ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Structure Sensitivity of NO Adsorption on a Smooth and Stepped Pt(100) Surface
NO adsorption was studied by LEED, photo-emission and AES at 300–500K on smooth and stepped Pt surfaces. The sticking coefficient was about 0.6 at 300K for all surfaces and at 400K the adsorbed NO dissociated on all surfaces. No adsorption of NO occurred on reconstructed surfaces above 380K. Unreconstructed surfaces adsorbed NO molecularly up to 410K and dissociatively at 423 and 435K for smooth and stepped surfaces, respectively. Thus surface reconstruction can play a more significant role on NO adsorption than monatomic steps.

Wear Properties of Electroplated Platinum Metals under Sliding Conditions
M. Huck, Metall, 1978, 32, (7), 685–689
The contact resistance and wear properties of electroplated Pd, Ru and Rh against 70 Ag–30 Pd contacts were studied under sliding conditions. Different wear mechanisms were investigated by comparing the shapes of the worn particles and studying the surface profiles.

Purity of Hydrogen after Passing through a Palladium Filter
A review on the purity of H after being passed through a Pd membrane is presented. (26 Refs.)

Thermodynamic Behavior of Dilute Palladium-Hydrogen Solid Systems
Temperature-composition isobars in the Pd–H system were measured at different pressures, and the thermodynamic functions of the dissolved H atoms at concentrations < 10−7 atom fraction were analysed. Both the partial excess entropy and enthalpy increase rapidly with temperature. Some indication has been found that the partial thermodynamic functions are composition dependent.

Diffusion in a Pd-Cu-Si Metallic Glass
The diffusivity of Au implanted in as-quenched and annealed Pd37.5Cu2Si4.5 glasses at 533–653K were measured using the Rutherford backscattering technique. The diffusivities (Dn) evaluated from viscosity data. Below the glass transition, the measured D was critically related to the state of structure and could be many orders of magnitude higher than Dn.

Specific Heat and Resistivity of an Amorphous Alloy, Fe34Pd46P20, near Its Ferromagnetic Phase Transition
Specific heat and resistivity values were found for the amorphous ferromagnetic alloy Fe34Pd46P20. A sharp well-defined phase transition into the ferromagnetic state occurred at 205K, despite the low concentration of magnetic Fe atoms. The specific heat only has a small anomaly at the ferromagnetic transition, and this is explained by the proximity of the alloy to the percolation threshold for a uniform ferromagnetic state.

Thin Resistive Thick-Film Layers Based on Precious Metal Resinate/Glass Systems
The resistivity, particle size and temperature coefficient of resistance of a Au/Rh resinate/glass system and of a Ru resinate/glass system, prepared by firing onto a 96% Al2O3 substrate, were examined. In the Ru system the particle size is about 200Å and because of this conduction occurs at a very low volume % conduction phase.

Pyrite-Like Phases in the Rh-Te System
The phase and structural relations in the Rh–Te system containing 66–74 at.% Te, were studied between 400–1100°C by X-ray, neutron diffraction, metallographic and other means. Rh1−x Te x (0.00 ≤ t ≤ 0.20) has a pyrite type structure with disordered distributions of Rh atoms and vacancies. In Rh5Te4, which has a Rh5Se4-type structure, Rh atoms and vacancies are ordered.

Iridium Alloys Contain Nuclear Fuel Safely
Ir-Hf and doped Ir alloys are preferable to pure Ir for containing radioisotopes. Ir-Hf alloys have high toughness, good oxidation resistance, and good compatibility with nuclear fuels and graphite, etc. Their mechanical properties improve linearly with increasing Hf, the best composition being Ir–0.65 Hf. Ir doped with Th and Al has high impact strength at temperatures over 1366K, and forms part of the radioisotope generator systems on Voyagers 1 and 2.
Thermopower and Magnetic Breakdown in Ruthenium


Thermopower and magnetoresistance measurements were performed on a hexagonal Ru sample since thermopower is a sensitive and useful probe in magnetic breakdown investigations. Peculiarities in the thermopower correlate with those in magnetic breakdown investigations. Peculiarities were performed on a hexagonal Ru sample since thermopower is a sensitive and useful probe of thermoresistance and anomalies in their behaviour are explained by magnetic breakdown, which should lead to decompensation of the electron and hole volumes of the Ru Fermi surface.

Application of Thin Films to Adsorption and Catalysis on Metals and Alloys


A review is given of the various applications of thin films on metals and alloys (including Pt group metals) for adsorption and catalysis purposes. The paper discusses developments in the analysis and characterisation of film surfaces, the surface and catalytic properties of multicomponent films and future developments. (57 Refs.)

CHEMICAL COMPOUNDS

Crystal and Molecular Structure of trans-Dichloro (dimethylsulfoxide) (cytidine) platinum(II)


The crystal and molecular structures of trans-[Pt(Me2SO)(cyd)Cl2] were determined. Nucleosides react with cis-[Pt(Me2SO)2Cl2] which is not an antitumour compound, but (Me2SO) has been used as a solvent for testing the antitumour activity of some Pt complexes, and has common features with cis-[Pt(NH3)2Cl2], a strong antitumour compound. The reaction mechanisms are thus interesting to understand the variations in antitumour activity of the Pt complexes.

Energy Transfer from Linear Stacks of Tetracyanoplatinates(II) to Rare Earth Ions


M4[Pt(CN)6]x.nH2O compounds (M is Sm, Eu, Tb . . . ) represent a new solid state class for investigations of nonradioactive excitation energy transfer. The donors are linear stacks of square-planar [Pt(CN)6]4– complexes, and the rare earth acceptors are located between the stacks. Radiationless energy transfer and sharp line rare earth ion emission have been observed for Sm and Eu with n = 18 compounds, but not for Tb. The energy transfer only occurs from the lower excited state of tetracyanoplatinate stacks.

Arene-Olefin Complexes of Zerovalent Iron and Ruthenium


Convenient syntheses of arene-olefin complexes of Ru(0) and Fe(0) e.g. M(n-4-C6Me4)(n-4-diene) (M = Fe, Ru; diene = 1,3-cyclohexadiene or 1,5-cyclooctadiene) and of Ru(n-4-C6Me4)(C2H4)2 are given. These zerovalent Ru and Fe arene-olefin complexes are potential catalysts for olefin oligomerisation.

ELECTROCHEMISTRY

The Effect of Adsorption Layers on the Electrocatalytic Oxidation of Organic Fuel on Pt Electrodes


X-ray studies were made of the poisoning by Pb salts of Rh electrodes prepared by electrodeposition of Rh onto Pt from 1% solution of RhCl3, at a current density of 2–15 mA/cm2. Pb and Pb oxides were found on the surface of the poisoned Rh electrodes.

The Oxygen Evolution Reaction on Platinum, Iridium, Ruthenium and Their Alloys at 80°C in Acid Solutions


Kinetic parameters for 50 at.% Ru-1Ir, Ru-Pt and Ir-Pt alloys were determined for the O2 evolution reaction and compared with results using Ru, Ir, Pt, and RuO2/TiO2 electrodes. These noble metals and alloys are about equally effective as electrocatalysts for the H2 evolution reaction, but very different for O2 evolution. The order of catalytic activity for O2 evolution being, Ru > Ru-1Ir ≈ RuO2/TiO2 ≈ Ir > Ir-Pt > Ru-Pt > Pt. The lower electrocatalytic activities when Pt is present are probably due to the formation of a Pt oxide film. The dual barrier model is used to interpret the results for the Pt containing electrodes. The best electrocatalysts for O2 evolution in acid solutions consist of noble metals which form oxide films such as RuO2, or IrO2.
A Study of Ruthenium Electrodes by Cyclic Voltammetry and X-Ray Emission Spectroscopy


H and O adsorption properties of Ru surfaces were studied on smooth foil Ru electrodes spot welded to Au wire, and on Ru electrodes electrodeposited onto a Pt wire substrate from a 4% RuCl₃ solution in diluted HCl at 25°C. Ru was found to dissolve on potential cycles, the rate of dissolution on cycles to 1.54V being much greater than for Pd, Rh, Ir, Pt and Au. Treatment in hot chromic acid or potential cycling to 1.3V resulted in significant changes in the voltamogram.

Behavior of Ruthenium in Fluoride-Volatile Processes. 3. Thermal Decomposition of RuOF₃


Solid RuOF₃ releases its oxygen at room temperatures and the rate of thermal decomposition, in mol of O₂/°C reaches a maximum of 70°C, then decreases rapidly with temperature. RuOF₃ is very unstable, contrary to earlier descriptions. In the range 0–70°C its vapour pressure is expressed by lnPₓₑₙₑ = 8.48–2.74 × 10⁻²(1/T). IR analysis of the solid indicates that Ru=O bonds change into single bonds upon condensation; this may be related to the instability of solid RuOF₃.

ELECTRODEPOSITION AND SURFACE COATINGS

A Stable Surface Modified Platinum Electrode Prepared by Coating with Electroactive Polymer


Polyvinylferrocene (PVF)-coated Pt electrodes were prepared and their electrochemical behaviour in acetonitrile (ACN) solutions was examined for comparison with Pt electrodes. After 24 hours in ACN solution the electrode behaviour was practically unchanged; other results were reproducible, and the electrodes were highly stable.

Effect of Electrodeposited Metals on the Permeation of Hydrogen through Iron Membranes


The permeability of H through annealed Fe membranes was examined after coating the Fe surface with thin layers of Pt, Cu or Ni. A 0.015 μm Pt coating was more effective in reducing H permeation than a thicker Ni coating, possibly because the hydrogen evolution reaction (h.e.r.) occurs more readily on Pt sites, thus reducing the overpotential and H coverage. The polarisation of the h.e.r. on the Pt-coated surface was less than on an Fe surface. The effectiveness of the coating in decreasing H entry to the Fe is Pd > electroless Ni > Cu > Watts Ni.

Deposition of Palladium-Cobalt Alloys from Ammine Electrolytes


Spectroscopic studies of the electrodeposition of Pd-Co alloys from ammine electrolytes were carried out, and the optimum conditions to produce semi-bright 30% alloys are recommended. The alloys were prepared from electrolytes containing (in mol/l) 0.17–0.20 ammonium Pd complexes, 0.05–0.07 ammonium Co(III) complexes in NH₃ solution of pH = 9–9.5. Electrodeposition was carried out at 18–20°C and at current density of 1–2 A/cm².

HETEROGENEOUS CATALYSIS

The Oxidation of Hydrogen and Carbon Monoxide Mixtures over Platinum


The oxidation of low concentrations of H₂ and CO over a Pt wire catalyst was studied. Temperature dependences of the oxidation rates of H₂, CO and a mixture of both were found and activation energies were computed. CO has zero activity at 463K up to a diffusion-controlled region at 478K. The mixture behaves as a single gas, oxidised initially at 429K. H₂ oxidation is inhibited by CO, but the CO oxidation by H₂ is promoted. The formation of species MCH,O is proposed and removal of this from the surface, at a temperature below that necessary for CO desorption, is responsible for these oxidation kinetics.

Platinum-Catalysed Recombination of CO and O₂ in Sealed CO₂ TEA Laser Gases


The rates of a hot Pt wire catalysed recombination of CO and O₂ at small partial pressures were measured in a basic gas mixture containing CO₂, N₂ and He at atmospheric pressure. The results were applied to the development of a long-lived, sealed, u.v. pre-ionisation CO₂ TEA laser operating with high CO₂ concentrations. The volumetric "pumping speeds" for O₂ and CO increased rapidly with the temperature of the Pt wire but were independent of both the reaction time and the partial pressures of O₂, CO and CO₂.
Model Experiments on the Poisoning of Pt Catalysts by Sulfur

Surface reactions on clean or S covered Pt(100) surfaces were studied to find S poisoning of catalysts on dissociation of H₂S, adsorption and desorption of CO, etc. Three poisoning mechanisms were found. When the surface is covered with one S atom per two surface Pt atoms it is chemically inert. For lower coverages, the strong chemical bond to S modifies the chemical properties of the Pt surface and weakens its interaction with adsorbates. When the S coverage is one to four Pt atoms, a regular S overlayer is established, molecules can adsorb on the surface but are prevented by the S structure from participating in Langmuir-Hinshelwood reactions.

Decane Isomerisation on Fluorine Containing Platinum-Alumina Catalysts
L. B. GALPERIN, B. E. GOKHMAN, E. G. LIRINA and I. D. YAKOVLEVA, Neftekhimija, 1978, 18, (2), 201-204

The mechanism of n-decane isomerisation over 0.6 wt.% Pt/γ-Al₂O₃ catalysts containing 4.0 wt.% F was studied in a flow reactor at 350-425°C using chromatographic methods. At 350-375°C the selectivity of the isomerisation reaction was up to 80%. However, at 400-425°C the rate of cracking reactions exceeded that of isomerisation reactions.

Metal-Support Interaction in Pt/Al₂O₃ Catalysts

The inaccessibility of Pt/Al₂O₃ to H₂ chemisorption upon H₂ treatment at temperatures over 500°C was studied using H₂ and O₂ chemisorption measurements, n-hexane conversions and NMR measurements of the Pt Knight shift. The chemisorptive capacity decreased for H₂ but not for O₂. The selectivity of n-hexane conversions and the Knight shift changed from low temperature values. The results agree with the assumption that the highly dispersed particles form an alloy with the Al support.

Characterization of Supported Platinum, Hydrogenation and H₂-D₂ Equilibration

The characterisation of Pt/Al₂O₃ using poisons COS, H₂S, SO₂, C₆H₆ and CS₂ and a pulse technique was investigated. CS₂ had the best poisoning properties for measuring Pt dispersions. Metallic dispersion, where each Pt atom contains two metallic centres, is compared with H₂-O₂ titration; the best agreement occurring at low metallic concentrations. The number of active centres found for 32Å colloidal Pt/Al₂O₃ is equal for all the hydrogenation equilibration processes and this is attributed to the mechanism occurring on two metallic centres. The hydrogenation may work by the olefin or benzene bonded to one metallic atom interacting with atomic H adsorbed on one Pt atom.

Synthesis and Catalytic Activity of Transition Metal Complexes with Ligands Fixed on Oxide Support Surfaces. II. Fixed Ni, Pd and Pt Complexes as Telomerisation Catalysts of Butadiene with Diethylamine

Pd, Pt and Ni complexes with ligands fixed on SiO₂ and Al₂O₃ were studied during catalytic telomerisation of butadiene with diethylamine. Catalysts of the type Si-OMR (M = Pd, Pt and Ni; R = allyl, etc.) with the metal atom covalently bonded to the carrier showed only low activity. Activity of the catalysts of the type Si-L₃PdL₃₉ with ligand L₉ co-ordinately bonded to the Pd, increased with the growth of instability constants of the surface compounds.

Acetylene Removal from C-5 Hydrocarbon Streams Particularly Those Containing Isoprene and/or Piperylene

Studies of the selective removal of α-acylenes from C₅ hydrocarbon mixtures, particularly those containing isoprene and/or piperylene, were carried out using Pd/support catalysts. The results show that the best removal of acetylenes is obtained using 0.1-0.5 wt.% Pd on α or γ-Al₂O₃. The catalyst must be in the form of highly dispersed Pd pellets, extrusions or spheres. The reaction temperature should be kept low, 0-100°C, to minimise the hydrogenation of the dienes, and the reaction pressure should be 10-15 psi above the boiling pressure of the hydrocarbon mixture at the reaction temperature.

Effect of Hydrogen Transfer through Membrane Catalyst of Pd-Ru Alloy on Rates of Isopropanol Dehydrogenation and Cyclopentadiene Hydrogenation
N. N. MIKHALENKO, E. V. KHRAPOVA and V. M. GRYAZNOV, Neftkhimiya, 1978, 18, (3), 354-357

The effect of H₂ transfer through membrane catalysts, made from Pd-Ru alloy foils preliminarily treated in air and H₂ at 350°C, on the rate of selectivity of the above reactions was studied. It is shown that the H₂ transfer through the membrane increases the rate and selectivity of cyclopentadiene hydrogenation to cyclopentane. By interlinking both the dehydrogenation and hydrogenation reactions, the rate of both reactions is greatly increased; transition of cyclopentadiene into cyclopentane being increased by the increase in the amount of H₂.
Catalysts Prepared by Interaction of Transition Metal Compounds with Support Surfaces. Specific Features of Ethane Hydrogenolysis over Supported (W+Pd)/SiO₂ and (Mo+Pd)/SiO₂ Catalysts


Studies of the hydrogenolysis of ethane over supported (W+Pd)/SiO₂ and (Mo+Pd)/SiO₂ prepared from organometallic Pd, W and Mo compounds showed a decrease of activation energy, and an increase of specific activity at constant temperature compared to that of Pd/SiO₂ catalysts. The catalytic behaviour of the bimetallic catalyst is explained in terms of changes of electronic and geometric characteristics of the dispersed particles.

Infrared Spectra of Chemisorbed CO on Rh/γ-Al₂O₃: Site Distributions and Molecular Mobility


Chemisorption of CO on a 0.92 wt. % Rh/γ-Al₂O₃ catalyst gave three adsorbed CO species: RhCO at 2000 cm⁻¹, Rh(CO)₂ with peak frequencies at 2100 and 2030 cm⁻¹ and a bridged species Rh₂CO with a broad band peaked from 1850-1900 cm⁻¹. Rh(CO)₂ and Rh₂CO were found on Ru in the β phase. The CO adsorbed as RhCO underwent a fast motion of characteristic time 0.1 x 10⁻¹²s, but when adsorbed as Rh(CO)₂ had a characteristic time 3 x 10⁻¹⁸s. This may be important in the selectivity and activity of the different catalytic sites and the directional properties of the metal-carbon bond orbitals.

Kinetics of the Reaction between Carbon Monoxide and Hydrogen over a Ruthenium Catalyst in a Continuous Stirred Tank Reactor


Studies of the catalytic reaction between CO and H₂ over a 0.5% Ru catalyst coated on cylindrical Al₂O₃ pellets were carried out in a stirred tank reactor at 225-300°C, the reaction yielding CH₄ and H₂O.

HOMOGENEOUS CATALYSIS

Use of Polymer Matrices to Activate Palladium(0) Catalysts and Reduce Catalyst Agglomeration


The dimerisation-alkylation of butadiene to 1-methoxy-3,7-octadiene and 3-methoxy-1,7-octadiene was studied in benzene at 100°C using homogeneous Pd[PPh₃]₄ resin-attached Pd(o) catalysts. At similar P/Pd ratios for these two catalysts the resin catalyst has a greater reaction rate, and large catalyst charges can be used with resin catalysts without reaching limiting rates. Resin retards the ability of polymer-attached phosphines to co-ordinate, and stops the catalyst agglomerating and precipitating from solution as an inactive material.

Advances in Metal Cluster Chemistry Detailed


Rh carbonyl catalysts [Rh₃(CO)₁₀]⁻³, [Rh₁₄(CO)₁₅]⁻⁴ and [Rh₇₂(CO)₆₂H₂]⁻² and large metal clusters arrange themselves as metals do, and may be useful for studying reactions on metal surfaces and on small metal crystallites. A newly developed Rh catalyst selectively synthesizes ethylene glycol from CO and H₂, and during the reaction catalyst [Rh₁₃(CO)₁₄]⁻³ and [Rh₁₂(CO)₉₄H₄]⁻² interconvert and some [Rh(CO)₉]⁻¹ may be formed. The [Rh₁₅(S)₃(CO)₁₃]⁻² cluster is the first with S atoms in the cavity formed by the metal atoms. Other elements, such as P, may similarly be encapsulated.

Photo-Enhanced Production of Hydrogen by Liquid-Phase Catalytic Dehydrogenation of Propan-2-01 with Rhodium-Tin Chloride Complexes


Photo-irradiation of a homogeneous solution of RhCl₃.3H₂O, SnCl₂.2H₂O catalyst in propan-2-01 markedly enhanced the endothermic reaction rate to produce acetone and H₂. An energy conversion efficiency of 23%, was attained. This reaction is interesting since over 100%, in energy conversion efficiency can be surpassed for the input photons since the quantum yield is determined by the turnover numbers of the photo-active catalyst.

ELECTRICAL AND ELECTRONIC ENGINEERING

Premature Failure in Pt-GaAs IMPATT-Recombination-Assisted Diffusion as a Failure Mechanism


An ageing effect is observed in Pt-GaAs IMPATT diodes operating in avalanche during temperature stress ageing. Below 300°C a change in activation energy of 0.2-0.4 eV gives a much lower life expectancy. The effect is caused by the diffusion of defects from the Pt-GaAs interface into the diode. This failure makes thick Pt-GaAs unsuitable for IMPATT devices, but problems can be avoided by using a thin Pt layer in conjunction with a diffusion barrier, such as Ti.
Thickness Dependence of an Amorphous Overlayer Ge Film on the Electrical Conductivity of Ultrathin Pt Films
The effect of amorphous Ge thin overlays on the resistance of ultra-thin Pt films was studied. The ratio of the resistance changes in the films is $10^{-2}$:1:10$^2$ for continuous, semicontinuous and discontinuous Pt films. The resistance changes for semicontinuous and discontinuous Pt films depend on the Ge thickness. With increasing overlay thickness the resistance for semicontinuous films increases at first, while for discontinuous ones it rapidly decreases, then decreases for both films to a saturation value.

Some Aspects of Multilayer Ceramic Chip Capacitors for Hybrid Circuits
The dimensions, electrical properties, inner electrodes and end terminations of multilayer ceramic chip capacitors were studied. For inner electrodes Pd is attractive for non-Bi containing ceramics since Pd has excellent conductivity. For end terminations resistance to leaching was improved as Pd content increased, the Pd preventing Ag migration. For storage purposes the more Pd that is added to the end terminals the greater the resistance against sulphurisation.

TEMPERATURE MEASUREMENT
Temperature Detection Using Platinum Film
The Pt film temperature detector uses thick or thin film techniques to deposit a layer of Pt on a ceramic substrate, which is then fired and trimmed to close electrical tolerances by automatic or semi-automatic means, such as laser cutting of the resistance track. These films conform to B.S. 1904 Grade II tolerance, i.e. at 0°C the resistance will be $1000 \pm 0.1 \Omega$. The response to temperature is almost linear. The maximum error from 0–100°C is 0.4%, but from 0–200°C it may rise to 0.8%, and the devices are entirely predictable. The uses include temperature compensation of electronic circuits and cold junction compensation of thermocouple amplifier circuits.

Glass Enclosed Resistance Thermometer for Temperature Measurement inside a High-Pressure Vessel
A Pt resistance thermometer, enclosed in glass to protect it from changes of hydrostatic pressure which would affect its resistance, is used to measure temperatures in a high-pressure vessel. Very fine wire of 0.1 mm diameter is used for the contacts to prevent the differences in compressibilities from cracking the glass at high pressures. Comparisons with an ordinary calibrated resistance thermometer at pressures up to 2500 bars showed the difference in measured temperature to be less than 0.005°C.

MEDICAL USES
Stiffening up Cell Membranes Could Stop Tumour Growth
A process, similar to that for hydrogenating vegetable oils, which hardens the outer walls of cells to prevent them dividing is described. It involves a homogeneous reaction with Rh contained in a soluble complex. The Rh breaks the double bonds in the lipid molecules in the cell, thus forming a more rigid structure which will not divide. Tests on living cells have been successful and may provide remission for cancer patients, enabling them to undergo treatment by other techniques. This process is more specific for hydrogenating particular bonds than heterogeneous catalysis.

NEW PATENTS

ELECTROCHEMISTRY

Electrodes
Sumitomo Chemical Co. Ltd.
British Patent 1,508,876
Electrodes for use in the production of Al by molten-salt electrolysis of Al oxide are coated with a binary metal oxide, in which preferably at least one of the metals is a Pt group or lanthanide metal. Examples are PtCoO$_2$, PtRhO$_2$, PdCoO$_2$, PdRhO$_2$, PdNiO$_2$, AgInO$_2$, or AgRhO$_2$.

Platinum Anodes for Electrolysis Apparatus
Norda Mines Ltd.
U.S. Patent 4,085,016
An electrolysis apparatus which is used to oxidise organic material present in concentrated sulphuric acid uses as its anode a valve metal substrate (Ti, Ta or Nb) painted with a coating of Pt and/or Ir which is then fired and electroplated with a Na hexahydroplatinate bath. This electrode is far more corrosion resistant than Ti cladded with Pt, pure Pt wire or a conventional electroplated Pt anode.

Platinum Metals Rev., 1978, 22, (4)