ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Thermal Stability of Coevaporated Al-Pt Thin Films on GaAs Substrates


Coevaporated thin films of Al-Pt on GaAs with Al concentrations between 45–70 at.% have suitable thermal stability in the composition range between AlPt and AlP for use in self-aligned gates on GaAs. The AlPt thin films have excellent adhesion properties, and increased stability compared to Al-Ni alloys.

Formation of Single-Phase PtAs Films on GaAs by Selective Oxidation and Etching


The oxidation of pre-reacted Pt films on (100) oriented n-GaAs substrates was studied at 550–750°C using Auger electron spectroscopy and Xe⁺ ion profiling. The GaPt/PtAs/GaAs structure formed during annealing in H₂, was oxidised using a mixture of H₂O vapour and H₂. The GaPt phase can be oxidised totally, whereas the inner PtAs; and GaAs interfaces are left unoxidised. The oxidation of the Pt-Ga phase is self-limited by the diffusion of the Ga through the Ga oxide overlayer. The oxide can be etched off to leave PtAs; on the GaAs substrate.

Reaction between Cu and PtSi with Cr, Ti, W, and C Barrier Layers


Studies of the reaction and thermal stability between Cu and PtSi with several barrier layers, Cr, Ti, W and amorphous C showed that Cu reacts with PtSi around 350°C. The low thermal stability of the Cu/PtSi structure is attributed to the high affinity of Cu to Si, with the Cu silicide formation starting around 200°C for a Cu/Si structure. Using an amorphous C barrier for the Cu/PtSi structure, a small amount of Cu silicide is observed at 400°C, but not at 660°C.

Specific Heat of a New Dense-Kondo System CeTIn (T = Ni, Pd, Pt)


Specific heat of a newly-found dense-Kondo system CeTIn (T = Pt, Pd, Ni) was measured at 60mK–80K. For CePdIn and CePtIn, the ratio of specific heat to temperature, C/T, increases greatly below 10K, indicating the heavy-fermion nature.

Electrical Resistivity of High Pressure D₂-Loaded Pd and Ti at Low Temperatures


The absorption and desorption of the D in Pd and Ti has been studied at pressures 5–90 atm by measuring their electrical resistivity under cyclic conditions of temperature from 77 K to room temperature. D starts to be absorbed in the bulk of Pd metal at >270 K and is not absorbed in Ti below the room temperature.

The Adsorption of CO on Pd Thin Films on Ta(1 10)


Studies of CO adsorption on Pd overlayers on a Ta(110) single crystal substrate were performed using TPD of Pd, AES and LEED. By directly using CO TPD, the Pd monolayer (ML) only weakly absorbs CO. The CO adsorption energy increases with Pd film thickness, returning to the value for bulk Pd for a 3 ML Pd film. Pd was shown to grow in a layer-by-layer mechanism at 77 K. Pd films annealed to 1075 K resulted in extensive alloy formation. However, the alloy is capped by a Pd monolayer that has a structure and surface chemistry identical to the as-deposited 1 ML Pd film formed at lower temperatures.

Solution of Hydrogen in Cold-Worked and Annealed Pd₉₅Ag₅ Alloys


The effect of cold-working and subsequent annealing on the H solubility of a Pd₉₅Ag₅ random substitutional alloy has been examined. A correlation between physical properties such as electrical resistance and hardness with H solubility has been made. Detailed data have been presented for the solubility at 323 K following annealing from 373 to 1073 K. The solubility correlates with mechanical property changes.

Laser Vaporization Generation of PdCH₃, ¹⁰⁵PdCH₃, and Pd¹³CH₃ for Electron Spin Resonance Neon Matrix Study at 4 K


The title radicals have been generated by reactive laser vapourisation and isolated in neon matrices at 4 K for ESR investigations. The results allow an experimental description of the electronic structure in the valence region to be obtained.
Auger Studies of the Effect of Mo, V and Pd Additions on the Oxidation Characteristics of Fe-24Cr Alloy
Studies of the effect of Pd, Mo and V additions on the oxidation behaviour of the Fe-24Cr alloy oxidised in air at 500°C were performed. The addition of 1 wt.% of Pd to the Fe-24Cr alloy was sufficient to promote the formation of a thinner oxide film than on the alloy without the Pd addition. There was no synergistic effect between Pd and Mo, or Pd and V in reducing the oxidation rate of the Fe-24Cr alloy.

Phase Relations in the Pd-Ti System
The Pd-Ti system was studied using differential thermal analysis, X-ray diffraction, electron probe microanalysis and reflected light microscopy. New phase relations in the 0-50 at.% Ti portion of the binary system are proposed. Eight binary phases exist in the system: Pd49Te, Pd31Te58, Pd30Te70, Pd24Te76, Pd,Te3, PdTe and Pd3Te2. Crystal structures, physical and optical properties of the phases in the system are reported.

Crystallization of Amorphous Ti-Pd
Studies of the phase formation in the Ti-Pd alloy system were performed by a physical vapour deposition technique. Upon heating this thin film amorphous structure, a direct transformation to a high temperature b.c.c. phase occurred, followed by ordering and phase separation. The amorphous structure and transformation were analysed using X-ray diffraction, hot stage transmission electron microscopy, Auger electron spectroscopy and differential scanning calorimetry.

Glass Transition Behavior of an Amorphous Pd48Ni32P20 Alloy Produced by Mechanical Alloying
A pre-alloyed Pd48Ni32P20 ingot with mixed compound phases was amorphised by mechanical alloying (MA) for periods longer than 72 ks (20h). The amorphous powder exhibits a large exothermic reaction due to irreversible structural relaxation, followed by a distinct glass transition to a supercooled liquid before crystallisation. Compared with the data on an amorphous Pd45Ni55P5 alloy prepared by liquid quenching, the onset temperature of structural relaxation decreases with an increase of the heat of structural relaxation at low temperatures <450 K. The results showed that the MA-induced amorphous phase has a disordered structure with more pronounced short-range ordering and contains a larger milling-induced stored energy.

A Study of Chemisorption Behavior of Carbon Monoxide on Rhodium Surfaces
A study of the chemisorption behaviour of CO on Rh(111), (001) and (113) planes and their vicinal stepped surfaces at low coverage was performed using a high resolution voltage-pulsed atom-probe. The results showed that CO is adsorbed only molecularly on the Rh(111) and (001) planes and with a trace of dissociation on the higher index (113) plane. It was found that closely spaced step and kink sites play a major role in promoting dissociation of adsorbed CO under the experimental conditions.

Study of the Fe-Rh-S Phase Diagram in Fe-Rh-Rh3S4-FeS1.09 Field
The Fe-Rh-S phase diagram was studied in the composition range Fe-Rh-Rh3S4-FeS1.09 by physico-chemical analysis and the existence of non- and monovalent eutectic and peritectic equilibria were observed. Studies performed in a broad range of temperatures and phases showed the presence of a Rh-containing pyrrhotinic solid solution of (Fe,Rh)1-xS.

Interfacial Reactions in the Ir/GaAs System
Interfacial reactions between Ir and GaAs in thin film and bulk forms were studied at 400-1000°C using TEM, energy dispersive X-ray analysis and electron probe microanalysis. The diffusion path was found to be Ir/IrGa/IrAs/GaAs and is consistent with the phase diagram between the initial stages of reaction (thin film) and long term annealing (bulk). For thin films, where the Ir supply is limited, the final configuration is Ir/Ga/IrAs/GaAs. Interfacial reactions between Ir and GaAs resulted in void formation at the GaAs interface.

Formation of Powder of Bi2Ru3O7 during Thermolysis of Products of Hydrolytic Deposition of Ruthenium and Bismuth
Studies were performed of formation of Bi2Ru3O7 powder during thermolysis of 0.1 M solutions of K1[Ru2OCl9] in HCl (pH=0.9) and Bi(NO3)3 in HNO3 (pH=0.4), which were mixed in equimolecular ratio followed by addition of a 20% solution of NaOH until the pH was 9.5-10.0. The heating of hydrolytic Ru and Bi deposits to 320°C resulted in their dehydration, retaining their mesoporous structure. At 320-500°C formation of mixed phases Bi3Ru4O11 and Bi2Ru3O7 occurred.
CHEMICAL COMPOUNDS

Formation of Platinum and Palladium Clusters with Carbonyl Phosphine Ligands
A general method for the synthesis of Pt and Pd carbonyl phosphine clusters has been found. Under mild conditions zero-valent Pd derivatives can form Pd₃(CO)₃ clusters with a carbonyl phosphine ligand shell of 38. The first high-nuclear carbonyl-phosphine Pt cluster has been synthesised by addition of phosphines to an oligomeric “Pt dicarbonyl” (Pt(CO))₂ in solution. However, this method only gives clusters with nuclearity not more than 5 atoms. Thermolysis of Pt₃(CO)₅(PPh₃)₄, in decane under inert atmosphere leads to Pt₃(μ-CO)₅(CO) in 14% yield.

Kinetics and Mechanism of Reductive Elimination of Hydrocarbons from (μ-H)Ru₃(μ₂-CX)(CO)₉ (X = Ph, Et, Cl, CO₂Me, SET, CHPPhCH₂Ph)
A study of the mechanism of reductive elimination of C-H bonds from the title compound under CO, yielding Ru carbonyls and alkanes or alkenes is presented. With β-hydrogens present alkenes and Et inverse deuterium isotope effects were measured. The proposed mechanism involves a sequence of C-H reductive eliminations, each of which is preceded by reversible migration of H from Ru-H-Ru bridging to Ru-H-C bridging. The rate determining step at high CO pressures is cleavage of the first Ru-H-C bond.

ELECTROCHEMISTRY

Changes in the Surface Morphology of Platinum Electrodes Produced by the Application of Periodic Potential Treatments in Alkaline Solution
The development of preferentially oriented crystalline surfaces of Pt with rough topographies in alkaline solution, produced by the application of a potential periodic square wave, is described. The effect of electrical variables is studied, and the different growth modes are followed by voltammetry in the H atom electroosorption potential range and by SEM micrographs. Strong OH⁻ ion-metal surface interactions are thought to favour the formation of hydrate Pt oxide layers. The electroreduction of the latter yields Pt overlayers with distinguishable growth modes and preferred crystalline orientations.

Co-adsorption of Bismuth with Electrocatalytic Molecules: A Study of Formic Acid Oxidation on Pt(100)
The adsorption of Bi and co-adsorption with CO, O₂, H₂O and HCOOH on Pt(100) surfaces was investigated by LEED. The “hex” reconstruction of clean Pt(110) is gradually and completely lifted by increasing Bi coverage to 0.25 monolayers (ML); saturation coverage is 0.5 ML. Bi < 0.25 ML has moderate attractive interactions, but repulsive interactions occur for higher coverages. Each adatom blocks two CO molecules and two O atoms. Bi is not hydrated by coadsorbed H₂O and a Pt(100) surface with 0.2 ML Bi is hydrophobic. Clean and Bi covered Pt(100) are inert to HCOOH.

Multilayer Oxide Growth on Platinum under Potential Cycling Conditions. – I. Sulphuric Acid Solution
Hydrous oxide growth on Pt under potential cycling conditions in 1.0 mol/dm³ H₂SO₄ yielded either a single or a two component product; the latter gave rise to two major reduction peaks in the region below 0.4 V. The Pt electrode was conditioned before use by a preliminary etch in aqua regia, followed by repeated hydrous oxide growth and reduction runs.

The use of a smooth electrode for DEMS is discussed. A new design thin-layer cell is presented and its feasibility is demonstrated for the cathodic desorption of benzene adsorbed on annealed Pt in 0.5 M H₂SO₄. Partial desorption in the H region occurred and complete desorption was only achieved under hydrogenation to cyclohexane at more negative potentials. Studies with C₂D₄ showed that no C-D bond rupture occurs upon adsorption. Various degrees of H/D exchange occur in the adsorbate.

Rapid Redox Reaction of Hemoglobin at Methylene Green Modified Platinum Electrode
The electrochemical processes of methylene green (MG) were studied using spectroelectrochemistry by in situ measurements in an optically transparent thin layer cell with the working electrode made of a piece of Pt gauze. A Pt auxiliary electrode and a Ag/AgCl reference electrode were used. A well-defined cyclic voltammogram of haemoglobin at the MG modified Pt electrode was observed.
The Influence of Electrode Porosity and Temperature on Electrochemical Gas Evolution at Platinum and Rhodium

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Electrodes of smooth Pt, platinised Pt, smooth Rh and Pt coated with an electrochemically plated layer of Rh were used to examine electrochemical gas evolution, using 0.5M H₂SO₄ for H evolution and 4M NaCl for Cl evolution. The pores are only effective for an irreversible gas evolving process (as with O₂), but its rate can be accelerated by increasing the porosity of the electrode surface layer and by increasing the temperature. For Cl or H evolution, which are reversible, the small pores of the surface layer do not operate if the overvoltage is determined by the gas supersaturation. Temperature dependencies of the rate of the Cl and H processes are different; the rate for Cl evolution increases with rising temperature.

Oxide Formation and Reactivity for Methanol Oxidation on Platinised Carbon Anodes


A XPS study of Pt and Pt+Ru PTFE bonded C electrodes for methanol oxidation in acid solution was performed. The role of Pt oxides in deactivating the Pt:C electrodes is discussed. Ru was found to act by promoting the formation of Pt-OH groups on Pt + Ru:C electrodes and a possible mechanism is presented. The effect of periodic potential relaxation steps on the life performance of the electrodes is presented. The results also showed that formation of inactive oxides groups on Pt:C electrodes appears to be improved by the presence of methanol.

Electroreduction of Gaseous Ethylene on a Platinized Nafion Membrane


The electroreduction kinetics of gaseous C₂H₄ on a platinised Nafion 117 membrane was studied at 1 atm, 20 or 100 mole % and 30°C<T<70°C, by polarisation and product measurements. The diffusion of hydrazine controlled the overall rate of the deposition, and the resulting metal was either dense (film like) or spongy (moosy like), depending on whether a high or low concentration, respectively, of platinic acid was used. The Pt deposit of the film morphology electrode was thinner and less porous. The Pt deposit of the film morpholgy electrode was thinner and less porous.

On Electrochemical Tritium Production


Tritium was formed in LiOD-D₂O solutions in which Pd cathodes are used to evolve D₂. Electrolysis was carried out for up to 4½ months, and excess heat was observed from 5 electrodes out of 28; T in 15 out of 53, but 9 out of 13 if the electrodes are of 1 mm diameter. The T production was ~ 10⁸ atoms/cm² s.

Thermal Neutron Measurements on Electrolytic Cells with Deuterated Palladium Cathodes Subjected to a Pulsed Current


The design of a highly efficient thermal neutron detection system is presented and the measurements are performed with it on electrolytic cells containing LiH dissolved in D₂O with Pd cathodes. A clear correlation between neutron production response and the pulsing of the electrolytic current through deuterated Pd cathodes is observed in a repeatable manner. The patterns are strongly dependent on the previous charging history of the cathodes. The technique appears to be useful in studies of the different variables of the cold fusion phenomenon.

Electrocatalysis on Microprecipitates of Palladium on Glassy Carbon Deposited at Various Potentials


Studies of the catalytic properties of Pd precipitates deposited on glassy C during various deposition potentials were performed during cathodic reactions of H₂ evolution and electrohydrogenation of acetophenone. The results showed a strong effect of Pd deposition potentials on the activity of the catalysts. The most effective catalysts were deposited at potential E=0.6 V.

Pt-Ru Anodes for Methanol Electrooxidation: A Ruthenium-99 Mössbauer Study


*Mössbauer spectra were obtained for a series of Pt-Ru methanol oxidation anodes. The presence of Ru(IV) species with a small quadrupole splitting was observed for the most catalytically active sample. For highly dispersed samples the data indicate that the Ru is present as a mixture of rutile-phase RuO₂ and a second Ru(IV) species. Comparison with electrocatalytic results suggests that the second Ru(IV) species is the active catalytic copromoter.

Electrochemical Reduction of Carbon Dioxide on Conductive Metallic Oxides


Faradaic efficiencies and I-V characteristics for the reduction of CO₂ on various conductive mixtures of Rh₂O₃, RuO₂, TiO₂, MoO₃ and Co₂O₃ were determined. Electrodes of RuO₂ + TiO₂ and of RuO₂ + Co₂O₃ + SnO₂ + TiO₂ show high current efficiencies for CH₄OH production when polarised near the equilibrium potential of H evolution in Na₂SO₄ solutions saturated with CO₂. Longtime polarisation shows good stability.
Formation and Properties of Highly Dispersed Electrolytic Deposits of Iridium on Carbon Fibre


Studies of the effect of deposition conditions on the formation and properties of Ir deposits on C fibre showed a strong effect of state of oxide groups on the surface of the C fibre. Highly dispersed Ir deposits were obtained during electrodeposition of Ir³⁺ on fibre subjected to reductive treatment. Electrocatalytic activities of Ir/C electrodes, obtained under various conditions, during the electro-oxidation of methanol and formic acid were compared.

A Lead-Iridium Pyrochlore Based Bifunctional Oxygen Electrode


Pb-Ir pyrochlore displays no change in its cyclic voltammogram over repetitive scans and can function as a stable bifunctional air electrode catalyst in a specific electrode configuration, thus preventing the erosion of the electrode by O evolution under high oxidation potentials during the recharge of metal/air cells. Thus this pyrochlore may be useful for energy storage in a secondary metal/air cell.

Study of Energy Saving Anodes in Metal Electrowinning

X. LI, Y. LIANG and N. LI, Youse Jinshu (Jikan), 1990, (2), 61-66

The lifetime of newly prepared IrO₂/PAN coated Ti activated anodes was measured by an accelerated lifetime test method at the anodic current density 20,000 A/m² in a Zn electrowinning electrolyte. An excellent activated anode with low O₂ evolution over-potential (150g H₂SO₄/l, 35°C, i = 500 A/m², n = 0.25 V) and long lifetime (t = 20,000 A/m², t = 13,8 h) was developed. The anodes can be used in metal electrowinning due to their being relatively cheap to produce and can save about 20% of the energy needed in the electrolyte cell.

Triruthenium Cluster-Polypyrrole Films: A Remarkably Stable Immobilized Relay at Highly Positive Potentials. Its Application to the Electrochemical Oxidation of Benzyl Alcohol


Ru clusters, of general formula [Ru₃O(OOC-CH₃)₄][L₄]⁺, as thick or thin film modifiers on Pt or C disc electrodes perform bulk electrocatalytic reactions. Thin polypyrrole films covalently substituted by μ-oxo-carboxylate clusters show high chemical and electrochemical stability, especially in the positive potential region. Thus, successful redox catalysis of the oxidation of benzyl alcohol was achieved.

Mechanism of Simultaneous Reaction of Acid-Base Ligands in [Ru(bpy)₂NOOH]²⁺


Studies of the mechanism of simultaneous reaction of acid-base conversion of [Ru(bpy)₂NOOH]²⁺ to [Ru(bpy)₂NO,H,O]²⁺ were performed under pseudo-monomolecular conditions ([OH⁻] = const).

The reaction mechanism proposed includes a stage of conjugated interaction of co-ordinated NO and OH with H₂O.

PHOTOCONVERSION

Preparation and Characterization of Pt(RuO₂)/TiO₂ Catalysts: Test in a Continuous Water Photolysis System


Aqueous suspensions of Pt(RuO₂)/TiO₂, photocatalysts, with Pt reduced by different techniques, were irradiated with UV light in a photoreactor with a continuous gas phase composed of Ar and photoprodus. Performance of the catalysts in the H₂O-splitting process was related to the different reduction methods by considering the physical characteristics of the powders, both the deposits and supports, such as crystal structure, specific surface area, particle size, quality of the metal dispersion and also of the oxidation state and doping changes caused by the techniques. The catalytic role of RuO₂ was specifically studied in connection with the preparative treatments followed.

Characteristics of Photoelectrochemical Cells Based on n/n⁺-Si and p/n⁺-Si Photoanodes Modified by Metal Films


Photoelectrochemical cells composed of different epitaxial n-Si photoanodes coated with evaporated metal films of Pt, Pr/Ni, Ni, and immersed in solution with redox couple Br⁻/Br²⁻ or Fe(CN)₄³⁻/Fe(CN)₄⁻² were investigated. The open circuit photovoltage and short circuit current density under optimum conditions were 0.494 V and 45.8 mA/cm², respectively.

Photoysis of Azomethane Adsorbed on Pd(111)


The photoysis of azomethane (CH₃N=NCH₃) adsorbed on Pd(111) was studied under ultrahigh vacuum conditions using TPD. In the condensed multilayer, photolysis breaks the C-N bond of azomethane, producing CH₃ radicals and N₂. The N₂ desorbs directly during photolysis at 87 K. The reaction of photoically generated CH₃ radicals with chemisorbed D atoms on Pd(111) has been observed to yield CH₃D below 150K.
Competitive Hydrogen Production and Emission through the Photochemistry of Mixed-Metal Bimetallic Complexes


The monometallic dihydride complexes RhH₃(PPh₃)₂, L⁺ undergo photochemistry and photophysics from two different excited states. Photophysics occurs from metal-to-ligand charge-transfer (MLCT) excited state generated by promotion of an n*-symmetry electron from Rh(III) into a π* orbital on L. When L is 2,2'-bipyrimidine (bpm), dpp, or dpq, results in the homonuclear photophysical properties of Ru(bpy)²⁺ are compared to those of Ru(bpy)²⁺ for the reduction of CO₂ to CH₄. The former is a superior photosensitizer for H₂ evolution and CO₂ reduction in the presence of Ru colloid as catalyst, with improved quenching of the excited state and effective charge separation of the primary encounter cage complex.

ELECTRODEPOSITION AND SURFACE COATINGS

Catalytic Anodes for High-Speed Electroplating and Electrogalvanizing


A comparison is given of insoluble anodes for high speed plating and electrogalvanising using valve metals with a coating of oxide mixtures, including Pt group metals oxides. It emphasises the advantage of catalytic anodes over Pb alloys. For electrolytic processes involving the anodic evolution of O₂, catalytic anodes such as the dimensionally stable anode (DSA) electrode are capable of stable, extended performance over a wide range of current densities. By comparison with Pb or PbO₂, the catalytic anode can substantially reduce the cell voltage and the energy required for electrolytic processes.

Electrodeposition of Silver onto Electrodes Coated with [Os(bipy)₂(PVP)₉Cl]Cl


Electrochemical deposition of Ag onto glassy C electrodes modified with the redox polymer [Os(bipy)₂(PVP)₉Cl]Cl, where bipy is 2,2'-bipyridyl and PVP is poly-4-vinylpyridine, was studied using cyclic voltammetry. For electrodes coated with the analogous Ru containing polymer (Ru(bipy)₂(PVP)₉Cl]Cl no electrodeposition was observed.

APPARATUS AND TECHNIQUE

Application of Pd Silicide in the Process of Silicon Detectors


A self-aligned metal-silicide process is described which improves detector leakage current, detector yield and junction contact resistance. A method of implanting impurity ions into Pd, Si uses a lift-off technique for fabrication of Si detectors for high energy physics. The method does not need a new mask step in the existing detector fabrication process, and may be used with other refractory metal silicides.
HETEROGENEOUS CATALYSIS

Gas Phase and Catalytic Ignition of Methane and Ethane in Air over Platinum


Fine wire experiments have been used to determine the kinetic rate data for C,H, and CH, oxidations on Pt at high temperatures. Under ultra lean conditions the oxidations have different mechanisms. Gas phase ignition of fuel-air mixtures by heated catalytically active surfaces involves dynamic surface and gas phase processes, and the independent monitoring of these two is discussed. The sharp maximum in surface temperature needed for gas phase ignition observed previously is caused by transient heating of the surface as ignition occurs.

Carbon Deposition on Supported Platinum Particles


Studies of coke formation and the associated changes in Pt particle morphology in real and model reforming catalysts were performed by a combination of electron microscopy and thermogravimetric techniques. Decoking studies showed that the deposit was predominantly isotropic in nature and did not contain any filamentous or graphitic components. During the catalytic hydrogasification the Pt particles undergo a wetting and spreading action with the carbonaceous residues on the support and thus maintain a small average particle size.

Structure Sensitivity of Methane Oxidation over Platinum and Palladium


A series of supported Pt and Pd catalysts were tested for CH, oxidation at 260–370°C, 50 Torr CH, and 110 Torr O, 900 Torr He and conversion below 2%. The intrinsic rate varies by >5000 from the least active to the most active catalyst, thus indicating that the reaction is structure sensitive. The catalytic activity of Pt depends on the distribution of the metal between a dispersed and a crystalline phase, while the catalytic activity of Pd depends on the metal particle size. The mean steady state turnover frequency at 355°C and the mean apparent activation energy are given for the different classes of catalysts.

Dispersion of Platinum on Silica and Alumina by Chemical Extraction


Chemical extraction combined with transmission electron microscopy (TEM) was used to study the dispersion of Pt in a series of Pt/Al,O, and Pt/SiO, catalysts. The results obtained with standard EuroPt-I catalyst showed that the “percentage extracted” of Pt after oxidation at ~400°C was identical with the “percentage exposed” of Pt evaluated by TEM.


Pt/Al,O, and Al,O, were chlorinated by CCI, at 573 K. Adding HCl in the early stages of the n-butane isomerisation at 573 K increases the catalytic activity. Preadsorption of HCl at 573 K converts the strongest Lewis acid sites into superacid ones able to isomerise n-butane at temperatures as low as 373 K. At 573 K, the role of the Pt is to produce important amounts of HCl by dechlorination of the support and to contribute to the formation of superacid centres.

Sintering-Redispersion of Pt-Re/Al, O, during Regeneration


The effect of temperature and gas flow rate on total metallic dispersion and specific surface area of Pt-Re/Al, O, reforming catalysts was studied during the burning of coke deposited on its surface. The actual temperature inside the catalyst during coke burning is the main parameter affecting the total metallic dispersion. The metallic phase is redispersed during catalyst oxychlorination and the total dispersion at values of 0.9–1% chloride on the catalyst is the same.

Hydrocarbon Conversion over Pt-Re/Al, O,-ZSM-5 Bifunctional Catalysts. II. Sulfur Resistance of Pt-Re/Al, O, Modified with ZSM-5


Sulphur resistance of Pt-Re/Al,O, and Pt-Re/Al,O,-ZSM-5 was studied during n-heptane reforming. On the basis of selectivity and product distribution, it appears that the incorporation of S improves the aromatics performance of both catalysts. It is concluded that while S acts as a poison for the existing reforming catalyst, it can play an important role in activity maintenance and aromatics production when ZSM-5 zeolite is present in the reforming catalyst bed.

Liquid-Phase Dehydrogenation of Cyclohexanol with Supported Noble Metal Hydrogenation Catalysts


Cyclohexanol dehydrogenation and cyclohexanone hydrogenation were performed with suspended noble metal particles. The orders of initial dehydrogenation rates are Pd>Rh=Pt>Ru and Rh>Pd–Pt>>Ru obtained for the catalysts supported on C and Al,O, respectively, were different from those for hydrogenation. The suspended states of catalyst metal/C were stable. Pt catalysts were most active for hydrogenation.
Hydrogenolysis and Related Reactions of Hydrocarbons (C₃ to C₅) on Silica-Supported Rh-Pt Bimetallic Catalysts


The reactions of propane, butane, 2-methylpropane, pentane, 2-methylbutane, 2,2-dimethylpropane and cyclopentane with H₂ have been studied in a static reactor using highly dispersed Rh-Pt/SiO₂ catalysts. The main reaction was hydrogenolysis with C-C bond breakage. Most compounds reacted at similar rates over Pt with activation energies in the range 132–144 kJ/mol. With Rh the rates varied with hydrocarbon structure by factors of >10¹. Rh was more active than Pt by factors of ~200 for branched hydrocarbons and of 10¹ or more for straight-chain compounds. At temperatures >455 K there was evidence of a change of rate-determining step over Rh, with the rate of CH₃ desorption controlling the overall reaction.

Isomerisation of n-Pentane on Pt/SO₄/ZrO₂: Role of Platinum and Reaction Mechanism


Studies of the catalytic characteristics of Pt/SO₄/ZrO₂ during n-pentane isomerisation by H₂-TPD showed that the H₂ adsorption ability of Pt/SO₄/ZrO₂ is much lower than that of Pt on Al₂O₃ or ZrO₂, but that it has enough activity for the hydrogenation of ethylene and cyclopropane under H₂ atmosphere. It is concluded that the role of Pt is to hydrogenate the coke precursor which causes the catalytic deactivation.

A HREELS Investigation of Ethylene on Pt Model Catalysts


The adsorption of C₂H₄ on supported Pt model catalysts is studied with high resolution electron energy loss spectroscopy for the case of Pt vapour deposited on an oxidised Al foil and single crystal TiO₂. At 160 K, the HREELS spectra show evidence of the di-σ bonded ethylene species present on the supported Pt clusters. However, upon heating to 325 K, only the TiO₂ supported model catalyst showed evidence of forming the ethyldiene species normally seen on Pt(111) single crystals. The oxidised Al supported species begins to decompose by 250 K, and no spectra characteristic of ethyldiene were seen.

Methanation Sites on a Pt/TiO₂ Catalyst


Studies of the adsorption of H₂ and CO and the hydrogenation of CO performed by temperature-programmed desorption and reaction (TPD, TPR) on 1.8% Pt/TiO₂ catalyst showed two types of adsorbed CO: CO was adsorbed on Pt and a new complex was adsorbed on the TiO₂ support. The CO transfers rapidly from Pt to TiO₂ at methanation temperatures.

¹²⁹ Xe NMR Proof for the Distribution of Platinum Species during Pt/NaY Preparation by H₂PtCl₆ Impregnation and Pt(NH₃)₄Cl₂ Cation Exchange Methods


The distribution of Pt species during the preparation of Pt/NaY catalysts by the impregnation of H₂PtCl₆ or the cation exchange of Pt(NH₃)₄Cl₂ into a NaY zeolite was measured by ¹²⁹Xe NMR spectroscopy. More uniform distribution of Pt species in the zeolite channel throughout the ion exchange, calcination and reduction. The result was consistent with the rate of H₂PtCl₆ adsorption on the NaY zeolite in aqueous solution and the Pt metal dispersion of the Pt/NaY samples.

Hydroconversion of n-Heptane on Catalysts Containing Platinum, Rhenium and Platinum-Rhenium on Sodium Mordenite


The hydroconversion of n-heptane on catalysts containing Pt, Pt-Re and Re on Na mordenite (NaM) was 61, 25 and 22 wt.%, respectively, at 400°C, 3.6 MPa, F/W=1.2 (vol. n-heptane (vol. catalyst)-1), and a H:n-heptane molar ratio of 10:1. The production of heptane isomers was 38 wt. % on Pt/NaM but <1% on the others under the same conditions. The metal dispersion in NaM was highest for Pt/NaM and lowest for Pt-Re/NaM while the total acidity and strength of acid sites were lowest for Pt/NaM and highest for Re/NaM. The weaker acidic character, assisted by Na⁺ ions combined with the higher dispersion of Pt in NaM appears to increase the isomerisation activity of the Pt/NaM catalyst and decrease the cracking activity.

X-ray Photoelectron Spectroscopy Study of Supported Noble Metal Catalysts Prepared by Spontaneous Electrodeposition


The chemical composition of the catalytic coating layer formed by the spontaneous electrodeposition of Pd and Pt on a stainless-steel support, under various catalyst preparation conditions for the purification of enamelling furnace exhaust gases was studied by XPS. The effect of the sequence of Pt and Pd deposition from separate baths on the noble metals content in the surfactant layers of the catalyst was observed. Addition of surfactant to the electrolyte resulted in a change in the relative concentration of noble metals in the coatings formed by successive deposition.
Relationship between Selectivity and Hydrogen Sorption of Carbon-Supported Palladium Catalysts


The relationship between the catalytic activity, selectivity and the H content of C-supported Pd catalysts was studied by examining how certain parameters, such as the duration and the medium (liquid or gas phase) of the prehydrogenation of the catalyst, control the amount of H sorbed on 10% Pd/C catalysts. The hydrogenation of allyl alcohol was studied at room temperature and 1 bar in 0.05 mol/dm³ H₂, SO₂, or Na sulphate solution. It was found that there is a relationship between the H content of a catalyst and the proportions of reduction and isomerisation. Surfaces poor in H favour isomerisation and those rich in H favour reduction. Under certain conditions the proportion of isomerisation may be as high as 70%.

Metal-Support Interaction in the Pd/SiO₂ System: Influence of the Support Pretreatment


Studies of the strong metal-support interaction in the Pd/SiO₂ system showed that heating of the Pd/SiO₂ in H₂ may lead to chemical (strong) interaction between metal and support, and growth of Pd₃Si. The magnitude of metal-support interaction, the agglomeration of metal particles, and the formation of an intermetallic compound are strongly affected by the thermal treatment of the SiO₂ substrate. The presence of SiOH groups on the SiO₂ allows metal particle migration and growth by coalescence, while for the OH-depleted SiO₂ the particle size changes proceed by atomic diffusion.

Alkali Addition to Silica-Supported Palladium: Infrared Investigation of the Carbon Monoxide Chemisorption


Studies of the effect of addition of alkali nitrates (Li, Na, K, Ca) to Pd⁹⁺/SiO₂ precursor after reduction under H₂ showed that the addition results in a moderate increase in the metallic particle size, but to drastic changes in the infrared spectrum of CO adsorbed on Pd. A direct interaction between the alkaline ion and CO bonded to Pd was observed and its extent increased with the reduction temperature. The behaviour of Li-doped solids is discussed.

Silica-Polyvinylpyridine-Pd(II) Complexes as Hydrogenation Catalysts

J. P. MATTHEW and M. SRINIVASAN, Chem. Ind., 1990, (8), 262–263

Silica supported polyvinylpyridine-Pd(OAc)₂ and -PdCl₂ complexes have been prepared and found to be very active catalysts for the hydrogenation of alkenes at room temperature and 1 atm. They are also more stable than other polymer-supported catalysts.

Catalytic Oxidation of L-Sorbose on Pd-Bi/Adsorbing Resin Catalysts


Supported bimetallic Pd-Bi catalysts were prepared by impregnating the non-polar polystyrene-divinyl benzene crosslinked adsorbing resin (D3520) with a solution of PdCl₂ and BiCl₃. The Pd-Bi/D3520 catalyst had good activity and selectivity for the oxidation of L-sorbose, which could be oxidised in one step into 2-keto-L-gulonic acid. Pd and Bi in the catalyst were identified as PdBi₀ or Pd,Bi phases by XRD measurements. The interaction between support and metals was confirmed; the active centre of the catalyst being in the form of Pd²⁺ + O²⁻ + Bi³⁺.

Hydrocarbon Conversions with Some Intermetallic Catalysts


The intermetallic pseudo-binary alloys ZrRhₓ₋ₓPdₓ and ZrRhₓ₋ₓRuₓ (0<x<3) were prepared, powdered and used as catalysts for the hydrogenation of oct-1-yn in the liquid phase at 101.32 kPa pressure and 70°C, hydrogenation of buta-1,3-diene in the gas phase at 101.32 kPa pressure at 45–225°C, and hydrosilylation of n-pentane in the gas phase at the same pressure and 200–400°C. Activities and selectivities for alkene formation for the hydrogenations and C₂ + C₃-alkane formation for the hydrosilylation were measured.

Structure Changes of Finely-Dispersed Rhodium Double Oxides on Silica Gel and Their Catalytic Properties


Rhodium double oxides, RhNbO₄, MoRhO₄, MnRhO₄ and CuRhO₄, were prepared as finely-dispersed states on a SiO₂ gel and their structural changes during reduction/oxidation treatments were studied. Fine particles of RhNbO₄ showed very high catalytic activities in hydrogenolysis of ethane and dehydrogenation of cyclohexane. The results suggest the important role of a highly-oxidised state of Rh ion, such as Rh⁹⁺.

Carbon Dioxide Reforming of Methane with Supported Rhodium


Rhodium supported on γ-Al₂O₃ was an effective catalyst for reforming CH₄ with CO₂ at low ratios of CO₂:CH₄. Kinetic experiments on a 0.5 wt.% Rh/Al₂O₃ catalyst gave rate equations for the reforming and shift reactions. A model was described for conversion in a pellet by incorporation of both the reverse reaction and the effect of external and internal diffusion. Adjustable factors were determined by matching measured temperature profiles.
Oxide dehydrogenation of Alkylbenzenes on Rh/AIPO₄ Catalysts

The oxidative dehydrogenation of several alkylbenzenes was performed at 673–823 K on Rh/AIPO₄. The reaction mechanism is described by the transfer of two H atoms to the molecule due to the action of the Lewis acid sites of the catalyst. This may explain the higher degree of AIPO₄ activity with respect to Rh/AIPO₄, caused by the higher number of acid sites in the support.

Promoter Effect of Alkali Metal Oxides and Alkali Earth Metal Oxides on Active Carbon–Supported Ruthenium Catalyst for Ammonia Synthesis

Promoter effects of alkali metal nitrates (Ca(NO₃)₂, KNO₃, RbNO₃) and alkaline earth (Mg, Ca, Sr, Ba) nitrates on Ru/A.C. (active C) were studied in order to prepare an effective catalyst for NH₃ synthesis. On active C, RuCl₃·3H₂O and (Ru(NH₃)₅Cl)₂ were found to be effective precursors of Ru catalysts. Alkali earth metal nitrates, especially Ba(NO₃)₂, were found to be as effective as alkali metal nitrates on Ru/A.C.

Partial Hydrogenation of Benzene with Ruthenium Catalysts Prepared by a Chemical Mixing–Spray Drying Procedure

Catalyst 1 wt.%Ru–0.1 wt.% Cu/SiO₂ for cyclohexene formation from benzene was prepared by chemical mixing and spray drying. Optimal conditions for catalyst preparation and source of support were found in order to increase cyclohexene yield. The most effective solvent for preparing the catalysts was ethylene glycol, at optimum amount 2.5–3.8 times in molar ratio to silica. When the catalysts were activated under H₂ at 400°C for 5h, the cyclohexene yield was 34.7%. Adding 1,4-butanediol and benzyl alcohol increased the cyclohexene yield to 40%.

HOMOGENEOUS CATALYSIS

A Highly Efficient Method for the Preparation of 2-Aryl Substituted Carbapenem Exploiting a Pd(0) Mediated Cross-Coupling Reaction

A remarkably mild procedure for the synthesis of 2-aryl substituted carbapenem via a Pd catalyzed coupling reaction of a vinyl triflate with aryl stannanes is described. Pd(DBA)₃, CH₃OH, where DBA is tris(2,4,6-trimethoxyphenyl)phosphine as the ligand provides generous yields of the desired β-lactams. Reaction times are brief while reaction temperatures never exceed ambient.

Desulfonylative Carbonylation of Arylsulfonyl Chlorides Catalyzed by Palladium Complexes

Carbonylation of arylsulphonyl chlorides with Pd complex catalysts in the presence of metal alkoxides M(OR)₃ (M = B, Al, and Ti) yielded the corresponding esters along with diaryl disulphides. Among the Pd catalyst precursors tested, PdCl₂[(PPh₃)₂] and Pd(PPh₃)₄, showed good catalytic activity. The reaction could also be completed with Pd(PPh₃)₄ and Ti(O-i-Pr)₄ at 160°C but decreasing the reaction temperature reduced the product yield. With metal carboxylates M(OCOR)₃ (M = Na, K, Ca, Mg and Zn), free acids are also obtained.

Palladium-Catalyzed Asymmetric Allylations of Chiral Enamines Bearing Phosphine Functionality. Effects of Anionic Counterparts of Allylating Reagents on Asymmetric Induction

Asymmetric allylations of chiral enamines bearing a phosphine group were catalysed by Pd(PPh₃)₄ using various allylating reagents to produce optically active α-allyl carbonyl compounds. A great effect of anionic counterparts of allylating reagents on the asymmetric induction was observed. This is the first example of the importance of anionic counterparts of allylating reagents in Pd-catalysed asymmetric allylations.

Phenyl-Phenyl Coupling in Triphenylantimonimy Catalysed by Palladium(0)

The Pd(0) induced coupling of phenyl groups in triphenylantimony(I) to give diphenyl and Sb(0) has been studied for possible intermediates. Two complexes containing Sb and Pd have been isolated, and their structures determined. One complex is made up of (I) co-ordinated to Pd diacetate.
Palladium-Catalyzed Carboannulation of 1,3-Dienes by Aryl Halides


The coupling of two reactions to produce a simple aryldiazo compound by 5% Pd(OAc)₂, functionally substituted aryl halides uses readily available starting materials and proceeds under mild conditions in high yield, completely stereospecifically giving a wide range of functionally substituted carbocycles. Best results were obtained by using 5% Pd(OAc)₂, 1 equiv. of n-Bu₄NCl, and carbonate or acetate bases in dimethylformamide at 60–80°C.

New Applications of Organopalladium Compounds in Organic Synthesis


The Pd-catalysed arylations and vinylations of cyclic alkenes provides a new route to 3-arylcycloalkenes and cyclic 1,4-dienes. This can be applied to the synthesis of blood platelet activating factor inhibitors and prostaglandins. Pd can migrate along C chains with Aryl Halides but it mechanistically resembles the previously reported Pd-catalysed arylations and vinylations of cyclic vinylidene carbonates was described. The Pd(o)-catalysed hetero- and carboannulation provides another convenient route to hetero- and carbocycles.

Palladium(0)-Catalyzed Carboxylative Cyclized Coupling of Propargylic Alcohol with Aryl Halides


The reaction of CO₂ with Na 2-methyl-3-buten-2-olate and aryl halides catalysed by a Pd(o) complex, Pd(PPh₃)₄, to yield cyclic vinylidene carbonates was described. The Pd(o)-catalysed reaction is different in the reaction pathway from the PdCl₂(CH₃CN)₂-catalysed carboxylative coupling of propargylic alcohols with allyl chloride, but it mechanistically resembles the previously reported Pd(o)-catalysed cyclisation followed by allylation of allylalkynoates.

Oxidative Coupling Reaction by Pd-Catalyst and Its Industrial Development

H. YAMANE, Shokubai, 1990, 32, (2), 121–122

Two new synthetic processes were developed by using an oxidative coupling reaction with Pd catalyst. The first process selectively synthesises biphenyl-3,3',4,4'-tetracarboxylic tetaester by dimerising phthalic ester in the presence of 1,10-phenanthroline Pd complex and Cu salt, while the other process produces diester oxalate by oxidative coupling of CO with Pd/C catalyst in the presence of alcohol and alkynitrile, and a combination of alkynitrile and Pd catalyst. The technologies are used in the coupling of various aromatics.

Synthesis, Characterization, and Kinetics of Functionalized Polybutadiene Using a Homogeneous Rhodium Hydroformylation Catalyst


The liquid-phase hydroformylation of a commercially available low molecular weight polybutadiene whose microstructure consists of 12 wt.% 1,2-polybutadiene and 88 wt.% cis/trans-1,4-polybutadiene using Wilkinson’s homogeneous Rh catalyst with excess PPh₃ is examined. ¹¹C and ¹H NMR studies showed that this catalyst system results in a polymer product whose olefin units are selectively converted to the corresponding internal and terminal branched aldehydes with negligible formation of hydrogenation products.

Oxidation of 2-Methylnapththalene to 2-Methyl-1,4-Napthaquinone with Ammonium Dichromate Catalysed by RuCl₃


The oxidation of 2-methylnapththalene (1) to 2-methyl-1,4-napthaquinone (2), by tetraalkylammonium dichromate and ammonium dichromate in acidic solutions of acetonitrile:H₂O catalysed by RuCl₃ was performed at 20–50°C. Increasing the temperature improves both the rate of oxidation of (1) and selectivity for (2) whereas increasing the concentration of RuCl₃ increases the selectivity rather than the rate of oxidation.

Oxidative Carbonylation of Cyclohexylamine to Cyclohexylethane Catalysed by Dichlorobis(Salicylaldehyde-o-Phenyleneiminate Ruthenate(III))


The complex [Ru(saloph)Cl₂] where saloph is bis(salicylaldehyde-o-phenylenediamine) catalyses the oxidative carbonylation of cyclohexylamine in ethanol medium to cyclohexylethane selectively at 160°C and at a CO+O₂ (1:0.50) pressure of 21 atm. A turnover number of 30 mol per mol catalyst per hour was observed. The rate of oxidative carbonylation of cyclohexylamine at 7–21 atm is first order with respect to catalyst, cyclohexylamine and dissolved CO concentrations and one-half order with respect to dissolved O₂ concentration.

New Chiral Ruthenium Complexes for Asymmetric Catalytic Hydrogenations


Mononuclear complexes, Ru(OCOR),(binap) where binap is bis(dipheny1phosphino)-1,1'-binaphthyl, and cationic [RuX(binap)(arene)]⁺ have been prepared and characterised. These complexes and their derivatives are highly efficient catalysts for asymmetric hydrogenation of enamides, allyl- and aryl-substituted acrylic acids, β,γ-unsaturated carboxylic acids, allylic and homoallylic alcohols, etc.
FUEL CELLS

Electrochemical Evaluation of Bis(tri-fluoromethylsulfonyl) Methane as a Fuel Cell Electrolyte

The kinetics of O₂ reduction on Pt were studied in a new type of perfluorinated acid, (CF₃SO₂)₂CH₂, containing acidic C-H bonds. The conductivity of this acid was higher than that of H₂PO₄ at 170°C. Even the room temperature conductivity of this acid was higher than that of H₂PO₄ at 100°C. Using standard fuel cell electrodes, the room temperature polarisation in 1.15 M (CF₃SO₂)₂CH₂ was 60 mV lower than with the same electrodes used in 85% H₂PO₄ acid at 70°C.

The Partial Oxidations of Benzene and Cyclohexane during Fuel Cell Reactions of O₂ and H₂

The partial oxidations of C₆H₆ and cyclohexane occurred in the cathode during a O₂–H₂ fuel cell reaction at 298 K. The anode was Pt-black/graphite and the cathode, of Pt-black/graphite, catalyses the formation of phenol from C₆H₆ and cyclohexanol and cyclohexanone from cyclohexane. The H₂O₂ generated at the cathode through the O₂–H₂ fuel cell reaction reacts with C₆H₆ and cyclohexane producing their oxygenates.

Platinum Dispersed on Carbon Catalyst for a Fuel Cell: A Preparation with Sorbitan Monolaurate

A highly dispersed Pt catalyst on acetylene black was formed by the reduction of chloroplatinic acid with MeOH containing sorbitan monolaurate (SM). Electrodes with the highest performance for O₂ reduction in phosphoric acid at 170°C were formed when the concentration of SM was 5 g/l and the catalyst was then heat treated at 500°C to decompose residual SM. The Pt particle diameter is hardly changed after 400 h at 0.8 V vs. RHE in phosphoric acid at 205°C.

Standard Gibbs Energies of Formation of RuO₂(s) and LaRuO₃(s) by Oxide e.m.f. Measurements

The e.m.f. of the galvanic cells Pt, Ru, RuO₂ | 15 YSZ | O₂ (Pₒ₂=0.21 atm), Pt and Pt, Cu, Cu₂O | 8 YSZ | RuO₂, Ru, Pt where YSZ is Y₂O₃-stabilised ZrO₂, were measured at 1050–1105K and 751–1200K, respectively, yielding the least squares expressions and the standard Gibbs energy of formation of RuO₂ was determined.

Selective Synthesis of Acetaldehyde Applying a Fuel Cell System in the Gas Phase

The partial oxidation of C₃H₆ using a fuel cell system with (C₃H₆ + H₂O, Pd/silica wool disk holding H₂PO₄(aq.)/Pd or Pt, O₂) produces CH₃CHO very selectively, at >97% in the gas phase, and also cogenerates electricity. The electrode prepared by hot-pressing a mixture of Pd black or Pt black with graphite and Teflon powder improved the current and the rate of formation of CH₃CHO, as compared to an electrode of the metal black alone. The optimum C₃H₆ pressure in the anode compartment is 30 kPa, while the O₂ pressure should be as high as possible. The optimum reaction temperature is 373 K. At an applied potential of 0.15 V the yield of CH₃CHO increased to 10.8% without decreasing the current efficiency.

GLASS TECHNOLOGY

Improved High Temperature Strength Claim for ZGS Platinum Material

F. RITCHIE and R. MCGRATH, Glass, 1990, 67, (7), 278
The requirements and developments which led to zirconia grain stabilised Pt alloy for extensive use in the glass industry, and its new sister alloy E300 ZGS 10% Rh-Pt are discussed. The E300 ZGS Pt, which is a new structural material, has been developed to supplement the existing range of ZGS Pt alloys.

The Use of Platinum and Its Alloys in the Glass Industry

The range of physical properties of Pt which make it invaluable in the glass manufacturing industry and those of an oxide dispersion strengthened Pt alloy are reviewed. Their uses in thermocouples, optical glass, crystal glass and glassfibre manufacture, and other applications are discussed.

ELECTRICAL AND ELECTRONIC ENGINEERING

Czochralski Crystal Growth in the System PtMnSb₁₋ₓ

Czochralski growth of crystals in the title system was investigated for semiconductor properties. Single crystals of p-type PtSb₁₋ₓ, with ~10¹⁴ carriers/cm³ were produced from BN crucibles. On doping with Te, n-type materials were formed. Melts of composition PtMnSb crystallised as PtMnSb single crystals. Single crystals of PtSb₁₋ₓ were obtained from a melt composition of PtMnSb₁₋ₓ, and several different phases subsequently formed.

Platinum Metals Rev., 1990, 34, (4) 233
Au/Pt/Ti Contacts to p-In\textsubscript{0.53}Ga\textsubscript{0.47}As and n-InP Layers Formed by a Single Metallization Common Step and Rapid Thermal Processing


Viable Au/Pt/Ti contacts on p-InGaAs and n-InP have been produced by electron gun evaporation of three layers of Ti (50 nm), Pt (60 nm) and Au (1 μm) under the same pumpdown process, followed by a single sintering by rapid thermal processing at 420–450°C. The lowest resistivities of these ohmic contacts were 0.11 and 0.13 Ωmm for p and n contacts, respectively, achieved after heating at 450°C for 30 s.

Effect of Energetic Bombardment on the Magnetic Coercivity of Sputtered Pt/Co Thin-Film Multilayers


The best magneto-optical properties have so far been achieved in vapour-deposited Pt/Co multilayers because films sputter-deposited in Ar have coercivities too small (100–350 Oe) to be practical in recording. However, the above studies showed that by sputter depositing multilayers in Kr or Xe instead of Ar, coercivities of ~1000 Oe are achieved, which are suitable for recording. The lower coercivity of Ar-sputtered films is attributed to interfacial mixing of Pt and Co layers by energetic bombardment from Ar gas atoms which recoil from the Pt target.

Film Thickness Dependence of Magneto-Optical and Magnetic Properties in Co/Pt and Co/Pd Multilayers


Studies of Co/Pt and Co/Pd multilayers prepared by two source DC-magnetron sputtering showed that magneto-optical and magnetic properties of the multilayers are affected by total film thickness. Kerr rotation angle of the films was greatly enhanced at film thicknesses below several hundred Å. The thickness-dependent rotation showed that the increase of Kerr rotation was due to optical interference and multiple reflection.

Magnetcization and Anisotropy of Co/Pd Multilayer Thin Films


Multilayered Co/Pd thin films were prepared by sequential electron-beam evaporation of Co and Pd onto Si substrate at room temperature with thicknesses of the Co and Pd sublayers of 2.0–10.3 and 4.3–22.3 Å, respectively. Broad maxima in the saturation magnetisation $M_s$ and intrinsic perpendicular anisotropy energy $K_u$ were observed at a Pd thickness of about 10 Å. At this maximum, $M_s$ per Co volume is larger than the saturation magnetisation of bulk Co.

Formation of Palladium Oxides by Mechanocmchemical Reaction on Pd and Ag-Pd Alloy Contacts


Pd contacts operated in mechanical break–make actions in air without switching load current showed the formation of Pd oxide on 70% Pd-Ag and 50% Pd-Ag contacts after 100,000 operation tests. The products show the non-linearity of contact resistance according to measuring current in both dynamic and static measurements.

The Effect of Annealing Temperature on Electrical Properties of Pd/n-GaSb Schottky Contacts


The thermal stabilities for Pd/n-GaSb Schottky contacts have been analysed, and at room temperatures they have a better performance than other metal/n-GaSb Schottky diodes, such as higher breakdown voltages and good adhesive properties on GaSb. However, when the annealing temperature is increased to 300–450°C for 30 min the contacts gradually become ohmic. Interdiffusion between Pd and Ga forming Ga$_2$Pd is the dominant factor for degrading the properties of the diodes.

Pd/Ge Ohmic Contacts for GaAs Metal-Semiconductor Field Effect Transistors: Technology and Performance


Non-alloyed Pd/Ge ohmic contacts were studied for applications to GaAs metal-semiconductor field effect transistors (MESFETs) and compared with conventional AuGeNi alloyed contacts. The Pd/Ge metallisation has a lower contact resistivity with a narrower spread than AuGeNi, and the lowest values were obtained when a Ti/Pt/Au overlayer was used. Similarly, parasitic source and drain resistances in 0.25 W MESFETs are slightly lower. A Ti/Pt/Au overlayer improves the thermal stability of the Pd/Ge metallisation at 300°C, giving a long-term degradation rate.

Reactivity of Ceramic Superconductors with Palladium Alloys


Pd alloy compositions were investigated for suitability as a non-reactive material for the processing of ceramic superconductors. Ba-based superconductors were tested on Pd-Au and Pd-Ag alloys, and Bi-based superconductors were tested on a Pd-Ag alloy. For Ba-based high-temperature superconductors 70% Pd-30% Ag was the least reactive, and 50% Pd-50% Ag was the least reactive for Bi-based high-temperature superconductors.
Stable and Shallow PdIn Ohmic Contacts to n-GaAs
A thermally stable, low-resistance PdIn ohmic contact to n-GaAs was developed based on the solid phase regrowth mechanism. Rapid thermal annealing of a Pd-In/Pd metallisation induces a two-stage reaction resulting in the formation of a uniform single-phase film of PdIn, an intermetallic with a melting point > 1200°C. Specific contact resistivities and contact resistances of 1 x 10^-4 Ω cm^2 and 0.14 Ω mm, respectively, were obtained for samples annealed at 600–650°C. The addition for a thin layer of Ge (2 nm) to the first Pd layer extends the optimum annealing temperature window down to 500°C. Specific contact resistivities remained in the low 10^-4 Ω cm^2 range after annealing at 400°C for over two days.

TEMPERATURE MEASUREMENT

Comparison of Resistance Versus Thermodynamic Temperature of Platinum Resistance Thermometers with the ITS-90
Experiments that relate the resistances of a group of five high temperature Pt resistance thermometers to thermodynamic temperatures at 600–962°C are reported. Within the accuracy of the photoelectric pyrometry involved, ±0.40°C at the freezing point of Ag, the measured thermodynamic temperatures agreed with the temperatures obtained using the ITS-90 (International Temperature Scale of 1990). In a 1.5 year period the typical random uncertainties, evidenced by variations in the resistance of Pt resistance thermometers at the triple point of H_2O, were equivalent to ±0.015°C at the Ag freezing point.

A High Temperature (1200°C) Probe for NMR Experiments and Its Application to Silicate Melts
A high temperature NMR probe has been developed and used to measure the 29Si nucleus in Na silicate glasses and melts. The probe uses Pt wire threaded through a two-hole tube of high purity alumina surrounding a core alumina tube. The heater current flows through two Pt wires in the alumina tube, opposite in direction so as not to produce an additional magnetic field across the sample volume. Sample temperatures were measured by a Pt:Pt-Rh thermocouple, attached below the bottom of the capsule. The highest temperature attained was 1200°C. The NMR spectra show narrowing above the glass transition temperature.

MEDICAL USES

Biophysical Studies of the Modification of DNA by Antitumour Platinum Coordination Complexes
The modification of DNA by cisplatin has been examined. Anti-tumour active Pt compounds induce in DNA, at low levels of binding, local conformational alterations which have the character of non-denaturing distortions. These changes in DNA occur due to the formation of intrastand cross-links between two adjacent purine residues. Conformational alterations induced in DNA by anti-tumour active Pt compounds may be repairable with greater difficulty than those induced by the inactive complexes. However, the non-denaturation change induced in DNA by anti-tumour Pt drugs could represent more significant steric hindrance against DNA replication as compared with inactive complexes.

Bending Studies of DNA Site-Specifically Modified by Cisplatin, trans-Diamminedichloroplatinum(II) and cis-[Pt(NH)₂(N3-cytosine)Cl]⁺
Duplex oligonucleotides containing a single intrastrand [Pt(NH)₂]²⁺ cross-link or monofunctional adduct and either 15 or 22 bp in length were synthesised and chemically characterised. The Pt-modified and unmodified control DNAs were polymerised in the presence of DNA ligase and the products and the extent of the DNA bending caused by the various Pt-DNA adducts was shown by their gel mobility shifts relative to unplatinated controls. When modified by the monofunctional adduct cis-[Pt(NH)_2Cl(N3-cytosine)(dG)]Cl the helix remains rod-like. These structural differences in DNAs modified by cisplatin and its analogs could be important in biological processing of adducts in vivo.

Synthesis and Antitumor Activity of Pt(II) Complexes of Benzyl-1,2-diaminoethane Ligands
Twelve new diamine ligands were synthesised and characterised in which a benzyl group and another vicinal substituent or a benzyl group, a 4-Cl-benzyl group, and a 4-MeO-benzyl group, respectively, and two other geminal substituents are attached to the 1,2-diaminoethane skeleton. The diamine ligands are transformed into the dichloroplatinum(II) complexes. The chloride ligands of four complexes are replaced by the lactate anion. Polyvinylpyrrolidone and α-cyclodextrin are used to increase the water solubility of the Pt(II) complexes. The antitumour activity of the complexes was tested for P388 leukaemia, and compounds with small alkyl substituents show higher antitumour activity than that of cis-platinum.