ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES

In situ Scanning Tunneling Microscopy of Platinum(111) Surface with the Observation of Monatomic Steps
In situ STM was used on single crystal Pt(111) surfaces before and after electrochemical potential cycling in aqueous H₂SO₄. Monatomic steps were resolved, and Pt adatoms produced by the reduction of the Pt oxide form islands with heights of a few atoms on atomically flat terraces of Pt(111). No change in the location of the steps, nor disappearance of the islands on the terraces was found with time.

Amorphization by Solid-State Reaction of Crystalline Aluminum and Platinum Multilayers Prepared by Cold Rolling
Amorphous Al₆Pt has been synthesised by cold rolling of composite metal multilayers, and its stability and crystallisation temperature determined from differential scanning calorimetry. Amorphisation occurs during mechanical deformation near ambient temperature, and also occurs in samples picked up during deformation and annealed. XRD and SEM were also used to investigate the amorphisation.

XPS-Investigations of the Oxidation of a Pt-4Cu Alloy
Pt-4 at.% Cu alloys have been heat treated in air at 500, 600, 700 and 800°C for 4 hours and the formation of the oxides was followed by XPS and weight measurements. After annealing below 600°C the surface is covered by Pt₂O₃, while at 600°C another oxide, PtOₓ, was observed. At higher temperatures the coverage by oxides decreases slightly and the ratio of PtOₓ/Pt₂O₃ increases.

Anomalous Solid State Reaction between SiC and Pt
Periodic structures of alternating layers of Pt, Si and C are generated by solid state reaction in the diffusion zone during interdiffusion in the Pt-SiC system at 900°C. The Pt-Si phase is stable at 900°C for at least 10h. At 1000°C Pt-Si is formed. The formation of the Pt silicides causes interfacial melting between Pt and SiC. The C is in either an amorphous state or a highly ordered graphite state depending upon its location. The periodic structures may be due to low solid solubility of C in the Pt-Si.

The Influence of Pd on the Surface Segregation of Cr and Impurities in High Chromium Stainless Steel
The surface segregation of the components in an Fe-4Cr-3Pd alloy as well as an Fe-4Cr alloy on which Pd layers of 600 and 1500Å were evaporated has been studied using AES and ESCA as surface probes. Evidence of an attractive interaction between Fe and Pd was found and it was shown that the Pd layer provides easy diffusion paths to Cr in contrast to Fe.

Thermodynamic Behaviour of Hydrogen in Palladium-Gadolinium Solid Solution Alloys
The thermodynamics of absorption of H₂ by disordered Pd-Gd solid solution alloys containing up to 8.0 at.% Gd were studied at 273–473 K and H₂ pressures up to 100 Torr by pressure-composition isotherms. Solubilities of H₂ at low H pressure increase with increasing Gd content, though the higher pressure solubilities decrease with solute content. The relative partial molar enthalpy of solution of H₂ at infinite dilution becomes more exothermic with Gd content, whereas the standard relative partial entropy at infinite dilution decreases with Gd content.

Atomic Displacements during Structural Relaxation in a Metallic Glass
Structural relaxation in the highly stable metallic glass Pd₉₄Ni₆P₉ has been studied by XRD. The structural changes occurring in reversible relaxation have been directly observed for the first time. The data analysis distinguishes effects due to processes where the density changes from those where it is conserved. There is a clear contrast between reversible and irreversible relaxation.

Radioactive Metal Tracer Investigation of Pd, Si Formation
A radioactive Pd isotope formed by neutron activation of natural Pd was used for the first time to probe the formation of Pd-Si. Application of this procedure to the formation of Pd-Si yields a Pd activity profile, the position and shape of which indicates that mainly Si moves during this reaction, while the observed spreading of the profile points to some Pd vacancy diffusion.
An in situ Observation of the Growth Kinetics and Stress Relaxation Pd;Si Thin Films on Si(111)

The growth of the Pd;Si thin films on Si(111) substrates was monitored by an in situ X-ray diffraction technique in vacuum and in He, at 160–250°C. The activation energies were found to be 1.34 and 1.37 eV for measurements performed in vacuum and He, respectively. Stress relaxation in the growing Pd;Si film was observed when the reaction temperature was >200°C. The rocking curve studies showed that the relaxed films have a higher degree of texture.

Helium Release from Aged Palladium Tritide

Studies on He introduced into PdTa via T decay show that the He is deeply trapped within the host matrix. The He: Pd atomic ratio saturates at ~0.5 under conditions of ambient-temperature storage. Below this value very little He release occurs. Release from a sample with He: Pd ~0.3 requires temperatures ~600 K, while a sample with He: Pd ~0.02 needs temperatures ~1300 K.

The Formation of Discontinuous Al2O3 Layers during High Temperature Oxidation of IrAl Alloys

Ir-Al alloys containing 50 at.% Ir were made and oxidised at 1300 and 1600°C in air for different times. Weight loss occurred, attributed to the formation of volatile Ir oxides. Microstructure of the oxidation zones showed internal oxidation; an Al2O3/Ir-rich phase layered structure occurred at 1300°C, while an entangled Al2O3 and Ir-rich phase was formed at 1600°C. The Al2O3 layer is discontinuous and gives rise to internal oxidation of the IrAl alloys.

CHEMICAL COMPOUNDS

K2PdH1, A Complex Hydride with Linear [PdH2]2− Group

The ternary Pd hydride K2PdH1, prepared by the reaction of K hydride with Pd sponge in pure H2, was studied by X-ray and neutron diffraction studies on powdered samples and on the deuterated compounds, respectively. The room temperature modification contains linear [PdH2]2− groups and additional hydride ions which are co-ordinated by K ions exclusively. In the cubic high temperature modification the movements of the linear groups result in a structure in which metal cation arrangements correspond to the CuAu type.

A Novel Cyclam-Nickel(II) Complex Appended with a Tris-(2,2′-bipyridine)-Ruthenium(II) Complex (Cyclam = 1,4,8,11-tetra-azacyclotetradecane)

A new class of heterometal-binuclear complex [Ru(bpy)2(bpy-cyclam)Ni2+]+ (where bpy = 2,2′-bipyridine) was prepared as a new complex for use in photocatalysts. NMR and X-ray structural studies show a close contact between a H atom of the pendant bpy and NiII in the cyclam.

ELECTROCHEMISTRY

Electrocatalytic Oxidation of Hydrogen, Formic Acid and Methanol on Platinum Modified Copolymer (Pyrrole-Dithiophene) Electrodes

Electrocatalytic properties of a conducting polymer modified by the inclusion of a small amount of dispersed Pt were studied during the electrooxidation of H2, of formic acid and of methanol using the copolymer electrode, modified with 0.1 mg/cm2 of Pt. The electroactivity of these active electrodes with a small amount of Pt dispersed into a conducting polymer matrix showed the possibility of obtaining good electrocatalytic anodes for fuel cells.

Electro-oxidation of Methanol on Pt Electrodes Modified by Metal Oxides and Noble Metals

Modification of Pt foil electrodes by various metals to give increased levels of electrocatalytic activity and stability has been studied. Modification with mixed oxides of In + Pb always yielded a higher activity than those of singly modified ones. Additional modification with Au resulted in an even higher activity. The low surface concentration of Pt (~1%) indicated that only a small portion of the surface is used in the reaction, at which Pt signals are strong.

Surface Electrochemistry of the Anodic Cl2 Evolution Reaction at Pt

The effect of co-deposited OH and O species in the surface oxidation process on the extent of chemisorption of the Cl2 intermediate during anodic Cl2 evolution has been evaluated. Pt anodes, either freshly reduced or pre-oxidised in the presence of Cl2 ions, were used for various times at various potentials. Coverage by surface oxide film has a major effect on the electrode kinetics of Cl2 evolution.
The Reduction of Dioxygen at Polypyrrole-Modified Electrodes with Incorporated Pt Particles


The electrodeposition of Pt particles in a polypyrrole layer leads to electrodes which show electrocatalytic activity for the reduction of dioxygen in aqueous media. The final product composition (ratio $\text{H}_2\text{O}_2$/$\text{H}_2\text{O}$) is influenced by how the Pt particles are incorporated in the polymer. When Pt particles are deposited with a high current density, $\text{H}_2\text{O}$ is produced predominantly. At low current densities of Pt deposition, $\text{H}_2\text{O}_2$ is the main product. These effects are explained in terms of the availability of the Pt surface for dioxygen.

**Electrocatalysis of Pt-Fe Alloys Produced by Ion Beam Mixing**


Ion beam mixing using 120 keV Fe$^+$ ions at doses $3$–$20 \times 10^{15}$ cm$^{-2}$ was carried on Pt-Fe bilayer samples at 298–523 K to produce alloys of varying compositions. Ion beam mixing and thermal annealing led to grain growth of the polycrystalline films and to alloy phase Pt$_x$Fe$_{1-x}$ formation. At $T < 373$ K mixing was athermal and occurred by ballistic collisional processes. At $T > 473$ K Fe migrated rapidly into the Pt. Surface Pt concentration in the mixed films was ρ 90 at.%, giving ρ 25% reduction in the cathodic overpotential compared to pure Fe electrodes for H$_2$ evolution in 30 wt.% KOH solution. An ion beam mixed Pt-Fe surface layer was more stable than Fe coated with evaporated Pt.

**Redox Processes at Iron Hydroxide Layers Formed on Platinum Substrates in Alkaline Solutions**


Redox processes taking place at precipitated hydrous Fe hydroxide layers chemically formed on Pt substrates in Na hydroxide solutions were studied at 25°C. The electrochemical behaviour of these layers depends considerably on the electrodeposition level reached in charge-discharge cycles.

**A Study of Glyoxylic Acid Synthesis in an Undivided Cell**


It has been shown that it is possible to synthesise glyoxylic acid from the reduction of oxalic acid solutions in an undivided reactor with reasonable current efficiencies and yields. Using a platinised Ti electrode current efficiencies > 70% were achieved provided the concentration of glyoxylic acid does not exceed ρ 5 g/dm$^3$. The benefits of an undivided cell are weighted against the reduced product concentration using this system, and methods to improve cell performance are suggested.

**Investigation of Microbiologically Produced Hydrogen Permeation through Palladium**


Hydrogen production and absorption were studied through the use of pure cultures of bacteria and permeation measurements through a Pd foil. A thin Pd foil separated the two halves of the test cell. H$_2$ generation by bacteria associated with the surface of the metal established a concentration gradient across the membrane that resulted in the transport of H from the “input” to the “output” surface. Test results indicate a clear correlation between the growth cycle of the bacteria and the permeation of H. Differences between reactions of bacteria and reducing agents incorporated in nutrient solutions were also apparent.

**Electrochemical Studies of Poly(mercaptohydroquinone) and Poly(mercapto-p-benzoquinone) Film Prepared by Electrochemical Polymerization. IV. Preparation of Palladium Microparticles on the Polymer Film**


The electrodeposition of Pd at µg levels onto electroconductive poly(hydroquinone/p-benzoquinone) film-coated glassy C electrodes is described. The polymer films were chemically modified with Pd pyridine complex and/or with Pd thiolate prior to the Pd electrodeposition. Controlled-potential electrolysis was applied to form Pd microparticles on the polymer film, from an acid PdCl$_2$ solution. The Pd particles on the pyridine complex-modified electrode were closely dispersed and were spherically shaped, while on the thiolate-modified electrode the Pd deposits were irregular in shape. Both the electrodes thus prepared exhibited high activity toward the generation of H$_2$ and had good stability in acidic solution.

**Kinetics of Oxygen Gas Evolution on Hydrous Rhodium Oxide Films**


The activity of Rh for O$_2$ evolution in base was found to be significantly enhanced by the presence of a thick, hydrous oxide film which is produced by repetitive potential cycling. An increase in O$_2$ evolution rate of up to three orders of magnitude was obtained on growing these films. The films were found to be stable to dissolution (in short term tests) at potentials below ρ 1.70 V (RHE). A mechanism for O$_2$ evolution is proposed involving cyclical formation-decomposition of higher Rh oxide species. The kinetic rate equation includes a term that takes into account the variation of Rh(IV) concentration at the interface, at constant overpotential, with pH changes.
Electrochemical Behaviour of an Electrodeposited Iridium Electrode in Acid Solution

The electrochemistry of an electrodeposited Ir electrode on a Ti substrate in 0.5 mol/dm³ H₂SO₄ has been investigated. The efficiency of electrodeposition is enhanced at elevated temperatures and satisfactory coating is achieved at 343 K.

Intercalation of Metal Complex Cations in Polyoxometallates: Formation of Composite Films with Distinct Electrocatalytic Centers

The codeposition of silicotungstates with complex metal cations, such as Os(bpy)₃⁺ or Ru(III), IV)-oxo species leads to the formation of novel composite polynuclear films on electrodes. These systems contain 3-dimensionally distributed, distinct reactive centres and can serve as multi-purpose electrocatalysts for oxidations or reductions of highly inert reactants.

Corrosion Behaviour of Cr-Ru Alloys in Sulphuric Acid Solutions under Active Dissolution Potentials

N. S. TOMASHOV and E. N. USTINSKII, Zaskh. Met., 1990, 26, (1), 121-124
Studies of corrosion behaviour of plastic Cr alloys containing 0.1-0.4 wt.% Ru and having surface area of 1.5-2.0 cm² were performed during cathodic polarisation in 25% and 40% H₂SO₄ solutions at 20 and 65°C in potentiostatic regime, and the dependence of the rate of active dissolution of cathodically modified alloys on effective H₂ evolution on their surfaces was established. The rate of H₂ evolution on the surface of cathodically modified Cr-Ru alloys increased by ~2 orders.

PHOTOCONVERSION

Colloidal Semiconductors as Photocatalysts for Solar Energy Conversion

The development of ultrafine colloidal semiconductor particles with photocatalytic properties is presented. Photochemical and photophysical processes which directly affect the photocatalytic properties, and factors that limit the charge transfer at the semiconductor/electrolyte interface are discussed. The use of these systems, such as Pt/RuO₂, and Pt/RuO₂ sensitised with Ru(bpy)₃⁺ in the decomposition of H₂O, and photocleavage of organic and inorganic wastes by RuO₂/CdS or Rh/CdS, etc., are described.

Photoreduction of Palladium Radical Cations. Transient Absorbance Kinetics of Electron Transfers to Photogenerated [Pd(CNMe)₃]⁺ Radicals

Photoreduction of organometallic radical cations by electron transfers to photogenerated [Pd(CNMe)₃]⁺ radicals is reported. The electron-transfer photochemistry which is described shows that the photogenerated, dissociated [Pd(CNMe)₃]⁺ transients are reducible by even modest electron donor ferrocenes. The studies show electron-transfer reduction of a photogenerated metal radical at rates approaching 10¹¹ M⁻¹s⁻¹ and thus the preparation of metal films.

Photochemical Generation of Formate via HCO₃⁻/CO₂ Reduction on Pd Dispersions

Formate ion and H₂ are simultaneously formed when solutions containing HCO₃⁻/CO₂, C₂O₄⁻ are irradiated in the presence of Pd/TiO₂ catalysts. The hydrogenation of aqueous solutions of HCO₃⁻/CO₂ as a function of catalyst HCO₃⁻ and added oxalic acid concentration is reported. Photolysis of the system over 24 h gave 2.3×10⁻¹¹ M formate (quantum yield ~3×10⁻¹1).

Rhodium and Rhodium Sulfide Coated Cadmium Sulfide as a Photocatalyst for Photochemical Decomposition of Aqueous Sulfide

The effect of the deposition of Rh and Rh₂S₃ on CdS on the photocatalytic activity of CdS is reported. The order of activity of the photocatalysts for the decomposition of aqueous sulphide was found to be Rh₂S₃/Rh/CdS>Rh₂S₃/CdS>Rh/CdS>CdS. X-ray photoelectron spectroscopic studies show that Rh as it is photodeposited on CdS is in the zero oxidation state but is prone to aerial oxidation. Photocatalytic decomposition of sulphides serves to destroy the pollutant and can also generate H₂.

Photochemical Hydrogen Production from CdS/RhO₂/Na₂S Dispersions

The effects of the amount of semiconductor, RhO₂-, loading and temperature were studied during H₂ generation over Cd/RhO₂/Na₂S system. The results show that the CdS/RhO₂ dispersion in an aqueous solution of sulphide ions works as a suitable H₂ system. The rate of H₂-evolution increases with increasing both the amount of CdS up to 10 mg/cm² and the content of RhO₂ up to 5%.
Photochemical Reduction of Carbon Dioxide to Formate Catalyzed by 2,2'-Bipyridine- or 1,10-Phenanthroline-Ruthenium(II) Complexes


Formate is photo-generated from CO2 and II) in photochemical reduction by visible light irradiation of systems containing (I) the [Ru(bpy)2Cl2]+ complex alone, or (II) a mixture of two Ru(II) complexes. System (I) produces the active catalytic species by photolabilisation of two bpy ligands. System (II), a mixture of [LRu(L),I]+ (L = bpy derivatives or 1,10-phenanthroline) as photosensitiser and cis-Ru(bpy)(CO)(X)n+ (X = Cl, H, n = 1 or X = CO, n = 2) or cis-Ru(bpy)2(CO)2Cl2, produced a maximum quantum yield of 15%. This CO2 photoreduction consists of two catalytic cycles, a photochemical one, and a dark-reaction pathway.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodeposition of Platinum by High Temperature Electrolysis

G.-B. DICK, Oberfläche Surf., 1990, 3, 8–12

Methods and uses of high temperature electrolytic (HTE) Pt plating are reviewed. The process parameters include a KCN-GaCN electrolyte, 500–600°C working temperature, a deposition rate of 17 μm/hour and cathodic current density of 1–5 A/dm². Pt as a cyanide complex reduces to metal at the cathode. The adhesion of these Pt layers is very strong. This method can also be used for coatings of other metals, including Rh and Ir. Advantages of these coatings include use of high purity Pt, thickness of 21.1 g/cm² and crack free layers. The main uses of HTE Pt layers include: electrodes for recycling, producing drinking water from brackish water, in chloralkali production and cathodic protection.

Studies of the Electrodeposition of Palladium from Baths Based on [Pd(NH3)2]X2 Salts. I. [Pd(NH3)2]Cl2 Baths


Spectroscopic studies of the deposition of Pd on vitreous C and freshly plated Pd were performed using potential sweep and pulse methods at both stationary and rotating disc electrodes in order to improve the selection of the parameters for electroplating Pd. The bath was based on [Pd(NH3)2]Cl2 in NH4Cl at pH 7–10. The Pd was stabilised by the L Nowadays, we use the enhanced version of plating Pd in the bath. The relative importance of O reduction, H absorption and evolution as competing cathode reactions under various conditions is defined and the advantage of strong convection for high rate plating is demonstrated.

APPARATUS AND TECHNIQUE

Electrochemical Solid-State Sensor for SO2 Determination in Air


The response time of an SO2 sensor as a function of the configuration of the measuring electrode as well as the thickness of the electrolyte were studied in the solid state galvanic chain Pt, Ag(Ag2SO4), Li, SO2, SO2(O2), Pt. The different response times which were observed during increasing and decreasing the SO2 concentration are attributed to a different rate of adsorption and desorption of SO2 on Pt films. The results show that a solid state sulphate galvanic cell is able to detect SO2 in air in the range 3–2000 ppm with an accuracy of ~ 5%.

Cu/Pd Thin-Film Thermopile as a Temperature and Hydrogen Sensor


A thermopile made of five thermocouples using Cu and Pd as thermoelectric elements was fabricated and tested as a H2 sensor. The results obtained using a H2 concentration as low as 88 ppm show that this device can be used in those applications where high resolution is required for measuring the H2 concentration. The H2 + N2 flux. The thermopile sensitivity increases on decreasing the H2 concentration. Response times depend on the temperature of both thermocouple junctions and the H2 concentration in the H2 + N2 mixture and are related to the adsorption-desorption processes of the Pd film itself.

Thick-Film Hydrocarbon Gas Sensors


The gas-sensing characteristics of Fe2O3 thick films with and without Pd catalysts were studied. The results show that the addition of 1 wt. % Pd to Fe2O3 enhances the sensitivity to butane gas. The sensitivity of Fe2O3/SnCl2 (50 wt. %)/Pd (1 wt. %) film heat treated at 400°C for 2 h to 1000 ppm C2H6 is 80% at an operating temperature of 300°C. The sensitivity of the sensor without Pd was 70%.

An Electrochemical Preparation of Palladium Oxide pH Sensors


Pd/PdO pH sensors which were produced by electrolysis in sulphuric acid using AC and DC potentials have characteristics and lifetimes highly dependent on the electrolysis conditions. The longest lived electrodes are those formed with a layer of large oxide crystals covered by a layer of much finer crystals, and the production of this structure needs delicate control of the oxidative and reductive cycles of the electrolysis.
HETEROGENEOUS CATALYSIS

Modern Concepts in Surface Science and Heterogeneous Catalysis

Surface science models for the examination of metal surfaces, and examples of typical uses are discussed. Concepts examined include relaxation, reconstruction, and atomic-scale structure of clean surfaces, experimental techniques for examining surfaces, the nature of the surface chemical bond, the gas-solid interaction and heterogeneous catalytic reactions. Among noble metals mentioned are adsorbed species on Rh surfaces, bonding of benzene in CO adsorption on Pt(III), Pd(III) and Rh(III), bonding geometries of pyridine on Ir, Pt, Pd and Rh surfaces, coadsorptions on Rh(III), H-D exchange reaction on stepped and flat Pt(III), CO structures on Pt and Rh and hydrogenation rates of ethylene on Pt(III) and Rh(III) (52 Refs.).

Influence of the Support towards Platinum Catalysed 1,3-Butadiene Hydrogenation
M. PRIMET, M. EL AZHAR and M. GUENIN, Appl. Catal., 1990, 58, (2), 241-253

Effect of support acidity on deactivation and selectivity, during gas phase hydrogenation of 1,3-butadiene over Pt supported catalysts with low metal loading (<1 wt.%) was studied at 333 K, under 101 kPa pressure of hydrocarbon and using a feed corresponding to P,H : P,H = 3, and Ar as balance. The acidic properties of the support modify both the initial selectivity for the hydrogenation of 1,3-butadiene to butene and the internal butene distribution. Catalysts supported on materials having a basic character are more selective for butene production and more specific for 1-butene formation. In addition, preadsorption of NH3 on Pt supported over acidic supports leads to an increase in butene selectivity.

Effect of Particle Size on the Reactivity of Oxygen-Adsorbed Platinum Supported on Alumina

A Pt/Al2O3 catalyst was aged in a CH2=CH- , O2, mixture at 873 K with O2/CH2 ratio of 4. The metal particle size increased from 2 to 12 nm. The catalytic activity for CH2=CH- oxidation was slightly increased for reaction temperature <700K and not modified at higher temperatures. Thus, the turnover number (i.e. the activity per surface Pt atom) is much higher on the large Pt particles. A decrease in the heat of O2 chemisorption was observed when the Pt particle size increased and the reactivity of chemisorbed O2 increased with increasing metal particle size. Changes in the strength of the Pt=O bond are proposed to take into account the increase in turnover number that accompanies a decrease in the dispersion of the metallic phase.

H-Erionite as a Component of Reforming Catalysts

Reforming catalysts based on Pt/Al2O3, with an erionite component of <25% promote the conversion of n-alkanes into cracking products and into aromatics. Studies were performed of this two fold selectivity using tracer methods and model substances. A mechanism is presented which takes into account the impact of acid centres on the external surface of erionite crystallites.

Effect of Hydrothermal Treatment on Alumina as Support for Noble Metal Catalysts

Boehmite was calcined with and without steam at 550-1000°C. Pt and Pt+Rh were deposited on hydrothermally and thermally treated Al2O3 by direct impregnation and ion exchange. The chemisorption of H2 on these metals was ~50% lower on hydrothermally treated supports than on thermally treated ones. Pt applied by direct impregnation on hydrothermally treated Al2O3 had lower light-off temperatures and produced more efficient catalysts for oxidation of CO, propene, xylene and propane than on thermally treated Al2O3.

The Hydrocatalytic Aromatisation of Naphtha. Part 1: Development of a New Catalyst for Aromatisation

A new Pt-Re/Al2O3 catalyst for a moving-bed reforming plant was developed using pure Al2O3 balls with high mechanical strength. Studies of the effect of the modification of the catalyst by a third metal, Cr, Cu or Sn, show that Pt-Re-Cr/Al2O3 catalyst has the best selectivity and stability and thus is most effective for the above application.

Coking, Ageing and Regeneration of Zeolites. XI. Coke Formation and Deactivation of Pt-Ultrastable Zeolite HY and PtH-Mordenite Catalysts during Hydrogenation of Benzene

Studies of the benzene hydrogenation on Pt-ultrastable zeolite HY (PtUSHY) and PtH-mordenite (PtHMOR) catalysts at 80°C showed the formation of molecules of carbonaceous (coke) compounds by the reaction of benzene and cyclohexane molecules, which are retained in the zeolite pores due to their low volatility. On PtHMOR they block the access of benzene to the Pt crystallites, causing almost instant deactivation of the catalyst. However, the deactivating effect of coke is very reduced on PtUSHY.
Two-Dimensional Compression and Catalysis: Acetylene → Benzene Conversion Induced by Spectator Nitric Oxide


Coadsorbed NO has been found to exert a very large promoting effect on the acetylene → benzene conversion on Pd(111). It was found that the two species are forced into mutually exclusive domains; this reduces the apparent acetylene threshold coverage for benzene formation to the extent that it becomes ten times less than the critical threshold exhibited by clean Pd(111). This can lead to effectively a 100% selective reaction, compared to a maximum of 25% previously reported.

Selective Hydrogenation of Styrene. II. Poisoning of Pd/Al₂O₃ by Thiophene and Pyridine


The poisoning of a commercial Pd/Al₂O₃ catalyst by pyridine and thiophene during the selective hydrogenation of styrene to ethylbenzene was studied. It was found that the Pd electronic state is the main factor controlling the interaction between the metal and the poisons. Pyridine added to the unpollided feed in a pulse produces a modification in the Pd electronic state and a decrease in conversion.

Activity and Selectivity of Pd/α-Al₂O₃ for Ethyne Hydrogenation in a Large Excess of Ethene and Hydrogen


The hydrogenation of ethyne in the presence of large amounts of H₂ and ethene was studied at 1520 kPa over Pd/α-Al₂O₃ catalysts of various dispersions. Both TON (turn over number) and selectivity for ethene decreased as the Pd dispersion increased. The result was consistent with a clear dependence of the rate order for ethyne on the particle size of the Pd, being 0 for large particles and −0.5 for small particles.

Hydrocarbon Synthesis from CO and H₂ in the Presence of Palladium Modified Cobalt-Attached Catalysts


Studies of the effect of the catalysts were performed during synthesis of liquid hydrocarbons from CO and H₂ on Pd modified Co catalysts supported on Al₂O₃, SiO₂, Al₂O₃ or SiO₂, which were prepared by saturation of the supports by Co carbonyl and Co nitrate. The addition of Pd into the catalysts resulted in an increase in liquid hydrocarbon yield and changes in their composition.

Palladium Catalysed Carbonylation of Aryl Chlorides to the Corresponding Methyl Esters


A series of aryl chlorides were carbonylated at 200°C to their corresponding methyl esters, in the presence of a 5% Pd/C catalyst. The results showed that the addition of K₂Cr₂O₇ increases the catalytic activity of the catalysts by increasing the initial rate of the reaction as well as the turnover number. The role of K₂Cr₂O₇ is to reoxidise large particles of metallic Pd into a highly dispersed Pd(II) species which can be reduced again under CO into an active zerovalent Pd complex. Deactivation of the catalyst by sintering would then be retarded.

Effect of Pd Dispersion on Methanol Decomposition over Supported Pd Catalysts


The turnover frequency (TF) for the methanol decomposition over various supported Pd catalysts is dependent on both supporting materials and Pd crystallite size. The highest dispersion of Pd was obtained with TiO₂ prepared from TiO2(CH3)4, or TiCl4, but at >773 K in the reduction treatment applied, suppressed activity was observed. Pd particles on ZrO₂ support gave a high value of TF when the Pd/ZrO₂ catalyst was calcined in air at 873–1073 K. TF curves for the methanol decomposition over TiO₂-, ZrO₂-, and ZrO₂-supported Pd catalysts change discontinuously at 10Å Pd particle size. Studies of the effect of heat treatment suggest that thermal stabilisation of the ZrO₂ support would play an important part in the development of catalytic properties of Pd.


The generation of paramagnetic Pd species in NaPd-Y and CaPd-Y zeolites adsorbed with H₂O, H₂, and benzene was studied by ESR and ESEM spectroscopies. The probable location of the Pd species is assigned on the basis of Pd-adsorbate interaction distances. Interaction of the Pd ions with adsorbates shows that they migrate toward the zeolite supercage in order to interact with the adsorbates. In contrast to NaPd-Y/Pd⁺ ions in O₂-pretreated CaPd-Y occupy relatively accessible sites in the β-cage (SiO₂) and the Pd⁺ ESR signal A disappears more rapidly in the presence of adsorbates with the appearance of signals due to Pd⁺ species.

Platinum Metals Rev., 1990, 34, (3)
The Effect of Lanthanum Promoter on the Selectivity of Pd/Zeolite-X in Methanol Synthesis


The promoting effect of various amounts of La on Pd/zeolite-X catalysts was nearly unchanged on La promotion. This is attributed to the cationic exchange method adopted to introduce La after Pd introduction into the zeolites. The zeolite lattice ensures the maintenance of small PdLaO₅ particles.

Chemisorption and Catalysis of Zeolite-Entrapped Palladium


The chemisorption of H₂, CO₂, and CO₂ in neopentane conversion was studied on two groups of Y-zeolite supported Pd samples. One group was of “grape-shaped” Pd particles filling adjacent supercages and the second one was pretreated yielding isolated Pd particles of the size of the supercages. The selectivity of neopentane conversion did not depend on Pd morphology but the activation energy was significantly higher for the samples of the first group.

Particle Size, Precursor, and Support Effects in the Hydrogenolysis of Alkanes over Supported Rhodium Catalysts


A series of Rh catalysts of varying dispersion were prepared using γ-Al₂O₃ as support and Rh acetylacetonate (Rh(acac)₃) as precursor. The hydrogenolyses of n-hexane (nH), methycyclopentane (MCP), and 2,3,3,3-tetramethylbutane (TeMB) were studied as model reactions. Clear dependence of turnover frequency on Rh particle size is observed for nH and MCP hydrogenolysis, but only small changes of selectivity occur with these alkanes. The effect of the precursor is appreciable and shifts the selectivity of TeMB hydrogenolysis toward that of large particles.

Hydrogenation of Carboxylic Acids by Rhenium-Osmium Bimetallic Catalyst


Hydrogenation of carboxylic acids to alcohols at low temperature and under low pressure was achieved in the presence of a new Re–Os bimetallic catalyst. The most active catalyst had Re:Os ratio of 1:2–3 and was prepared by reduction of Re₂O₇ and OsO₄ with H₂ in the presence of succinic acid. Decanoic acid was hydrogenated to decanol in high conversion at 35–100 atm and 100–120°C. The selectivity of alcohol was improved by the addition of thiophene as a modifier of the catalyst.

HOMOGENEOUS CATALYSIS

Palladium-Catalyzed Cycloisomerizations of Enynes and Related Reactions


A review is given of Pd-catalysed cycloisomerisation of enynes and related reactions, especially of the development of such catalytic systems. Investigations of a tandem Pd(0)-catalysed alkylalenylation-Aldredene cyclisation, palladacyclopentenes in a cyclotrimerisation and a cycloisomeration, hydricopalladation catalyst in reductive enyne cyclisations and semihydrogenation of acetylenes, and others are included. (69 Refs.)

New Aspects of Oxypalladation of Alkenes


The studies of the Wacker-type oxidation showed that the redox catalysis of the conventional Wacker process is not operative, but the formal oxidation state of Pd(II) remains constant throughout the reaction. The Pd-OOH species which derived from the oxygenation of the Pd-I species by O₂ is the active catalyst. The intramolecular version of the Wacker reaction provides a unique approach to preparation of various heterocycles. The Pd(II)-catalysed acetalisation of alkenes with diols is also a promising process for the synthesis of optically active acetalts and aldehydhydr derivatives.

Catalysis of Pd(II)-Catalyzed Acetalisation of Alkenes with Diols


Alkenes bearing electron withdrawing substituents are catalytically acetalised with 1,3-propanediol only by the use of PdCl₂(MeCN) as a catalyst under O₂ atmosphere. The results show that acetalisation proceeds effectively when a combination of BiCl₃ and LiCl is used as co-catalyst. A hydroperoxopalladation(II) species was found to be an active catalyst in the present reaction.

Palladium-Catalyzed Desulfonylative Homo-Coupling of Arylsulfonyl Chlorides in the Presence of Titanium(IV) Isopropoxide


The desulfonylative homo-coupling of arylsulphonyl chlorides proceeds efficiently on treatment with Ti(IV) isopropoxide in the presence of a catalytic amount of PdCl₂(PhCN)₂ to yield corresponding biaryls in good yields. The present reaction using arylsulphonyl chlorides appears to be particularly advantageous, if the corresponding halide cannot be obtained by direct halogenation. In addition, the reaction can be completed in a fairly short time compared with that using aryl halides.
Palladium-Catalyzed Synthesis of Aromatic Acids from Carbon Monoxide and Aromatic Compounds via the Aromatic C-H Bond Activation
A single step synthesis of aromatic acids from aromatic compounds and CO under very mild conditions by Pd-based catalysis via direct C-H bond activation is presented. With Pd(II) catalysts the reaction is electrophilic and proceeds with ortho-para orientation when an electron-donating group is attached to the benzene ring. Addition of t-BuOOH and allyl halides makes the reaction catalytic with respect to Pd(II).

The Rhodium-Catalyzed Deuteration of Unsaturated Triglycerides
Unsaturated triglycerides were deuterated with deuterium gas in the presence of Wilkinson’s catalyst [{Rh(CO)},RhCl(I)] and recrystallisation of the products from acetone yielded highly pure deuteron-labelled triglycerides (TG). The deuterated TG were converted to methyl esters and studied by gas chromatography/mass spectroscopy. Since the deuteron labelled TG were to be used in human metabolism studies, atomic absorption spectroscopy was used to determine if any residual Rh was present. No Rh was detected at the minimum detection level.

Asymmetric Synthesis in Carbon-Carbon Bond Forming Reactions of α-Diazoketones Catalysed by Homochiral Rhodium(II) Carboxylates
The first use of homochiral Rh(II) catalyst in C-C bond forming reactions of α-diazoketonyl precursors is reported. Partial asymmetric synthesis was observed in intramolecular C-H insertion, aromatic diazoketone reduction and cyclopropanation of α-diazoketones catalysed by homochiral Rh(II) mandelate and Rh(II) carboxylates derived from L-proline.

Hydrogenation of Carbon Monoxide by the Use of Rh₄(CO)₁₂ Catalyst in 1-Methylpyrrolidine Solvent
The hydrogenation of CO was studied using Rh₄(CO)₁₂ catalyst in 1-methylpyrrolidine (MPD) solvent at 210–270°C and syngas pressures of 500–1800 kg/cm² (H₂/CO = 1). The Rh₄(CO)₁₂-MPD system showed a high catalytic activity for ethylene glycol (EG) formation at a low catalyst concentration. The selectivity to EG increased as the reaction pressure increased.

Ruthenium Catalysed N,N'-Diaryleurea Synthesis from N-Aryl Substituted Formamides and Aminoarenes
Formanilide reacted smoothly with aniline in the presence of catalytic amount of RuCl₃(PPh₃)₂ to give N,N'-diphenylurea in 92% yield. A stoichiometric amount of H₂ was evolved spontaneously into the gas phase. Various symmetrically N,N'-disubstituted ureas were obtained in good to excellent yield.

FUEL CELLS
One Step Synthesis of Hydrogen Peroxide through Fuel Cell Reaction
A new method for the production of H₂O₂ uses a fuel cell system at room temperature. The fuel cell system (O₂, HCl (aq) or H₂SO₄ (aq), M(cathode)/Nafion-H/Pt(anode), H₂), where M is Pt, Pd, Au, graphite, or Au-mesh, cogenerates H₂O and electricity with a current efficiency of 100% in the early stages of the reaction. The risk of explosion is reduced by the lack of organic materials and by the separation of O₂ and H₂ by the Nafion-H SPE membrane.

Recent Advances in Solid Polymer Electrolyte Fuel Cell Technology with Low Platinum Loading Electrodes
The effects of Pt localisation in electrodes, and the type and thickness of membrane, on the performance of solid polymer electrolyte (SPE) fuel cells is discussed, as well as electrode kinetic criteria for attaining high power densities. The chloroplatinic method of treatment of the electrodes provides a satisfactory and considerably more economic alternative to sputtering treatment of the electrodes provides a satisfactory and considerably more economic alternative to sputtering for the deposition of a thin layer of Pt on the front surfaces of the electrodes, essential for the attainment of high power densities. SPE fuel cells with low Pt loading electrodes had power densities approaching those with ten times the Pt loading.

Porous Carbon Anodes for the Direct Methanol Fuel Cell—II. The Role of the Reduction Method for Carbon Supported Electrodes
The efficiency of platinised porous-C electrodes for the electro-oxidation of methanol in H₂SO₄ has been found to vary quite markedly with the method used to deposit the Pt. This is due to both the size and electronic nature of the Pt crystallites. The most efficient electrodes had small crystallite sizes of ~20 Å diameter, and a minimum amount of ionic Pt species.

Platinum Metals Rev., 1990, 34, (3)
Oxygen Electrodes for Rechargeable Alkaline Fuel Cells—II

A number of electrocatalysts and supports for the positive electrode of moderate temperature, single-unit, rechargeable fuel cells has been studied. Five electrocatalysts were identified for further development: RuMnO₂, Pb₆(Ir,Ru)O₂, Pb₆(Ir,Ru)O₂, Pb₆(Ir,Ru)O₂, Pb₆(Ir,Ru)O₂. Of these Na₈Pt₅O₁₂ was found to be the best candidate bifunctional O₂ electrode catalyst in terms of stability and O₂ reduction/evolution performance.

Electrocatalysis for Oxygen Electrodes in Fuel Cells and Water Electrolyzers for Space Applications
J. PRAKASH, D. TRYK and E. YEAGER, *J. Power Sources*, 1990, **29**, (3&4), 413–422

The pyrochlore Pb₆Ru₂O₁₂, in both high- and low-area forms, has been characterised, and O₂ reduction and generation kinetic-mechanistic studies were made. Mechanisms are proposed. Compounds in which part of the Ru is substituted by Ir have also been prepared and showed somewhat better performance for O₂ reduction in porous gas-fed electrodes than the unsubstituted compound. Anodic corrosion resistance of the electrodes was improved by using two different anionically conducting polymer overlayers.

Corrosion Testing of Candidates for the Alkaline Fuel Cell Cathode
J. SINGER and W. L. FIELDER, *J. Power Sources*, 1990, **29**, (3&4), 443–450

The pyrochlore Pb₆Ru₂O₁₂, and the spinel NiCo₃O₄, are candidates for the O₂ reduction electrode of the alkaline fuel cell. Current/voltage data for these specially made corrosion electrodes has been obtained in order to develop corrosion test screening for these materials. The data consist of measurements of current at fixed potentials and cyclic voltammograms. Initial data for the pyrochlore Pb₆Ru₂O₁₂ indicate relative stability.

CORROSION PROTECTION

The Corrosion Behavior of Double Pressed, Double Sintered Stainless Steel Containing Noble Alloying Elements

Double pressed, double sintered stainless steels show a clear and stable passive behaviour in a 1 N H₂SO₄ environment, due to closed and round pore morphology obtained by this process. Noble alloying elements Pt, Pd, Au, Ag, Ni, and Cu have been found to enhance the self passivation processes. Noble alloying elements also enable passivation of samples obtained by a single process of hot pressing and sintering, even where some degree of open porosity is observed.

Effects of Pt on the High-Temperature Oxidation of Fe-Cr and Fe-Cr-Al Base Alloys

The effects of sputter-deposited Pt thin films on the isothermal oxidation of Fe-24Cr alloys, Fe-24Cr alloys containing 0.063 and 0.87 wt.% Y, and Fe-24Cr-4Al alloys containing 0.07 and 0.5 wt.% Y at 1173–1523K have been studied. Pt coating on the Y-free Fe-24Cr alloy resulted in a marked suppression of the isothermal oxidation rate. Pt coating on Y-containing Fe-24Cr-4Al alloys had no influence on oxidation rate, while Pt coating on Y-containing Fe-24Cr alloys increased the oxidation rate.

HIGH-TEMPERATURE CORROSION OF ALUMINIDE FORMING COATINGS FOR SUPERALLOYS

The cyclic oxidation and hot corrosion of diffusion aluminide and CoCrAlY overlay coatings on Ni-base superalloys have been investigated. Pt additions to aluminide coatings produce a substantial increase in resistance to cyclic oxidation and high temperature hot corrosion, and improve the low temperature hot corrosion resistance of diffusion aluminide coatings, but the effect is not as dramatic as in high temperature hot corrosion.

CHEMICAL TECHNOLOGY

Control of Polymer Gel Morphology by Small Potential Electric Stimulation with a Conducting Polymer Electrode

A polypyrrole thin film was prepared on a Pt deposited glass electrode by electrochemical polymerisation of pyrrole. Poly(methacrylic acid) (PMMA)-Ca⁺⁺ microgel was made responsive to pH. A small potential shift, of the order of 1V, caused a morphological change of the microgels which were in contact with the polypyrrole film/Pt deposited glass electrode. A microscope and a video recording system was used to observe the reversible deformation/reformation of the PMAA Ca⁺⁺ microgels on the electrode.

Bending of High Strength Polymer Gel in an Electric Field

Deformation of high strength poly(vinyl alcohol) hydrogel which contains poly(sodium acrylate), PVA-PAA gel, in an electrolyte solution under the influence of an electric field has been studied. A micro robot with several soft fingers consisting of the PVA-PAA gel and two Pt electrodes was designed. This biomimetic machine could catch and release an object in an electrolyte under a DC electric field.
Simulation of Bifunctional Palladium Membrane Reactor


The performance of a bifunctional membrane reactor using Pd which can function both as a H₂-permeable membrane and as a catalyst for oxidation, has been studied utilizing isothermal and adiabatic models. Under an isothermal condition, the dehydrogenation taking place in a catalyst packed bed was enhanced owing to a continuous removal of the H₂, produced in the course of reaction through the membrane. H₂ removal was remarkably increased by the subsequent hydrogenation on the Pd surface of the permeation side. The adiabatic model shows further enhancement of dehydrogenation.

ELECTRICAL AND ELECTRONIC ENGINEERING

Platinum-Platinum Oxide Gate pH ISFET


Platinum-platinum oxide gate ISFETs (ion sensitive field effect transistors) have been designed and fabricated for a stable pH microsensor. The Pt-Pt oxide ISFET was found to be more stable than a Si,N, bare gate ISFET. The Pt oxide layer, formed by a solid-oxide ISFET was found to be more stable than a Si,N, bare gate ISFET. The Pt oxide layer, formed by a new process using an RF sputtering technique, was identified as PtOₓ by XPS.

Evidence for Multiple Barrier Heights in p-Type PtSi Schottky-Barrier Diodes from I-V-T and Photoresponse Measurements


Current-voltage-temperature (I-V-T) characteristics of p-type moderately doped PtSi Schottky barrier diodes have been measured at 77–120 K, and it was thought that the barrier formed at the metal-semiconductor interface is not homogeneous, but made up of multiple barriers. A normal distribution of barrier height fits the distribution remarkably well, and a mean barrier of 0,242 eV with a standard deviation of σ = 0,011 eV is obtained. Further evidence of multiple barriers is given.

Pt/Ti Ohmic Contacts to Ultrathin Carbon-Doped p-GaAs Formed by Rapid Thermal Processing


Adding C doping of 1 x 10²⁰ and 5 x 10²⁹/cm² to p-GaAs layers enables low resistance ohmic contacts of 7 x 10⁻⁴ and 8 x 10⁻⁷ Ωcm², respectively, to be made with Pt/Ti metallisations. The electrical properties of the contacts to C-doped GaAs are temperature independent up to 500°C. The carrier transport mechanism was a field emission quantum-mechanical tunnelling.

Recording Experiments in Magneto-Optical Disks Using Ultrathin Co/Pt and Co/Pd Media


Ultrathin Co/Pt and Co/Pd films were deposited on photopolymer glass substrates with a double layer disk structure. Successful thermomagnetic writing was made in these magneto-optical disks by a relatively low laser power > 3 mW. The C/N ratio was 50 and 45 dB for Co/Pt and Co/Pd, respectively, at a bit length of 5 µm. The recorded bit domains were very clear and regular even at the shorter bit length.

Magneto-Optical Recording in Co/Pt Multilayers


Studies of magnetic and magneto-optical properties as well as recording performance have shown that Co/Pt layered structures can be successfully applied in magneto-optical recording. Two different structures were studied: 4Å Co/9Å Pt layers and 4Å Co/18Å Pt. Lorentz microscopy was used to show that very regular domains can be written in these layers. The results are related to measured recording performance.

Magneto-Optical Kerr Rotation Spectra and Perpendicular Anisotropy in Compositionally Modulated Multilayer Films of Co/Pt and Fe/Pt


Magnetic compositionally modulated multilayer films (CMFs) of Co/Pt and Fe/Pt have been prepared and their structure characteristics such as magneto-optical Kerr rotation (θₖ) spectra, and magnetic properties have been studied. An enhancement of θₖ was observed at wavelengths about 290 and 250 nm in Co/Pt and Fe/Pt CMFs, respectively. It was found that Fe/Pt CMFs turn into perpendicularly magnetised films in the same manner as Co/Pt CMFs when the Fe layer becomes thinner than about 5Å.

Magneto-Optical Effects in Compositionally Modified Co/Pd Thin Films


The magneto-optical effects in compositionally modulated Co/Pd thin films have been studied by measuring both the polar Kerr and ellipticity loops at a wavelength of about 780 nm. A squared magneto-optical Kerr rotation of magnitude ± 20° was measured in such Co/Pd thin films.
Crystallization of TeO$_2$-Pd Films for Optical Recording Materials


The crystallisation speeds of TeO$_2$ films can be substantially enhanced (to around 300ns) by the addition of Pd, so that TeO$_2$-Pd thin films become suitable candidate materials for write-once optical recording. The crystallisation of TeO$_2$-Pd films has been studied by differential thermal analysis, X-ray diffraction and transmission electron microscopy. The optical transmittance changes accompanying crystallisation are not monotonous, but step-wise with increasing annealing temperature. Although laser irradiation is considered to cause melting of the film by heating the film to >740°C, the degree of crystallinity and the grain size in laser recorded spots was similar to those in films annealed at 270°C.

**Low Resistance Ohmic Contacts onto n-InP by Palladium Electroless Bath Deposition**


A new electroless Pd deposition bath is described, which is highly stable and shows deposition speeds around 0.8 μm/h. The morphology and structure of the Pd film and the deposition mechanism of the Pd have been studied. Just after deposition, Pd metal is present with a crystallised compound like InPd. This phase evolves with annealing temperature to InPd, InPd$_2$, In$_3$Pd. Specific contact resistance of $\rho_C = 5 \times 10^{-7}$ Ωcm$^2$ has been obtained in the annealing temperature range 300–350°C. This value is held even after 20h of an annealing temperature of 400°C.

**Possibility of LiPdH$_2$ as a New Ionic Superconductor**


Local-density-approximation-based electronic-structure calculations for the compound LiPdH$_2$ indicate that it may be a metal with substantial ionic character. The band-structure results were used to calculate the McMillan-Hopfield parameters within the rigid muffin-tin approximation. These parameters have values close to those of PdH$_2$, which shows that LiPdH$_2$ may be a good superconductor.

**Application of Electroless Ruthenium Deposits for Electronic Materials**


The characteristics and applicability of electroless Ru deposits for connectors in the electronics industry has been studied. Electroless Ru deposited in a bath containing hydrazine hydrate as a reducing agent is a hard coating and a deposit of <1μm shows good resistance to corrosive fumes and solutions. Contact resistance remains <100mΩ after exposure to such environments. It is concluded that electroless Ru is a good candidate for electrical contacts.

**Advanced Double Layer Capacitors**


A three-dimensional RuO$_2$-ionomer composite structure has been successfully formed and could lead to a high-energy-density electrochemical capacitor. An ionomer ionic linkage appears to be provided throughout the composite structure. The all-solid electrochemical capacitor concept offers the advantages of greater reliability and safety. Capacitance values of approximately 0.6 F/cm$^2$ were obtained.

**TEMPERATURE MEASUREMENT**

The International Temperature Scale of 1990 (ITS-90)


An English version of the official French text of the ITS-90 is reproduced, and is authorised by the Comité Consultatif de Thermométrie and approved by the Comité International des Poids et Mesures. The International Temperature Scale of 1990 is defined. Between the triple point of equilibrium hydrogen (13.8033 K) and the freezing point of silver (961.75°C) the International Kelvin Temperature ($T_K$) is defined using Pt resistance thermometers.

**Thin Film Platinum Resistance Thermometer for Measurements in High Magnetic Fields**


The resistivity of thin Pt films at high magnetic fields, up to 140 kOe, was measured at 30 and 77 K. The films were deposited by magnetron sputtering on an Al$_2$O$_3$ substrate. A Chebyshev type polynomial description is given at zero magnetic fields of the function $R(T)$ in the temperature range 10–300 K. The sensitivity of the new sensors was better at temperature <100 K, than that of a wire thermometer.

**MEDICAL USES**

The Coordination Chemistry of Platinum Anticancer Drugs and Related Compounds with DNA


A review of the literature on the mode of action of various Pt anti-cancer drugs is presented. The progress made in understanding the interactions of Pt(II) with a specific macromolecular receptor, DNA is highlighted by considering the kinetics of binding, the regioselectivity and structure of DNA adducts and mechanism of actions. Pt compounds as DNA intercalators and linked Pt-intercalator complexes are also considered. (198 Refs.)