/TiO₂ loading represented the minimum concentration for maximum contact.

HOMOGENEOUS CATALYSIS

Application of Ultratine Metal Particles to Organic Syntheses


The application of ultratine metal particles to organic syntheses are reviewed. Ultratine particles of Pt, Pd, Rh, Ru, Cu and others show high catalytic activity and selectivity in various organic syntheses. Catalytic reactions involve: hydrogenation of C = C double bonds, nitro groups and aromatic rings; hydrogenation of dienes to the corresponding mono-enones; hydrogenolysis of cystine to cysteine; hydration of acrylonitrile to acrylamide, and hydration of C = C double bond followed by dehydrogenation of the alcohol. (51 Refs.)

Palladium Compounds with Some Azocompounds and Their Catalytic Properties


Studies were made of the reaction of K₂PdCl₄ with azocompounds in hydro-alcoholic media and Pd : azocompound molar ratio of 1 : 1 using ortho-substituted azocompounds of 4-(2-pyridylazo)reocryl, 1-(2-pyridylazo)-2-naphthol and 1-(2-naphtholazo)-4-sulphobenzene. The Pd(II) complexes yielded by the reaction were highly stable and catalytically active during hydrogenation of nitrobenzene under mild conditions.

Synthesis of Aryltrimethylnitins by the Reaction of Me₃SnSnMe₃ with ArL Catalysed by “Ligandless” Palladium


The dependence of the nature of various solvents on the final product yield made during the reaction of Me₃Sn₂ with 2,4-dinitrobenzene in the presence of I using ortho-substituted azocompounds of 4-(2-pyridylazo)reocryl, 1-(2-pyridylazo)-2-naphthol and 1-(2-naphtholazo)-4-sulphobenzene. The Pd(II) complexes yielded by the reaction were highly stable and catalytically active during hydrogenation of nitrobenzene under mild conditions.

Homogeneous Asymmetric Catalysis by Means of Chiral Rhodium Complexes


Synthetic and mechanistic aspects of homogeneous asymmetric hydrogenation and hydroxylation catalysed by Rh complexes with chiral phosphine ligands are described. A sample of the reactions discussed include: asymmetric reduction of α, β-enones and keto esters via hydroxylvlation, asymmetric reduction of β-keto esters and ketopantoyl lactone by hydrogenation, remarkable effects of H₂ pressure on the stereoselectivity and efficiency of typical chiral diphosphine ligands. (45 Refs.)
Hydroformylation of Unsaturated Fatty Acids


A review is given of hydroformylation of unsaturated fatty materials in the presence of Rh catalyst. With Rh, the reaction can be carried out at pressure as low as 200 psi, at double bond location in a polyunsaturated fatty acid and in high yield and conversion. The reconstituted catalyst is more active than the original catalyst and can be recycled. (74 Refs.)

Chemistry of Continuous Rhodium Hydroformylation


Novel alkylidiphenylphosphine based Rh complex catalysts were found to increase thermal and operational stability over known commercial Rh complex systems based on triphenylphosphine, during continuous t-olefin hydroformylation. In the product flash-off mode of the commercial process, the reconstituted catalyst is more active than the original catalyst and can be recycled. (74 Refs.)

Homogeneous Hydrogenation of α, β-Unsaturated Aldehydes Catalyzed by Ruthenium and Osmium Complexes


The Ru and Os hydridophosphine and carboxylato-phosphine complexes were found to be effective catalysts for the homogeneous hydrogenation of α, β-ununsaturated aldehydes. The activity and selectivity of the reaction may be controlled by suitable choice of reaction conditions and by small variations in the catalyst structure. High selectivity C=C bond reduction is achieved with Ru complexes, while for the more difficult selective reduction of the C≡C bond, the use of Os complexes is more suitable.

Ruthenium Complexes of 1,3-Bis(2-pyridylimino)isoindolines as Alcohol Oxidation Catalysts


The complex (1,3-bis(4-methyl-2-pyridylimino)isoindoline) trichlororuthenium(III) catalyses the autoxidation and electrochemical oxidation of alcohols in basic alcoholic solutions. Primary and secondary alcohols are oxidised, with the principal products being aldehydes and ketones. The best results were obtained with Na ethoxide as base. Turnover numbers of 10–30 per day were observed in 1 atm O₂ at ambient temperatures. But >200 turnovers were observed in the oxidation of ethanol at ambient temperature with no loss of catalytic activity.

FUEL CELLS

Electrocatalytic Oxidation of CO in a CO/O₂ Fuel Cell

J. WU and C. P. KUBIAK, Book of Abstracts, 187 ACS Natl. Meeting, St. Louis, Missouri, Apr. 8–13, 1984, Division of Inorganic Chemistry, Abstract No. 131

A laboratory scale fuel cell was constructed with 2 mM [Rh(III)Br₂] as anodic electrocatalyst which oxidised CO to CO₂ at glassy C electrodes with a turnover of 15.1, and produced 1.211 mmol CO₂ and 262°C of electric charge.

CHEMICAL TECHNOLOGY

Ruthenium Tetroxide—A Reagent with the Potential for the Study of Oxygen Functionalities in Coal


The oxidation of coals by RuO₄ gives a variety of products. Among these are the esters formed by the oxidation of ether linkages. Infrared spectra were taken of the neat coals, their oxidation products and two ether soluble fractions. These initial observations justify further studies on the behaviour of RuO₄ towards known organic substrates having typical coal (oxygen) functionalities.
Chemical Vapor Deposition of Ruthenium
M. E. GROSS, L. E. PAPA, M. L. GREEN and K. J. SCHNOES,
Extended Abstracts, 84-1, Spring Meeting, Cincinnati, Ohio, May 6–11, 1984, Abstract No. 101, 149–150
A low temperature organometallic chemical vapour deposition process for Ru is described. Three organometallic Ru compounds were tested as sources for chemical deposition of the metal on Si and SiO2 substrates at low temperature and pressure. The decomposition of Ru(CO)12 in vacuum produced the most uniform metallic films. During runs at temperatures 250–450°C, the film thickness and grain sizes decreased. Resistivity values of the Ru films increased with increasing deposition temperature. Samples deposited at 250–300°C compare favourably with pure Ru. Ru from Ru(CO)12 deposited on a device wafer at 300°C gave excellent conformal step coverage. This Ru was subsequently oxidised to RuO2.

NEW PATENTS
METALS AND ALLOYS
Silver-Plastic Moulded Body
JOHNSON MATTHEY P.L.C. U.S. Patent 4,410,475
Articles such as jewellery may be fabricated by moulding under pressure and at elevated temperature a mixture of metallic particles and thermostatic particles. The metals may be platinum group metals, Au, Ag and base metals such as Ni, Cu, Zn or Sn.

Amorphous Magnetic Alloy
T.D.K. ELECTRONICS CO. LTD. U.S. Patent 4,416,709
An alloy highly resistant to corrosion for use in the core of a magnetic head has a composition of formula (Fe1-xCoxNi1-yMoxCr1-zXy, where M is Ru alone or a mixture with Pt, Pd, Ir and/or Rh, M' is a transition metal other than those in the formula, X is a vitrification element, p + q + r = 100%, a + b + c + d + e = 100% and e is 20–26%. A typical alloy is (Fe0.4Co0.4)704Ru2Cr(Si10B80)13.05Ti.

CHEMICAL COMPOUNDS
Amorphous Zirconium Phosphosilicate
DAIICHI KIGENSO KAGAKU KOGYO CO. LTD. European Appl. 105,128
New ion exchange agents of increased resistance have the formula Zr[PO4]2/3(SiO2)n.H2O or M1/2Zr[PO4]2/3(SiO2)n.H2O where I is the valence of the cation of the matrix, y is 0.02–2, z is 0.05–16.00 and n' is 0–100. The cation may be derived from Groups IA, IB, IIA, IIB, IIIA, IIIB, VA, VIA, VIIA and VIII. Platinum group metals, Ag and the lanthanides are among the cations proposed.

ELECTRICAL AND ELECTRONIC ENGINEERING
A Hydrogen Sensitive Pd-MOS Structure Working over a Wide Pressure Range
A Pd-MOS structure, made of p-doped Si wafer, thermally oxidised to an oxide thickness ~100nm, with Pd evaporated to a thickness of ~100nm, has been developed. It is sensitive to H2 both in air at atmospheric pressures and in UHV. It is sensitive to H2 pressure from 5 x 10–11 to 2 Torr. It has applications in studying catalytic reactions involving H on metal surfaces, leak detection on underground telephone cables and water tubing, and monitoring H in breath for medical diagnosis. Under different experimental conditions the H pressure range could be extended by at least two orders of magnitude.

Palladium and Platinum Sulphur Complexes
NEW PATENTS
METALS AND ALLOYS
Silver-Plastic Moulded Body
JOHNSON MATTHEY P.L.C. U.S. Patent 4,410,475
Articles such as jewellery may be fabricated by moulding under pressure and at elevated temperature a mixture of metallic particles and thermostatic particles. The metals may be platinum group metals, Au, Ag and base metals such as Ni, Cu, Zn or Sn.

Amorphous Magnetic Alloy
T.D.K. ELECTRONICS CO. LTD. U.S. Patent 4,416,709
An alloy highly resistant to corrosion for use in the core of a magnetic head has a composition of formula (Fe1-xCoxNi1-yMoxCr1-zXy, where M is Ru alone or a mixture with Pt, Pd, Ir and/or Rh, M' is a transition metal other than those in the formula, X is a vitrification element, p + q + r = 100%, a + b + c + d + e = 100% and e is 20–26%. A typical alloy is (Fe0.4Co0.4)704Ru2Cr(Si10B80)13.05Ti.

CHEMICAL COMPOUNDS
Amorphous Zirconium Phosphosilicate
DAIICHI KIGENSO KAGAKU KOGYO CO. LTD. European Appl. 105,128
New ion exchange agents of increased resistance have the formula Zr[PO4]2/3(SiO2)n.H2O or M1/2Zr[PO4]2/3(SiO2)n.H2O where I is the valence of the cation of the matrix, y is 0.02–2, z is 0.05–16.00 and n' is 0–100. The cation may be derived from Groups IA, IB, IIA, IIB, IIIA, IIIB, VA, VIA, VIIA and VIII. Platinum group metals, Ag and the lanthanides are among the cations proposed.

ELECTRICAL AND ELECTRONIC ENGINEERING
A Hydrogen Sensitive Pd-MOS Structure Working over a Wide Pressure Range
A Pd-MOS structure, made of p-doped Si wafer, thermally oxidised to an oxide thickness ~100nm, with Pd evaporated to a thickness of ~100nm, has been developed. It is sensitive to H2 both in air at atmospheric pressures and in UHV. It is sensitive to H2 pressure from 5 x 10–11 to 2 Torr. It has applications in studying catalytic reactions involving H on metal surfaces, leak detection on underground telephone cables and water tubing, and monitoring H in breath for medical diagnosis. Under different experimental conditions the H pressure range could be extended by at least two orders of magnitude.

Palladium and Platinum Sulphur Complexes
NEW PATENTS
METALS AND ALLOYS
Silver-Plastic Moulded Body
JOHNSON MATTHEY P.L.C. U.S. Patent 4,410,475
Articles such as jewellery may be fabricated by moulding under pressure and at elevated temperature a mixture of metallic particles and thermostatic particles. The metals may be platinum group metals, Au, Ag and base metals such as Ni, Cu, Zn or Sn.

Amorphous Magnetic Alloy
T.D.K. ELECTRONICS CO. LTD. U.S. Patent 4,416,709
An alloy highly resistant to corrosion for use in the core of a magnetic head has a composition of formula (Fe1-xCoxNi1-yMoxCr1-zXy, where M is Ru alone or a mixture with Pt, Pd, Ir and/or Rh, M' is a transition metal other than those in the formula, X is a vitrification element, p + q + r = 100%, a + b + c + d + e = 100% and e is 20–26%. A typical alloy is (Fe0.4Co0.4)704Ru2Cr(Si10B80)13.05Ti.

CHEMICAL COMPOUNDS
Amorphous Zirconium Phosphosilicate
DAIICHI KIGENSO KAGAKU KOGYO CO. LTD. European Appl. 105,128
New ion exchange agents of increased resistance have the formula Zr[PO4]2/3(SiO2)n.H2O or M1/2Zr[PO4]2/3(SiO2)n.H2O where I is the valence of the cation of the matrix, y is 0.02–2, z is 0.05–16.00 and n' is 0–100. The cation may be derived from Groups IA, IB, IIA, IIB, IIIA, IIIB, VA, VIA, VIIA and VIII. Platinum group metals, Ag and the lanthanides are among the cations proposed.