ABSTRACTS

PROPERTIES

Electrical Properties, Stability, and Applications of Ultrathin Porous Pt Films on SiO₂


The morphology of 25 Å porous Pt films deposited on thermally grown SiO₂ at room temperature and 250°C is presented. The impedance was measured over the range 100 Hz to 1 MHz. At 1 kHz, the impedance was measured in electric fields up to 250 V/cm at temperatures –192 to 140°C. The AC impedance of the 25 Å Pt film deposited at room temperature decreased by 25% in 21 days at 150°C in room air, but the AC impedance of the Pt film deposited at 250°C did not change.

Volatilization of Pt-Rh Alloys at High Temperature


Studies of the volatilisation of Pt-7Rh and Pt-Rh-Au alloys at high temperature showed that the volatilisation loss of the alloys at 1200–1350°C obey a parabola-straight line rule, and the transposition time from the parabola loss to straight line loss decreased with increasing temperature. The volatilisation loss increased with increasing Rh content and by addition of Au to Pt-Rh alloys. The activation energy of volatilisation of Pt-7Rh-3Au alloy is 167 kJ/mol.

Columnar Epitaxy of PtSi on Si(111)


Columnar grains of PtSi surrounded by high quality epitaxial Si were obtained by ultrahigh vacuum codeposition of Si and Pt on Si(111) substrates heated to 610–810°C. The areal density of columns varied from 120 to 3.8/μm², and layers with thicknesses from 100 nm to 1 μm were displayed. The PtSi grains are also epitaxial and have one of three variants of the relation defined by PtSi[010]/∥Si(111), with PtSi[001]/∥Si<110>.

Properties of a Platinum-Yttrium-Boron Alloy

K. SCHWARZ and W. MOLLE, Neue Hütte, 1990, 35, (10), 391–393

The properties of a Pt-0.03Y alloy were improved by adding a small amount of B. The addition of B resulted in an increase in the rate of internal oxidation and a fine dispersion of the Y oxide particles was obtained. High creep rupture strength, a high creep resistance and a decreased grain growth were found.

Magnetic and Transport Properties of the UTIn Series (T=Rh, Pd and Pt)


Magnetic susceptibility, magnetisation, electrical resistivity and magnetoresistivity measurements have been performed for the U(Rh, Pd, Pt)In series crystallising in the hexagonal Fe₂P type structure. Results for URhIn are reported for the first time. Antiferromagnetic ordering in URhIn and UPtIn with a Neél temperature of 7 and 22 K and metamagnetic transitions in fields of ~1.5 and 3.5 T at 4.2 K have been observed, respectively. Resistivity anomalies at low temperatures have been observed. UPdIn was antiferromagnetic with a Neél temperature of 20 K.

Effects of High Concentration CO and CO₂ on Hydrogen Permeation through the Palladium Membrane


The effects of high concentrations of CO and CO₂ on the H permeation characteristics of a Pd membrane 0.7 mm thick, 12 mm diameter cut from cold-rolled Pd plate, followed by annealing were investigated using pure H₂, H₂-CO (10%,50%), and H₂-50%CO₂ at 423–723 K and pressures 0.9–250 kPa. Deterioration in H permeability and diffusivity in the Pd membrane occurred for H₂-CO(10%,50%) gas below 523 K with a concentration dependence on CO, while only slight deterioration occurred for H₂-50%CO₂ gas below 473 K. Results are explained by different adsorption energies of CO and CO₂ at the Pd surface. Deterioration in H₂ permeability is attributed to a decrease in effective area for H₂ dissociation by the weak adsorption of CO.

Kinetic Description of the Transition from a One-Phase to a Two-Phase Growth Regime in Al/Pd Lateral Diffusion Couples


The kinetics of the solid-state reaction between Al and Pd is studied in the geometry of a lateral Al-Pd diffusion couple at 250–430°C. The first reaction phase is the crystalline AlₐPd₇ (6) phase and after its growth to a critical length, the quasicrystalline decagonal Al₉Pd(γ') phase starts to grow in between the Al and the AlₐPd₇ phases. The first-phase AlₐPd₇ and second-phase Al₉Pd(γ') grow simultaneously. Excellent agreement between the data and the model is found. From the analysis the effective interface growth constant for the AlₐPd₇ is extracted as a function of temperature.
Electrical Resistivity Changes Due to Interstitial Hydrogen in Palladium-Rich Substitutional Alloys


The changes in electrical resistivity of Pd solid solution alloys, alloyed with Ag, Au, Cu, Y, Ce, Ti, Zr, V, Nb and Ta, with H concentration were measured at 301 K up to t(WM)=1.5. The H was introduced by electrolysis and measurements of electrode potential were also made. The specific electrical resistivity of H-free Pd alloys increased with increasing solute contents.

Interstitial Hydrogen Electrical Resistivity Changes Due to

The resistivity of H-free Pd alloys increased with increasing volume fraction of H. The changes in electrical resistivity of Pd solid solution alloys, alloyed with Ag, Au, Cu, Y, Ce, Ti, Zr, V, Nb and Ta, were studied. The specific electrical resistivity of H-free Pd alloys increased with increasing solute contents.

Internal Oxidation of Pd-40Ag-1RE (RE=Sm, Eu, Gd) Alloys and Their Properties

Y. Li, H. Dai and Y. Ning, Guijinshu (Precious Met.), 1990, 11, (2), 18–22

The internal oxidation of Pd-40Ag-1RE (RE=Sm, Eu, Gd) alloy wires and their properties were studied in air at 800–1200°C. For the alloys containing Sm or Gd, the oxidation rate along the grain boundaries was higher than that of grains in some parts. It is concluded that the internal oxidation of Pd-40Ag-1RE alloys is controlled by volume diffusion.

Microstructural Stability of Diluted Pb-Cu-(Sn-Se-Pd) Alloys

A. De la Torre, P. Adeva, G. Caruana and M. Aballe, Z. Metallkd., 1990, 81, (8), 594–600

The evolution of microstructure was followed in homogeneous, fine-grained Pb-Cu, Pb-Cu-Sn-Se and Pb-Ca-Sn-Se-Pd alloys optically, by SEM and by microanalytical identification of phases and measurement of several microstructural parameters, at temperatures between 323 and 423 K for 4 to 700 h. Small Cu and Se additions substantially reduce Pb grain size; Pb acts as a grain stabiliser during heat treatments. Grain size distributions in one or two dimensions are lognormal and invariant with treatment temperature and time. The Pb containing alloys have high structural stability at the temperatures studied, making them suitable for chemical plant application.

Magnetic Properties of Nonequilibrium Fe-Pd Alloys Produced by DC Triode Sputtering


Sputter-deposited Fe–xPd alloys of ~100 µm thickness were prepared by DC triode sputtering. The single b.c.c. phase was obtained for x= 0–0.25 in contrast to the narrow single b.c.c. of x=0–0.05 in the equilibrium phase diagram. The lattice constant and the magnetisation increased by annealing below 500 K and decreased by annealing above 500 K.

The (α+β) Hydrogen Miscibility Gaps in Hydrogenated Palladium-Rich Pd-Y(Gd)-Ag Ternary Alloys


Pd-rich Pd-Y(Gd):Ag ternary alloys were investigated as possible diffusion membranes for H purification, and their alloying behaviour and the extent of (α+β) H miscibility gaps in hydrogenated alloys were studied. Metallographic and X-ray studies of annealed Pd_{90-x}(Y(Gd)):Ag, alloys with a Ag content y of 5–24 at.% and x in at.% giving the value of the content of Y and/or Gd, indicate that every one of these alloys forms as a single α-Pd phase. It was found that the (α+β) H miscibility gaps in the hydrogenated alloys with any given Ag content decrease gradually as the content of Y and/or Gd increases, and the critical compositions for the disappearance of the miscibility gaps are approximately isoelectronic.

Do Thermal Spikes Contribute to the Ion-Induced Mixing of Ni into Zr, Ti, and Pd?


Low-temperature ion beam mixing rates for Pd-Ni, Ni-Ti and Zr-Ni bilayers greatly exceeded binary collision estimates, and appeared quite sensitive to thermodynamic driving forces. In the absence of a temperature dependence such a behaviour is usually ascribed to interdiffusion within thermal spikes. It is suggested that interdiffusion within a thermal spike of the Vineyard-Johnson type is not the dominant mechanism.

On the Constitution of the Pd-Te System up to 28 at.% Te


The constitution of the Pd-Te system was completed in the Pd-rich range up to 28 at.% Te and at >600°C. The solid solution between Pd and Te has a maximum Te content of 16.3 at.% at ~770°C. The system shows a eutectic with 23.0 at.% Te at 773°C. Three phases Pd, Te, (19 at.% Te), Pd, Te, (26 at.% Te) and dimorphic Pd, Te (25 at.% Te) were observed in the subsolidus region.

Structure Changes on Relaxation of Differently Cooled Pd_{0.83}Si_{0.165} Alloy Glass


The radial distribution function (RDF) of X-ray diffraction was studied for liquid-quenched Pd_{0.83} Si_{0.165} alloy glasses in relation to cooling conditions. The atomic distance (r,) total co-ordination number (n) and volume (V) were obtained by a first peak of RDF. The faster the cooling rate, the larger the r, n and V become. Based on the relaxation theory, it is shown that linear changes in r, n and V with the thickness (D) indicate the reciprocal cooling rate.
High-Temperature Oxidation of Rhodium


The oxidation kinetics of Rh were measured in air at 1 atm at temperatures 600–1000°C. The oxidation weight gain proceeds logarithmically at 600–650°C, followed by power law behaviour at >800°C. The logarithmic growth kinetics comes from thickening of hexagonal Rh₂O₃ scales. The transition reflects a thickening of hexagonal and orthorhombic Rh₂O₃ scales. Over 800°C the growth kinetics result from thickening of a predominantly orthorhombic Rh₂O₃ scale. At 1000°C the oxide becomes volatile.

The Controlled Oxidation of the High Chromium Steel Alloys Fe₄₀Cr and Fe₄₀Cr₃Ru


Fe₄₀Cr steel with and without 3% Ru added were exposed to O at different temperatures in an UHV system to find out how the Ru enhanced the corrosion resistance of the alloy. Cr was oxidised before Fe in both Fe₄₀Cr and Fe₄₀Cr₃Ru, but only in the Ru alloy did the Cr also enrich the surface, at temperatures over 275°C, to form a substantial oxide, possibly because of an attractive interaction between Fe and Ru in the bulk.

New Compounds in the 30–40 at.% Ru Range of the Rare Earth-Ruthenium (R-Ru) Systems


New compounds were prepared and identified in the rare earth-Ru (R-Ru) systems and a complete compound formation scheme was constructed. Two new crystal structures were found and completely resolved. YₓRuₓ and ErₓRuₓ, while for a third one (RₓRuₓ) the complexity of the structure prevented any structural determination.

CHEMICAL COMPOUNDS

Complex Formation of Platinum with Tin(II) in Aqueous Solution of Maleic Acid


Studies of the interaction of K₂PtCl₄ with SnCl₂·2H₂O in 1 M maleic acids at 20°C showed the formation of bimetallic Pt(II) complexes of anion type with maximum content of SnCl₂H₂O⁻ ligands, with the molar ratio=5. Chloride ions in [Me₃N]₂Pt(SnCl₂)₂ and [Me₃N]₂Pt(SnCl₂)₂ dissolved in the maleic acid were completely replaced by maleate-anesions, thus preserving the Pt-Sn bond. During heating, Pt-Sn complexes undergo intermolecular conversion, which result in the formation of bimetallic compounds with Pt oxidation order −1.

Synthesis and X-Ray Crystal Structure of Trimesilylrhodium(III)


The first neutral homoleptic aryl of Rh(III), Rh(2,4,6-Me₃C₆H₃)₃, was prepared by interaction of RhCl₃(C,H₅S) and mesitylmagnesium bromide. X-ray crystal studies showed that there is “agostic” interaction between Rh and an ortho-CH₃ group in a distorted fac-octahedral geometry but no evidence for agostic H bonding was found. ¹H NMR spectra over a temperature range indicate synchronised rotation of the mesityl group about the Rh-C bond.

A Novel Zwitterionic otho-Metallated Ruthenium(II) Phenolate


Decarbonylative metallation of the dialdehyde by [Ru(PPh₃)₂Cl₂] produced the unusual complex [Ru(MeL)(CO)(PPh₃)₂(Cl)]. X-ray crystallographic studies showed that the Ru¹¹¹Pt₃C₃IO co-ordination unit has a single net negative charge and the Ru(MeL) fragment incorporates a four-membered C,O-chelated phenolato function with a neighbouring monoprotonated azomethine moiety.

Preparation of Uniform Colloidal Metallic Ruthenium and Its Compounds


Colloidal spherical particles with narrow size distribution of a Ru double salt, (NH₄)ₓRu(III)O(NO)₂RuIVOC₃H₇O were obtained by ageing solutions of RuCl₃ containing K₂SO₄ and urea at elevated temperatures. The amorphous product was readily converted to RuO₂ by calcination at 400°C. The same original powder, dried and heated at 250–300°C in a stream of H₂ yielded metallic Ru.

ELECTROCHEMISTRY

Electrochemical Behaviour of Basal Single Crystal Pt Electrodes in Alkaline Medium


The electrochemical behaviour of basal single crystal Pt electrodes in 0.1 M NaOH has been studied. The voltammogram for the Pt(111) surface orientation shows two clearly defined zones; one corresponds to weak H adsorption states and the other could tentatively be assigned to strong H adsorption states. The voltammogram for a Pt(100) surface shows four different H states while for the Pt(110) orientation only one H state is obtained.

*Platinum Metals Rev.*, 1991, 35, (1) 34
Electrochemical Oxidative Cleavage of the Platinum-Hydrogen Bond in
trans-[PtHCl(PEt₃)₂]

The electrochemical oxidation of the Pt(II) hydride, trans-[PtHCl(PEt₃)₂], in CH₂CN containing NBu₄ClO₄ at a Pt gauze electrode produces almost exclusively Pt(II) complexes as products, none of which contain Pt-H bonds; trans-[PtCl(solvent) (PEt₃)₂]⁺ is the major oxidation product. Titration on the electrochemically oxidised solutions show that Pt-H cleavage occurs with H⁺ formation. The overall oxidation process is therefore: H⁻ → H⁺ and not Pt(II) → Pt(IV).

Rectifying Bilayer Electrodes: Layered Conducting Polymers on Platinum

The preparation of sequential bilayer structures made from any pair of polybithiophene, (I), polypyrrole, (II) and poly(3-bromothiophene), (III) by anodic electropolymerisation on Pt electrodes is described, and the electrochemical properties of the junctions between the two conducting polymers are discussed. The polymers in the outer layers of the electrodes Pt/I/II and Pt/III/II can be trapped in the oxidised state for several hours and can be released from the outer layers via an appropriate redox couple in solution.

Hydrochloric Acid Electrolysis Using Solid Polymer Electrolytes. II. Gas Purity and Current Efficiency

Current efficiencies and purities of H and Cl in HCl acid electrolysis by membrane-electrocatalyst composites of Ir-Pt/Nafion 117/Pt-Ir prepared by chemical plating were investigated over the range 1.7–12 mol/kg HCl concentrations, and temperatures 25–75°C and current densities up to 100 A/dm². Cathodic current efficiencies of 97–98% were found.

The Electrooxidation of Methanol in the Potential Region of Platinum-Oxygen Layer

Methanol oxidation at a Pt electrode in 0.5 mol/dm³ H₂SO₄ at high potentials was retarded by the formation of an O layer and a new type of retarding substance from MeOH. During retardation due to the formation of O layer, the rate of MeOH oxidation decreased and increased with increasing O coverage and potential, respectively. Reverse effects in O coverage and potential concurrently occurred when the potential was variable. At low O coverage, the decreased effect from O coverage was more notable than the increased effect from the potential, but this reversed at medium coverages.

Electrochemical Activity of Silicides of Some Transition Metals for the Hydrogen Evolution Reaction in Acidic Solutions

The H evolution reaction was examined on silicides of transition metals in H₂SO₄ solutions. The highest rates were observed on Pt and Pd silicides, followed by those of Cu, Cr and Ni. If Fe silicides are used as typical transition metal silicides their electrocatalytic activity for the H evolution reaction is enhanced considerably by electrodepositing traces of Ru, and especially Pt on their surfaces.
Morphological Changes in Silver Colloidal Particles during Oxidative Treatment in Complex Solutions of Gold and Palladium

The treatment of polychromatic imaging Ag particles in HgPdCl₄ and HgAuCl₄ solutions resulted in a change in the spectral and colour properties of an image. During the process, the spectral Ag particles transform to Ag shells with Pd and Au particles being ultradispersed on a surface.

Poly(pyrrrole-2,2'-bipyridyl) Rhodium(III) Complexes Modified Electrodes: Molecular Materials for Hydrogen Evolution and Electrocatalytic Hydrogenation

The synthesis and electropolymerisation of new [Rh(III)(L₂Cl₄)BF₄] complexes, where L = 2,2'-bipyridine bearing pendant pyrrole units, and the electrochemical behaviour of the resulting polymers are examined. Films of this material are highly stable for bulk electrocatalytic reactions, especially for efficiently reducing water to H₂, and for the hydrogenation of cyclohexanone to cyclohexanol.

The Electrochemical Reduction of Cp*Rh Complexes

The electrochemical reduction of [Cp*RhCl₂] (1) or [(Cp*Rh)(μ-Cl)]PF₆ (2) in methylene chloride and acetone and of [((Cp*Rh)(μ-OH))PF₆ and Cp*Rh(acetone)]⁺ in acetone was investigated. An involved stepwise reduction sequence with electron transfer, Cl⁻ loss and disproportionation from (1) or (2) produces the novel blue, air-sensitive, binuclear RuII species [Cp*RhCl]⁺.

Application of Ion Implantation/RBS to the Study of Electrocatalysis

Ir-implanted Ti near-surface alloys were prepared by ion implantation, characterised by Rutherford backscattering (RBS) and subsequently anodically oxidised to form electrocatalytically active Ir₂Ti₆O₁₉/Ti electrodes, and their electrochemical behaviour in acidic chloride, sulphate and perchlorate solutions was studied. The specific catalytic activities (rate per catalyst surface site) of Ir₂Ti₆O₁₉/Ti and Ru₄Ti₁₉O₅/Ti and their relative catalytic activities were evaluated. Ir₂Ti₆O₁₉/Ti was only 45% as effective a catalyst for Cl₂ evolution as Ru₄Ti₁₉O₅/Ti, but it was far more stable, with a corrosion rate of only 5% that of Ru₄Ti₁₉O₅/Ti.

Catalytic Oxidation of Methanol by Ruthenium Oxides

The electrocatalytic behaviour of Ru oxide/C electrodes for O evolution and MeOH oxidation in acid solutions is reported. The electrodes were characterised by various techniques which showed the Ru to be present as a mixture of RuVI oxides, including the stable rutile phase. Electrochemical studies show that a RuVI species promotes the catalytic oxidation of MeOH, while surface-bound RuO₂ is involved in the O evolution reaction.

Topotactic Two-Phase Reaction of Ruthenium Dioxide (Rutile) in Lithium Nonaqueous Cell

Electrochemical and X-ray diffraction studies were performed for the reduction of RuO₂ with rutile structure in IM LiClO₄ propylene carbonate:1,2-dimethoxyethane (1:1) solution. RuO₂ was topotactically reduced to LiRuO₂, which is orthorhombic via an intermediate phase having a tetragonal lattice. The reaction was reversible. Although three phases coexisted during the reduction of RuO₂ and oxidation of Li,O₁/₂RuO₂ the reaction was classified as a topotactic two-phase reaction where an intermediate phase existed between the RuO₂ and LiRuO₂ phases.

PHOTOCONVERSION

An Ultramicrostructured Photocathode System Composed of TiO₂ Single Crystal and Layered SiO₂ and Pt Thin Film

An ultramicrostructured photocathode system composed of a TiO₂ single crystal and thin films of SiO₂ and Pt was prepared by exposing the vertical section of the layered SiO₂ and Pt film. The SiO₂ layer is ~140 nm thick. The electrode showed photosresponse under irradiation in the presence of NH₃, water vapour, EtOH and acetone. This may be the first microphotocathode system which can work in the gas phase.

Photocatalytic One-Step Syntheses of Cyclic Imino Acids by Aqueous Semiconductor Suspensions

Photocatalytic cyclisation using aqueous suspensions of TiO₂ or CdS loaded with Pt oxides under Ar at room temperature was applied to the one-step synthesis of optically active cyclic imino acids, N-carboxylic acid, and proline from the α-amino-carboxylic acids and their N₅-substituted derivatives.
A Direct Absorber Reactor/Receiver for Solar Thermal Applications


A novel catalytic reactor concept of 3.5 kW is described where concentrated radiant solar energy is directly absorbed on Rh/Al₂O₃, thus avoiding the heat-transfer limitations of conventional tubular reactors for high-flux conditions.

Photocatalytic Asymmetric Reduction of 3-Methyl-2-Oxobutanoic Acid with Chiral Rh(I) Complexes and Powdery Semiconductors


Photocatalytic asymmetric reduction of the title acid giving 2-hydroxy-3-methylbutanoic acid has been performed at up to enantiomeric excess of 60% in aqueous MeOH with chiral BINAP-Rh(I) complexes and semiconduct powders, TiO₂ or CdS. The efficiency of the asymmetric reduction is still low, but the asymmetric hydrogenation of α-ketocarboxylic acid has been obtained without using H₂.

Simultaneous Photodissociation of H₂ and PMe₄Ph from OsH₂(PMep₄Ph): Production of Dimeric and Paramagnetic Osmium Polyhydrides

J. W. Bruno, J. C. Huffman, M. A. Green, J. D. Zubrowski, W. E. Hatfield and R. G. Caulton, Organometallics, 1990, 9, (9), 2556-2567

Concurrent photodissociation of H₂ and PMe₄Ph (→ P) from OsH₂P₄ in benzene, THF and EtOH has been proved by chemical trapping. It is the first polyhydride to undergo two distinct photoprocesses with comparable efficiencies. The final products observed on photolysis of OsH₂P₄ under vacuum is an equilibrium mixture of Os₃H₄P₄ and Os₅H₅P₅. The former is also photosensitive, leading to products of P-CH₃ cleavage (Os₃H₄(PMep₄Ph)(μ-PMe₄Ph))₂, as well as to a product of Os₅H₅ heterolysis, [Os₅H₅P₅⁺¹(trans-OsH₅P₅⁺¹)], which contains a unique paramagnetic polyhydride anion.

Spectral, Photophysical and Photochemical Properties of Ru(bpy)₃²⁺ on Porous Vycor Glass


The properties of Ru(bpy)₃²⁺ adsorbed on porous Vycor glass have been characterised. The complex is immobilised on the glass surface and can be quenched by O₂, N₂O and SO₂. Other forms of quenching are discussed, as are the few differences in behaviour due to the Ru being on a solid support and not in a fluid medium. The net photooxidation chemistry initiates with a two-photon ionisation of Ru(bpy)₃²⁺. Electron conduction may occur by a surface mechanism.

A Luminescence Quenching Study on the Localization Problem of Ru(bpy)₃²⁺ in Micelles and Hemimicelles


Quenching studies on the luminescence emission of compound Ru(bpy)₃²⁺ with ferrocyanide ion, 9-methylnaphthrene and dioxyissteaeric acids were carried out in hemimicellar and micellar aggregates to gain insight into the location of this Raman and luminescence probe. Ru(bpy)₃²⁺ is bound to a more nonpolar hemimicellar hydrophobic region. Stern-Volmer constants for the dioxyissteaeric acid quenching of its luminescence in micelles indicated that the optical electron in the metal-ligand charge-transfer state of the probe molecule resides in a bipyridyl ring which appears to be close to position 7 of the stearic acid chain.

Conversion of Light into Electricity with Trinuclear Ruthenium Complexes Adsorbed on Textured TiO₂ Films


A series of CN-bridged trinuclear Ru complexes of structure [RuL₂(μ-(CN)Ru(CN)L₂)₂] for L = 2,2'-bipyridine-4,4-dicarboxylic acid and L’ = 2,2'-bipyridine (1), and other bipyridines, etc, have been synthesised. The two carboxyl functions act as interlocking groups through which the dye is attached at the TiO₂ film surface. The interlocking groups provide strong electronic coupling, allowing charge injection to proceed at quantum yields close to 100%. Monochromatic incident photon-to-current conversion efficiencies are >80% in some cases. Regenerative cells with these trinuclear complexes and ethanolic triiodide/iodide redox electrolyte have optimal results with (1), giving a fill factor of 75% and a power conversion efficiency of 11.3% at 520 nm.

Design of Antenna-Sensitizer Polymeric Nuclear Complexes. Sensitization of Titanium Dioxide with [Ru(bpy)₃(CN)₂]Ru(bpy(COO)₂)₂²⁻


The use of antennae-sensitizer molecular devices is proposed as a possible strategy to increase the light harvesting efficiency of sensitised semiconductors. The cyano-bridged trinuclear complex [Ru(bpy)₃(CN)₂]Ru(bpy(COO)₂)₂²⁻ was prepared and studied. The complex absorbs on TiO₂ via the negatively charged -Ru(bpy(COO)₂)₂²⁻ central unit. Photophysical and photoelectrochemical studies were performed and emission and excitation spectra showed that in this complex the light energy absorbed by the terminal Ru(bpy)₃(CN)₂ (antenna) groups is efficiently funnelled to the central -Ru(bpy(COO)₂)₂²⁻ (sensitiser) fragment.
ELECTRODEPOSITION AND SURFACE COATINGS

Deposition of Transition Metal and Mixed Metal Thin Films from Organometallic Precursors

Y.-J. CHEN, H.-J. MÜLLER, H. D. KAESZ, R. S. WILLIAMS, R. F. HICKS, J. I. ZINK.

High purity films of Pt, Ir, Rh and Ni and Re have been grown by organometallic chemical vapour deposition OMCVD (a), while thin films of Pt, Rh or Ir have been grown by photo-assisted OMCVD of volatile hydrocarbon precursors, but these contained more C than films grown under (a). Short-path OMCVD for OMCVD (a), while thin films of Pt, Rh or Ir have hydrocarbon precursors, but these contained more C than films grown under (a). Short-path OMCVD for organometallic precursors of limited volatility was used to deposit films of intermetallic compounds, PtGa, and CoGa. Substrates to be coated are placed in the reaction tube at the temperature needed for controlled decomposition of the precursor complexes. The various hydrocarbon derivatives, carrier gases, substrates, light sources, temperatures and means of producing thin films are discussed.

Preparation of Thin Palladium Films by Use of an Electroless Plating Technique


An electroless plating technique was used to prepare supported thin Pd films permeable only to H. Before plating, Pd nuclei were deposited on the outer surface of a porous tube by sensitisation and activation treatments with Sn(II) chloride and Pd(II) chloride solutions, respectively. The rate of Pd deposition during plating was related to the Pd nuclei concentration, which increased with repeated number of treatments. Sn deposition retarded Pd deposition, but treating with AgNO₃ solution before activation promoted the formation of Pd nuclei. An alkaline solution was used to plate the Pd on the porous glass tube, twice as fast as conventional plating methods.

APPARATUS AND TECHNIQUE

An Oxygen Sensor Composed of Tightly Stacked Membrane/Electrode/Electrolyte


An O₂ sensor which operates at room temperature has been constructed using Nafion, a porous Pt cathode directly deposited on Nafion and a polyethylene (PE) film directly covering the cathode surface. The sensor is amperometric and all the components are tightly stacked. The O₂ reduction current is limited by the O diffusion rate through the diffusion-limiting PE film and it changes in proportion to O concentration of gases up to 100%.

Platinum Metal Etching in a Microwave Oxygen Plasma


The etching of Pt foils in an O plasma generated in a flow-type microwave system was studied as part of a general effort to understand the etching of metals in both plasma and chemical systems. It was found that very rapid etching (−6 Å/s) took place even at low power inputs of 200 W. The principal plasma parameters, including oxygen atom and ion concentrations, and electron temperature, were measured as a function of distance below the microwave coupler. Etching of Pt in an O plasma jet resulted from the concomitant action of O atoms and high energy electrons.

Use of Oxide Electrodes for Proton-Conductor Gas Sensor

N. MIURA, K. KANAMARU, Y. SHIMIZU and N. YAMAZOE, Solid State Ionics, 1990, 40/41, (Part I), 452–455

An amperometric proton-conductor CO sensor operative at room temperature was developed by using a Pt/SnO₂ and a Pt/WO₃ electrode. The CO sensitivity of this sensor was about 7 times higher than the H₂ sensitivity and the 90% response time was ~3 minutes. The sensor became H₂ selective when a Pt-black electrode was combined with a Pt/WO₃ electrode. Sensing mechanisms are discussed.

The Hydrolysis Products of cis-Dichlorodiammineplatinum(II). 3. Hydrolysis Kinetics at Physiological pH


The rate of hydrolysis of cis-PtCl₂(NH₃)₂ has been measured in non-buffered aqueous solutions at I=0.2 M NaClO₄ and T=45°C at constant pH over the range 4.0–8.5; the reverse reaction was also monitored. This allowed models for the hydrolysis of cis-PtCl₂(NH₃)₂ under physiological conditions to be tested, and shows that the Rosenberg model for Pt(II) transport in vivo may need modification.

Study by UV-Visible Potential-Modulated Reflectance Spectroscopy of the Chemisorption of CO, Methanol and Ethanol on Several Noble Metal Electrodes


The title method has been used as a technique to determine the energy of electronic transitions in chemisorbed carboxyls and the type of bonding of CO. This was used to examine the electroadsorption of CO, MeOH and EtOH on Pt, Pd, Rh, Ru and Au electrodes. A maximum is reported, which depends only on the type of bonding of CO to the surface, i.e. linear, bridge-bonded or multiply bonded.
A diode r.f. sputtering technique was used to produce Rh/C multilayers for application in the soft X-ray region. In situ kinetic ellipsometry, grazing X-ray reflectivity and absolute soft-X-ray reflectivity are used to make measurements. A model assuming a quasi-sharp C-Rh interface (4 Å thick) and a diffused Rh-C interface (22 Å) in the stack is used to fit the reflectivity curves at three experimental wavelengths. Reflectivities as high as 22% at 13.3 Å and 24% at 44.7 Å were measured on a 17-period multilayer structure having a period of ±69 Å. One interface is relatively ideal and it is sufficient to give good reflectivities.

The Use of RuO$_2$ in Studies of Polymer Blends by Scanning Electron Microscopy


Flat samples of blends of polypropylene (PP) and styrene-ethylene-butylene-styrene (SEBS) were contrasted with RuO$_2$ and studied by SEM having a back-scattering electron (BSE) detector. The SEBS phase had bright areas with dark dots and the PP phase was dark. The dots were unstained EB-domains of the triblock SEBS polymer. This method gave high resolution images due to the intrinsic electrical conductivity on the surface from the deposited Ru species; the RuO$_2$ vapour gave electrical conductivity to the stained areas. This method allows a BSE detector to be used in morphological studies.

HETEROGENEOUS CATALYSIS

A Heterogeneous “Ligand-Accelerated” Reaction: Enantioselective Hydrogenation of Ethyl Pyruvate Catalyzed by Cinchona-Modified Pt/Al$_2$O$_3$ Catalysts


The effect of low modifier concentrations on the rate and enantioselectivity of ethyl pyruvate hydrogenation catalysed by Pt/Al$_2$O$_3$ modified with 10,11-dihydrocinchonidine (HCD) was studied in order to test the concept of “ligand-accelerated” catalysis for a modified heterogeneous system. The reaction mechanism was found to be in complete agreement with a simple two-cycle mechanism. The adsorption of HCD on the Pt surface must be reasonably strong and/or only a small fraction of the surface Pt is modifiable. Simple geometric considerations indicate that a modified ensemble should be one adsorbed cinchona molecule and 10–20 Pt atoms.

Sulphur-Resistant Character of Titania-Supported Platinum Catalysts


The resistance of Pt/TiO$_2$ catalysts to H$_2$S was studied by pulse reactions with Pt/Al$_2$O$_3$ as a reference. Pt/TiO$_2$ was found to be much more resistant than Pt/Al$_2$O$_3$ to H$_2$S poisoning. The results showed that in TiO$_2$, there is labile O that can react with H$_2$S to form SO$_x$ or SO$_y$, which leave the catalyst. Thus, with the Pt/TiO$_2$ system a considerable part of S contamination is “auto-regenerated” and the poisoning effect of S on Pt is therefore mitigated. However, for the Pt/Al$_2$O$_3$ system, H$_2$S decomposes on Pt giving H$_2$ and PtS.


The reduction and chemisorption properties of the Pt-Ga/Al$_2$O$_3$ catalysts were studied during n-hexane conversion in a flow microreactor. The addition of Ga into Pt/Al$_2$O$_3$ improved its stability, and the catalyst containing >3.5% Ga promoted n-hexane conversion. The selectivity for aromatisation, isomerisation and hydrocracking could be adjusted by changing the Ga content of the catalyst.

Role of Sulfur in Catalytic Reforming of Hydrocarbons on Platinum-Rhenium/Alumina


Cyclohexane and n-heptane reforming were studied on 0.3–0.3% Pt-Re/Al$_2$O$_3$-0.95% Cl catalyst in the presence of S. The combined effect of Re-S and Pt-S$_i$ (where S$_i$ is the irreversible form of Pt) that modified the Pt ensemble size and the electronic interactions caused the hydrogenolysis and dehydrocyclisation activities to decrease. Due to the added effect of Re-S decreasing the ensemble size, the fewer “available” free Pt crystallites on Pt-Re/Al$_2$O$_3$ compared to Pt/Al$_2$O$_3$ means the toxicity of irreversible S was greater for the bimetallic catalysts.

XPS Studies of Pt-Sn Naphtha Reforming Catalysts


XPS studies of Pt-Sn catalysts with porous and nonporous Al$_2$O$_3$ and SiO$_2$ gel surface areas of 250 m$^2$/g and 110 m$^2$/g, and 700 m$^2$/g, respectively, were performed. Both Pt(0) and Sn(0) were observed in the reduced samples. Sn(0), and alloy formation, occurs when Pt and Sn are added as a complex dissolved in acetone. The ratio of Pt(0) to Sn(0) varies, at constant Pt loading, with the total amount of Sn added in the preparation. This Pt:Sn ratio varies from about 0.4 to about 6 for the catalysts studied.
Molecular Die Catalysis: Hexane Aromatization over Pt/KL
Studies of n-hexane aromatization over 0.6-0.8% Pt/KL, prepared by exchanging zeolite L powder with Pt(NH₃)₄Cl₂ solution at room temperature for 20 h, and 1%Pt/SiO₂ catalysts were performed at 510°C, 100 psig pressure, with a H₂/hexane mole ratio of 6. Pt/KL catalysts showed a much greater selectivity for hexane aromatisation than Pt/SiO₂ catalysts and a strong preference for cracking the terminal C-C bond as opposed to interior bonds.

Preparation of Platinum Cluster Catalyst Supported on Porous Chelate Resin-Metal Complexes for Hydrogenation of Olefin and Diene
Catalysts of Pt clusters/chelate resin-metal complexes of Na(I), Mg(II), and Al(III) were prepared by reduction of Pt ions immobilised on the high porosity supports. The catalytic activity of the supported clusters increased in the order: Na(I)<Mg(II)<Al(III), which is consistent with increase in surface area of the resin.

Kinetics of Liquid-Phase Hydrogenation of Cinnamaldehyde over a Pt-Sn/Nylon Catalyst
The kinetics of liquid-phase hydrogenation of cinnamyl alcohol and cinnamaldehyde over Pt/nylon and Sn-Pt/nylon catalysts were studied. The kinetics of cinnamaldehyde hydrogenation over Sn-Pt/nylon at 10-60°C were interpreted on the basis of a two-site model, where B sites, associated with Sn, were involved in hydrogenation of cinnamaldehyde and hydrocinnamaldehyde, whereas A sites, associated with Pt, catalysed cinnamyl alcohol hydrogenations. The results show strong adsorption of cinnamyl alcohol on Pt sites, which also explains the apparent negative activation energies of some rate constants.

Carbon Monoxide Restructuring of Palladium Crystalite Surfaces
Six Pd/Al₂O₃ catalysts, with dispersions ranging from 3 to 86% were studied during repeated cycles of exposure to CO at 25°C and reduction at 300°C. CO cycling lowers the dispersion of all the samples by 20 to 50%. The loss of surface sites was higher on the small crystallites. The adsorption capacity recovered with oxidation at 550°C and reduction at 300°C. The H₂ solubility in the bulk of the Pd crystallites was not affected by CO cycling. Surface restructuring may be used to enhance the catalytic activity of Pd.

Selective Acetylene Hydrogenation in Mixtures with Ethylene in the Presence of a Palladium Catalyst
Studies of hydrogenation of C₂H₂-C₂H₄ mixture on Pd/γ-Al₂O₃ catalyst performed at 311-373 K in a wide range of reagents concentrations showed the formation of C₂H₄ from the intermediate compound systems ZH₂-C₂H₆ (where Z are new active centres of the catalyst) which proceeds in two parallel routes. It is shown that in the case of C₂H₂-C₂H₄ interaction, the mechanism of ethylene and acetylene with H₂ is the same as that during hydrogenation of individual hydrocarbons.

The Effect of Bismuth on the Selective Oxidation of Lactose on Supported Palladium Catalysts
The selective oxidation of lactose by O₂ has been studied in a batch reactor containing an aqueous slurry of 0.5 kmol/m³ and 1.0 kg/m³ of Pd/C promoted by Bi. This resulted in 100% selectivity to Na lactobionate up to conversions of 95% in the pH 7-10 range and at up to 333 K. A maximum initial reaction rate of 0.47 mol/kg s occurred at molar Bi:Pd of 0.5-0.67. Other aldoses could be oxidised with similar selectivities.

Activity and Selectivity of 1-Hexene Conversion on SAPO-11 and Pd/SAPO-11
The activity and selectivity patterns for 1-hexene reactions were compared at 150-450°C for four different kinds of acidic zeolites (H-mordenite, HZSM-5, SAPO-11 and Pd/SAPO-11) with different acid properties and geometric structure. The Pd/SAPO-11 catalyst gave enhanced double bond shift (DBS) selectivity and less cracking at higher temperatures in comparison to unloaded SAPO-11. There was a strong correlation between the shift from DBS to cracking with total acidity.

An Infrared Study of the Hydrogenation of Carbon Monoxide and Carbon Dioxide at High Pressure over Pd/La₂O₃
A new high-pressure IR cell reactor has been used to study the reactions of CO and CO₂ with H₂ over Pd/La₂O₃ films at a pressure of 8300 Torr. The activation energy for the CO₂ hydrogenation (25.1 kcal/mol) which produces MeOH is higher than that reported elsewhere for the analogous CO hydrogenation reaction. The CO₂ reaction may proceed through hydrogenation of adsorbed CO, rather than by direct hydrogenation of CO₂ over Pd/La₂O₃.
Structure-Sensitivity of the Deactivation of Pd/SiO₂ for Methylcyclopropane Hydrogenolysis by CO


Pd/SiO₂ catalysts with 5–80% metal exposed have been characterised for reactivity for methylcyclopropane hydrogenvolysis as a function of CO. The CO surface coverage and metal crystallite size are important in the deactivation behaviour of the catalyst. Pretreatment conditions help to determine reaction and deactivation structure sensitivity patterns. As CO coverage increases a monotonic decrease in activity occurs for large Pd particles, while catalysts with >40% metal exposed have a near-step drop in activity between 20–30% coverage.

Effects of Promoters of Palladium/Silica Catalysts for the Synthesis of Methanol


Methanol synthesis from syngas on promoted Pd/SiO₂ catalysts was carried out at 1–20 atm (H₂:CO = 2) and 230–310°C. The effects of Ca, K or La promoters on the activity and selectivity for methanol formation were studied. The highest methanol activity was achieved with 0.5 wt. % Ca-promoted Pd/SiO₂ catalysts and was about four times higher than that of non-promoted catalyst.

Effects of Cerium Addition on the CO-NO Reaction Kinetics over Alumina-Supported Rhodium Catalysts


Laboratory reactor studies showed that the addition of Ce to a low-loaded Rh/Al₂O₃ catalyst resulted in changes in CO-NO reaction kinetics, mainly suppression of N₂O formation, decreased apparent activation energy, and a shift to a positive-order dependence of the rate on NO partial pressure. The Ce-induced modification of the kinetics leads to increases in the NO reduction activity at low temperatures.

Effect of Potassium on the Formation of Isocyanate Species in the NO + CO Reaction on Rhodium Catalyst


Adsorption and IR spectroscopic studies of the effect of K on the formation of isocyanate species in the NO + CO reaction on supported Rh catalysts showed that the addition of K to 5% Rh/Al₂O₃ significantly decreased the uptake of H₂, CO and NO at 300 K. Preadsorbed K caused a significant increase in the formation of the NCO complex, with the maximum intensity obtained for a sample containing 2.5% K. The same effect was observed on Rh/SiO₂ catalyst where two NCO species were identified (2180 cm⁻¹ for Rh-NCO and 2310 cm⁻¹ for Si-NCO).

CO Adsorption on Rhodium(I) and on Metallic Rhodium Supported on Titanium Dioxide


The interaction between a cationic organometallic Rh(I) compound and TiO₂ in acetone leads to Rh(I)/TiO₂. The reduction with H₂ at atmospheric pressure and ambient temperature yields a supported metallic Rh catalyst which is active in 1-hexene hydrogenation. The precursor and catalyst have been characterised, and the predominant species is dicarboxyl on both. Dissociative CO adsorption is discussed.

Selectivity Changes in the Ring-Opening Reaction of Methylcyclopentane over Rhodium Catalysts Caused by the Addition of Silver and Metal-Support Interactions


The hydrogenolysis of methylcyclopentane (MCP) was studied over Rh-Ag/TiO₂ catalysts after various reduction/oxidation treatments. The addition of Ag resulted in a decrease in activity, accompanied by an increase in the selectivity toward n-hexane (n-Hx). This increase in selectivity was enhanced when Ag and Rh are impregnated simultaneously and when the catalysts are reduced at 773 K. The selectivity changes can be interpreted in terms of a shift in the ring-opening mechanism. This shift is caused by a blockage of large ensembles required to constitute the multi-site complexes. This blockage would be more effective when Ag and TiO₂ species are simultaneously present on the Rh surface.

Carbon Dioxide Hydrogenation on Rhodium Supported on Transition Metal Oxides. Effect of Reduction Temperature on Product Distribution


Studies of the effects of metal reduction conditions during CO hydrogenation on Rh/TiO₂ and Rh/Nb₂O₅ catalysts showed the presence of C₁–C₄ hydrocarbons which followed Anderson-Schulz-Flory statistics. For Rh/TiO₂, the role of CO as an intermediate in CO₂ hydrogenation was clearly evident. In both catalysts, the formation of the SMSI state (strong metal-support interaction) during high temperature reduction greatly affected catalytic activities and selectivities. The differences in the general behaviour of the two oxides as far as the reversibility of the SMSI in the reaction conditions was concerned was ascribed to thermodynamic and/or kinetic constraints in the formation of SMSI during high temperature reduction.
Synthesis of Hydrocarbons and Alcohols from CO and H₂ over Co-Rh Catalysts

Studies of synthesis of hydrocarbons and alcohols from CO and H₂ (CO:H₂ = 1:2) over Co catalysts promoted by addition of Rh and Cu were performed at 250–300°C and pressure of 0.1–6.0 MPa. The results show that 4.5% Co-0.1% Rh-5:10% Cu/TiO₂ catalysts are highly active in the above synthesis and have much higher selectivity in regards to the formed alcohols as compared to the traditional Co-catalysts.

Immobilization of Rhodium Complexes with Chiral Cationic Water Soluble Ligands on Nafton-H and Other Strongly Acidic Cation Exchange Resins

Rhodium complexes of the chiral cationic water soluble ligands, [(S)-2,4-bis-[bis-(p-N,N-dimethylammoniumphenyl)phosphino]pentane]²⁺, etc., were immobilised on cation exchange resins. All these supported complexes catalyse the asymmetric hydrogenation of dehydroaminoacid derivatives with no detectable loss of Rh into the substrate phase. Rates and enantioselectivities depend on the ligand and the nature of the exchange resin.

IR Study of CO Adsorption and Its Interaction with Oxygen over Ir/Al₂O₃ Catalyst

An IR study of the behaviour of CO adsorption and its interaction with O over Ir/Al₂O₃ catalyst showed that CO adsorption on Ir/Al₂O₃ with high Ir loading was an activation process, and the intensity of the adsorbed CO band increased with the increase in adsorption temperature from ambient to 300°C. The amount of adsorbed CO at 150°C was approximately one half that of the maximum. The migration of adsorbed CO and O was increased by increasing the temperature.

Zeolite A-Supported Ru Catalysts

A number of zeolite A-supported Ru catalysts were prepared either by addition of Ru precursor to the zeolite A synthesis gel (ZS) with resulting metal being dispersed intrazeolitically, although not uniformly, or by surface deposition of Ru on zeolite A with metal particles primarily on the external surfaces of the zeolite crystallites. With the exception of the strong molecular sieving effect on the reaction of cyclopropane found for RuNaAl₂ZS₅, the most important effect on the catalysis was Ru particle size.

Surface Structure and Catalysis for CO Hydrogenation of the Supported Ru Species Derived from the Ru₃(CO)₁₂ Inorganic Oxides

Supported Ru cluster particles were prepared by the surface reaction of Ru₃(CO)₁₂ with inorganic oxides followed by H₂ reduction at 723 K. On V₂O₅ the cluster was converted to three-atomic-layer Ru metal particles, while one-atomic-layer [Ru₃] clusters were formed on SiO₂ (n=12) and TiO₂ (n=6). Clusters [Ru₃(OZ)₆] (Z=Al or Mg) with Ru-O surface bonds were formed on Al₂O₃ (n=6), K-doped Al₂O₃ (n=6) and MgO (n=3). CH₃ was predominantly formed on [Ru₃]/SiO₂. The 6-Ru atom clusters with Ru-Ru distances of 0.262–0.265 nm had the highest selectivity for C₁–C₄ hydrocarbon formation. Metallic [Ru₃] clusters on TiO₂ had higher activity than [Ru₃(OAl)₆] clusters bonded to the surface through O atoms. The smallest surface-bound clusters on MgO produced mainly CH₄ and CO₂.

HOMOGENEOUS CATALYSIS

A New Platinum-Based Catalyst System for Olefin Asymmetric Homogeneous Hydroformylation

A number of Pt(II) diphosphino complexes in combination with SnCl₂ are known to be active in olefin hydroformylation. It is now reported that the complex [Pt(C₅H₅)(+](-DIOP)] interacts with [PtCl₂((+)-DIOP)] to give catalysts active in the hydroformylation of styrene and 1-hexene. The activities of the systems depend upon the molar ratio of the two Pt complexes and the nature of the substrate. The systems display good chemoselectivity and induce asymmetry in the branched aldehydes formed.

Evidence for a Bis(alkylidene) silacyclobutene Intermediate in the Platinum-Mediated Formation of a Silacylobutene

The treatement of Ph₃Si(C≡CCMe₃)₂ with a cationic Pt-H reagent resulted in the formation of a 4-alkylidene-1-silacylobutene ring system. Acetic acid cleaves at Pt-C bond to yield alkynylsilane products, showing the intermediate formation of a Pt-Si-μ-alkynylidene complex. ROH reagents react with a proposed bis(alkylidene) silacyclobutene intermediate to initiate ring opening and to form 4-alkylidene-1-silacyclobutadienyl complexes (where R=H, Me, Et or Ph). The R=H complex ion structure was confirmed.
Hydroformylation with Platinum Phosphinito Complexes
Pt complexes containing phosphinito ligands afford active hydroformylation catalysts at 30–100 bar and 80–100°C. The hydroformylation rates for α-alkenes are the same as those obtained with Pt-trichlorostannate catalysts. Products are a mixture of alcohols and aldehydes with linearities in excess of 90%. Internal alkenes can also be hydroformylated with linearities as high as 70%.

Homogeneous Catalysis of Platinum Blue Related Complexes in Photoreduction of Water into Hydrogen
The evolution of H₂ is reported on dissolving platinum blue complexes [Pt(NH₃)₃(C₂H₄NO₂)₂][PF₆]₀, [Pt(NH₃)₃(C₂H₄NO₂)(PF₆)]⁻, [Pt(NH₃)₃(C₂H₄NO₂)]²⁻, and [Pt(NH₃)₃(C₂H₄NO₂)(H₂O)]⁻ in water. The H₂ seems to be due to an interaction between [Pt(NH₃)₃(C₂H₄NO₂)]²⁻ and proton. A homogeneous photochemical H-producing catalyst system is made with (1) or [Pt(NH₃)₃(C₂H₄NO₂)]²⁻, using EDTA as sacrificial electron donor, and Ru(bpy)₃²⁺ as photosensitiser and MV⁺ as electron relay. Quantum yields for their H₂ production are 0.022 and 0.11, respectively.

Palladium-Catalyzed Hetero- and Carboannulation of Vinylic Cyclopropanes and Cyclobutanes
ortho-Functionally substituted aryl iodides react under mild conditions with vinyl- and isopropenylcyclopropane and isopropenylcyclobutane in the presence of Pd(II) acetate and an appropriate base, K acetate, triethylamine or Na carbonate to give 2-(1-alkenyl)-substituted 2,3-dihydrobenzofurans, indolines and indans in good yield. This gives a novel versatile route to a variety of heterocycles and carbocycles, amenable to unsaturated cycloalkanes, 1,2-, 1,3- and 1,4-dienes as well as alkynes.

Carboxylic Acid Transvinylisation as Catalysed by Complexes of Palladium Acetate with Phenanthroline-Like Ligands
The complexing of Pd acetate with di-imine ligands results in a promotion effect on the vinyl exchange processes and ensures excellent selectivity and stability of the catalyst under reaction conditions. Vinylation of both saturated and unsaturated carboxylic acids by vinyl acetate proceeds smoothly even at an increased concentration of H₂O in the mixture.

Heteropoly Anion-Modified Palladium Catalyst for Reductive Carboxylation of Nitrobenzene
An efficient catalyst system of PdCl₂ and Keggin-type heteropoly anions containing Mo and V which had a noticeable promoting effect on the Pd, were used in a reductive carboxylation of nitrobenzene to form N-phenylcarbamate in the presence of alcohol in dimethyloxane solvent. Turnover numbers were 98 and 196 in terms of moles of Pd and heteropoly anion.

π-Olefin-Palladium-Copper Complexes as Intermediates in Formation of Propylene Glycol Monoacetate during Oxidation of Propylene in the System PdCl₂/CuCl₂/HOAc
Studies of the kinetic and physical-chemical mechanisms during propylene oxidation by O₂ in the system PdCl₂/CuCl₂/HOAc were performed by various electron spectroscopic techniques. The contact of propylene-oxygen gaseous mixture with acetate solutions of PdCl₂, CuCl₂, LiCl and LiOAc resulted in a catalytic reaction yielding propylene glycol monoacetate and acetone.

Phase Transfer Pd(0) Catalyzed Polymerization Reactions. III. Polymerization by Cross-Coupling of Alkyl-Boron Compounds and Aromatic Halides Catalyzed by PdCl₂(dppf) and Bases
A novel one flask polymerisation of a sequence of hydroboration of a diolfin with 9-borabicyclo[3.3.1]nonane followed by the intermolecular cross-coupling of the resulting α-ω-bis[B-alkanediyl-9-borabicyclo[3.3.1]nonanes with dihaloarenes is described. The reactions are catalysed by PdCl₂(dppf) and a base and are performed in a two-phase (organic liquid-liquid or solid-liquid) phase transfer catalysed system. This provides unique synthetic routes to the preparation of functional polymers containing C-C bonds in the main chain.

Hydrodechlorination of CCl₄ in the Presence of Pd(OAc)₂
Methane was produced by the reaction of H₂ on CCl₄ in acetic acid in the presence of Pd(OAc)₂ catalyst under 0.1 MPa and at 20–80°C. In the presence of aliphatic alcohols, CH₃OH in the reaction products decreased sharply yielding chloroform and ethyl chloride as main hydrodechlorination products.

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Synthetic Methodology Involving the Carbopalladation of Allenes


Carbopalladation of allenes by vinyllic or arylid Pd species (vinyllic or arylid halides + Pd(0)/L, catalyst) gives new 2-substituted ally Pd complexes, which have interesting stereochemical properties due to the conjugated unsaturated system on the central C atom of the ally ligand, and react with high regio and stereoselectivities with delocalised carbonucleophiles. The overall process creates two new C–C bonds in a single reaction and leads to functionalised 1,3-dienic (or styryl) compounds of known stereochemistry.

Expanding Industrial Applications of Palladium Catalysts

J. TSUJI, Synthesis, 1990, (9), 739–749

A review of Pd in industry as homogeneous and heterogeneous catalysts classifies them into having oxidative reactions with olefins and aromatic compounds and oxidative carbonylation, by Pd(II) salts and appropriate reoxidants; and Pd(0) complexes for reactions of organic halides and reactions via allylPd complexes. Careful selection of reaction conditions, solvents, choice of ligand and catalyst modifiers are necessary to achieve long catalyst life and high selectivity. (89 Refs.)

Rhodium Phosphine Complexes as Acetalisation Catalysts


Complexes containing Rh(III) triphos moieties as catalyst precursors have been studied for acetalisation and trans-acetalisation reactions. The complexes are reactive under mild conditions and give a high turnover rate and induce interesting diastereoselectivities. For methyl-substituted acetals, the in situ catalysts prepared from [Rh(Diol)Cl], [(Diol=1,5-hexadiene or 1,5-cyclooctadiene) and 3-alkyphenanthrolines display extremely high catalytic activity in the transfer hydrogenation of acetophenone. Turnover rates up to 10,000 cycles/h have been recorded in 2-propanol solution at 83°C, with KOH as promoter. Asymmetric inductions up to 65% e.e. have been obtained, using a ligand with a chiral trimethylpropyl substituent. In the asymmetric process the most active and stereoselective catalytic species might be a Rh hydride complex containing two phenanthroline ligands in a chiral C₂ array.

Asymmetric Metal Complexes Catalysis. V. Asymmetric Hydroxysylation on the Phosphine Complex [Rh(COD)Cl], (S)-Phephos


Studies of the asymmetric hydroxysylation of acetophenone by diphenylsilane in the presence of [Rh(COD)Cl], (S)-Phephos showed high activity and enantioselectivity of the catalysts. Enantioselectivity of the catalyst increased with increase in the reaction temperature, and the reaction still proceeded at acetophenone:Rh ratio of up to 20,000.

Optically Active Phenanthrolines in Asymmetric Catalysis. III. Highly Efficient Enantioselective Transfer Hydrogenation of Acetophenone by Chiral Rhodium/3-Alkyl Phenanthroline Catalysts


The in situ catalysts prepared from [Rh(Diol)Cl], (Diol=1,5-hexadiene or 1,5-cyclooctadiene) and 3-alkyphenanthrolines display extremely high catalytic activity in the transfer hydrogenation of acetophenone. Turnover rates up to 10,000 cycles/h have been recorded in 2-propanol solution at 83°C, with KOH as promoter. Asymmetric inductions up to 65% e.e. have been obtained, using a ligand with a chiral trimethylpropyl substituent. In the asymmetric process the most active and stereoselective catalytic species might be a Rh hydride complex containing two phenanthroline ligands in a chiral C₂ array.

An Experimental and Modelling Study of Polybutadiene Functionalization to Polyaldehydes Using a Homogeneous Rhodium Catalyst


The liquid-phase hydroformylation of a polybutadiene containing 1,2 and 1,4 olenic units can be performed using a homogeneous Rh-phosphine ligand catalyst (Wilkinson’s) with excess phosphine ligand at mild reaction temperatures. The product is a polybutadiene whose degree of olenic unit functionalisation can be controlled through use of proper reaction conditions. The olenic units in the polybutadiene are selectively hydroformylated to the 1,2 terminal branched and 1,4 internally branched aldehyde products. The aldehyde addition is reasonably uniform in the range of polymer molecular weight.

Unusual Activity and Selectivity in Alkyne Hydrosilylation with an Iridium Catalyst Stabilized by an O-Donor Ligand


Studies of alkyne hydrosilylation by Ir in the O-donor ligand environment of Grim’s triso ligand (tris(diphenylmethylphosphoranyl)methane) showed that the reaction is selective for 1-alkynes and regioselective for β-products. However, it gave the thermodynamically less favoured cis-vinylsilane products by an unexpected anti addition of Si–H to the triple bond. Mechanistic studies suggest that the alkyne first inserts into the M-Si, not the M-H, bond and that a trans to cis rearrangement occurs via an η′-vinyl intermediate before reductive elimination. A number of Rh and Ir complexes of the type [(triso)ML₃] are prepared.
Selective Oxygenation of Aliphatic Ethers Catalyzed by Ruthenium(II) Complexes


Studies of selective and fast conversions of primary ethers to esters (or lactones) were performed using Li hypochlorite in the presence of catalytic amounts of Ru(II) complex catalysts RuX₃L₃, (L is (CH₃)₂SO and (L₃) is 1,3-bis(diphenylphosphino)propane). Isopropyl ether undergoes oxidative cleavage to acetone, while secondary ethers bearing methylene groups in the β-position are converted into β-keto ethers. Methyl ethers are unaffected by the oxidation.

A New Ruthenium(VI) Oxidant: Preparation, X-Ray Crystal Structure, and Properties of (Ph₄)[RuO₄(OAc)Cl₂]


The title compound was obtained by the addition of RuO₄ in CCl₄, to a slight excess of PPh₃ and glacial acetic acid in acetonitrile, followed by recrystallisation or by recrystallisation from dichloromethane–CCl₄. The compound has a quasi-trigonal bipyramidal structure with a symmetrically bound acetato ligand and cis-dioxo ligands in the trigonal plane. It is an effective oxidant for halides, alcohols, sulphides and phosphines, functioning catalytically in the presence of N-methylmorpholine-N-oxide.

Autocatalysis and Free Radical Mechanism in a Ruthenium Cluster Catalysed Hydrogen Transfer Reaction


The mechanisms of the [(Ph₃P)₂N][H₂Ru₄(CO)₁₂] (1) catalysed disproportionation and transfer-hydrogenations of cyclohex-2-en-1-one have been shown to involve free radicals. In the latter reaction (1) is converted to other carbonyl species via autocatalysis. Spectroscopic analyses at the end of a catalytic run at 82°C and 5h, and > 100 turnovers of cyclohexanol with (1) as the precatalyst showed that all of (1) was converted into a mixture of soluble carbonyl and hydridic species.

Ruthenium-Catalysed C-H Bond Activation. Evidence for a Concerted Mechanism in Oxyfunctionalization of Cyclic Saturated Hydrocarbons


Oxidation of bridged polycyclic alkanes with in situ generated RuO₄ occurred by a concerted mechanism involving interaction of the highly electrophilic oxo Ru species with tertiary unhindered C-H bonds. However, it is not yet clear whether an alkoxo-hydroro- or alkoxo-hydrido-oxo Ru species was involved as a key intermediate.

Oxo Transfer and Metal Oxidation in the Reaction of [Ru(PPh₃)₃Cl₂] with m-Chloroperbenzoic Acid: Structure of [Ru(PPh₃)₃(m-CIC₆H₄CO₃)Cl₂]


One mol and 0.5 mol of peracid were consumed for oxo transfer to PPh₃ and oxidation of metal, respectively, in the reaction of [Ru(PPh₃)₃Cl₂] with m-CIC₆H₄CO₃H. X-ray studies of the product [Ru(PPh₃)₃(m-CIC₆H₄CO₃)Cl₂] showed that after oxo transfer the carbonylate residue remains chelated to the metal centre. The trans,cis,cis-RuP₃O₁Cl₂, co-ordination sphere has two-fold symmetry. The complex undergoes one-electron quasi-reversible reduction but only at low potentials.

FUEL CELLS

“Development of Advanced Noble Metal-Alloy Electrocatalysts for Phosphoric Acid Fuel Cells (PAFC)”


Highly dispersed Pt and Pt alloys for PAFC electrocatalysts of crystallite size 12 Å diameter are discussed. For the cathodes advanced alloys have been developed of higher performance than Pt. For anodes diluting the Pt with less expensive materials gives a superior performance to Pt alone. For O reduction modifications to produce ordered alloys have given stability for over 9000 hours in the hot PAFC environment, as have alloys of Pt-Co and/or Cr containing Ga additions. For H oxidation Pt-Pd alloys show greater tolerance to poisoning and greater stability against crystallite growth. For successful commercialisation fuel cells must achieve high performance, low cost and long life.

ELECTRICAL AND ELECTRONIC ENGINEERING

Display of Wide Dynamic Range Infrared Images from PtSi Schottky Barrier Cameras


Twelve-bit digitised infrared images taken with PtSi Schottky barrier detector arrays have been processed on work stations. Two techniques for 8-bit global display are compared. The projection technique gives superior results based on an extensive set on indoor, day and night imagery. The new projection algorithm can be used as a powerful and robust local contrast enhancement technique. A real-time implementation of the projection algorithm is now incorporated into a specially designed camera and gives a very satisfactory automated alternative to the offset/gain controls.

Temperature Dependence of the Resistance in the Pt/Ti Nonalloyed Ohmic Contacts to n-InAs Induced by Rapid Thermal Processing


The temperature dependence of the resistance in the Pt(60 nm)/Ti(50 nm) nonalloyed ohmic contacts to p-InAs (Zn doped $1 \times 10^{18}$ to $1 \times 10^{19}$/cm$^3$) induced by rapid thermal processing at 300–600°C was studied. The ohmic nature of these contacts was attributed to both the low metal-semiconductor interfacial barriers and to the heavily doped semiconductor contacting layers. The results showed conversion from thermionic emission as the dominant carriers transport mechanism across the interfacial barrier for the as-deposited sample to a combination of thermionic and field emission mechanisms for the heat-treated samples.

Electrical and Structural Properties of Pt/Ti/p+-InAs Ohmic Contacts


The thermally stable Pt/Ti metallisation scheme was applied to Zn doped p+-InAs layers to evaluate the influence of the outstanding electrical properties of the p+-InAs, such as the narrow band gap and the surface Fermi level pinning in the conduction band on the ohmic contact performance. Zn doping was $1 \times 10^{18}$ to $1 \times 10^{19}$/cm$^2$. After rapid thermal processing for 30 s the specific contact resistances were lowered to $<6 \times 10^{-9}$ Ω cm$^2$ for a 450°C anneal. This heat treatment enhanced limited reactions in both the Pt/Ti and Ti/InAs interfaces, but did not degrade the stable microstructure.

Hole Trap Level in Pt-Ti/p-InGaAs/n-InP Heterostructures Due to Rapid Thermal Processing


Deep level transient spectroscopy and I-V-T measurements were performed on Pt-Ti/p-InGaAs/n-InP heterostructure mesa diodes annealed by rapid thermal processing (RPT). Four electron trap levels with activation energies of 0.61, 0.45, 0.35 and 0.30 eV were observed which are believed to be native defects in InP, and they were independent of RTP conditions. A new hole trap, with an activation energy of 0.89 eV was found only for samples annealed at >500°C and thought to be introduced by Ti diffusion at high temperature. I-V-T data were consistent among all samples, indicating that the hole trap level is not dominant in the current mechanism.

Stability of Amorphous Ir-Ta Diffusion Barriers between Cu and Si


Thin film amorphous Ir-Ta (a-IrTa) was tested as a diffusion barrier between (100) Si and Cu. Sandwich structures of (100) Si/a-IrTa/Cu/a-IrTa were stable during annealing in vacuum up to 700°C. At 750°C interdiffusion of Cu and Si occurred. The crystallisation temperature of thin film a-IrTa, was reduced from 900 to 750°C in the presence of Cu. The high stability of the metallic a-IrTa buffer layer makes it useful for application in miniaturisation of very large scale integrated electronics.

MEDICAL USES

Metal Complexes as Anticancer Agents. The Future Role of Inorganic Chemistry in Cancer Therapy


A review of the background and reasons for the success of cisplatin in the treatment of various tumours is discussed. Other metal complexes with cancer inhibiting properties for chemotherapy are examined; these include Ru compounds, Ti compounds and possibly Au and Sn compounds; as well as drug targeting with Pt complexes showing affinity to hormone receptors and osteotropic properties. (77 Refs.)

[Bis(aminomethyl)dimethylsilane] platinum(II)dichloride: A Potential Antitumor Agent


The title compound was synthesised by a three-step procedure and its anti-tumour activity was investigated against L1210 leukaemia in mice. With suitable dosing it extended the life span by at least 100% and resulted in 40–50% survivors (day 30) in two experiments. It appeared to be as active as cisplatin under these conditions.

Effect of Palladium Addition on the Tarnishing of Dental Gold Alloys


Tarnishing tests were performed on Au-Cu-Pd and Au-Cu-Ag alloys. Tarnish resistance was almost perfect for the alloys with nobility of >50%, but it seemed to relate to the Pd:Cu atomic ratio for the alloys with low nobility. Pd inclusion reduced the tarnish susceptibility up to ~ 10 at.%. Tarnishing of the alloy with low nobility was very sensitive to its microstructure. Pd-bearing alloy showed no increase in the degree of tarnishing by phase separation. This may be attributed to the enrichment of Pd in the Cu-rich phase.