ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Microstructures and Magnetic Properties of Fe-Pt Permanent Magnets
The magnetic properties of Fe-38.5Pt, Fe-39.5Pt and Fe-50.0Pt (at.%) alloys were studied after various heat treatment conditions. The magnetic hardness of the Fe-39.5Pt alloy showed a maximum after annealing for 10 h at 873 K. This alloy had the highest coercivity, and was a fully ordered single phase, γ1, composed of small antiphase domains of size ~10 nm. The magnetic hardness degraded greatly with the formation of a poly-twinned structure.

Hydrogenation Characteristics of TiFe1-xPdx (0.05 ≤ x ≤ 0.30) Alloys
The crystal structure and hydriding behaviour of pseudobinary TiFe1-xPdx (0.05 ≤ x ≤ 0.30) alloys are reported. Increasing the amount of substituted Pd increased the lattice constant while maintaining the CsCl type crystal structure. Partial substitution by Pd, which has superior catalytic and hydriding properties, effectively lowered the activation temperature of the intermetallic TiFe alloy.

Preserved Interfacial Magnetism and Giant Antiferromagnetic Exchange Coupling in Co/Rh Sandwiches
The interlayer coupling in Co/Rh/Co sandwiches prepared by UHV evaporation was studied using magnetisation and transport experiments. The antiferromagnetic coupling strength for thin Rh layers was the largest ever found in magnetic systems, reaching ~34 erg cm⁻³ for a 5 Å thick Rh interlayer. This is 7–8 times larger than previously reported for a Co/Ru system.

A Study of the Al-Ni-Ru Ternary System below 50 at.% Aluminium
Studies of the Al-Ni-Ru system showed two ternary invariant reactions, peritectic and eutectic, with a binary eutectic between. The Ru-rich solid solution had greater solubility for Ni (~30 at.%) than for Al (~9 at.%). The Ni-rich solid solution and the phase based on AlNi, extended into the ternary to ~14 at. %. The extent of the B2 solidification surface was large.

CHEMICAL COMPOUNDS

Preparation of Pd-Pt Bimetallic Colloids with Controllable Core/Shell Structures
Nanosopic polymer-protected Pd-Pt bimetallic colloids with controllable core/shell structures have been prepared by a so-called H₂-sacrificial protective strategy. H₂ was used as reducing agent to produce a thin Pt or Pd shell on the preformed poly(N-vinyl-2-pyrrolidone)-protected 1–3 nm Pd or Pt core prepared in ethylene glycol. Pd-core/Pt-shell and Pt-core/Pd-shell structures were confirmed by IR-CO probe results.

Formation of a Pt-Carbonyl Colloid by Reaction of Colloidal Pt with CO
The formation of Pt-carbonyls from the reaction of CO on colloidal Pt in aqueous media by the citrate method was investigated. The resultant Pt-carbonyls were aggregates of the Pt-carbonyl family [Pt₃(CO)₆]⁺ with n = 1 to ~10. The Pt–colloid converted into carbonyls in 80–90% yield, but not if the colloid was pretreated with H₂. When the Pt-carbonyl was treated with KOH, isolated [Pt₃(CO)₆]²⁻ clusters were observed.

A Novel Type of Amidato Coordination: The Metallocycle Rh-Rh-NH₂(C(Me)=N)₃(CO)=O
The reaction of [RhCl₃(Cp*)(μ-CH₃)₂(μ-OCO)] and with acetonitrile in aqueous solution followed by addition of KPF₆ gave the Rh-Rh complex [RhCl₃(Cp*)(μ-CH₃)₂(μ-OCO)]²⁻ which is the first example of an amidato complex where the ligand [NHC(N=NMe)₃] links the metal-metal site forming a new type of metallocycle. It is also among the first examples of hydrolysis of NHCR species in Rh complexes.

Activation of Hydrogen on Iridium(I) Centers in Water: Solvent Effects, pH Effects, and Iridium-Hydride Exchange with D₂O
The water-soluble Ir complexes trans-Ir(CO)₂Cl₂(X = Cl, OH; L=PPh₃(m-C₆H₄SO₃K) (TPPMS), P(m-C₆H₄SO₃Na)₃ (TPPTS)) were used to examine the range of solvent effects for H₂ activation at an Ir(I) centre and of pH changes on the rate of H₂ addition to an organometallic centre. In H₂O the hydride ligands undergo H/D exchange with D₂O with the rate dependent on the trans ligand.

Incorporation of Ru₃(O,C(CH₃)₃CH₃), into Extended Chains: Interaction of Ru₃(O,C(CH₃)₃CH₃), with Pyrazine, 4-Cyanopyridine, TCNE, and p-Benzquinone


Ru₃(O,C(CH₃)₃CH₃), (1) was reacted with bridging ligands possessing extended-systems in order to form conductive polymers. With pyrazine, the polymer [(1)(pz)], was isolated, but 4-cyanopyridine (4-cp) gave only the bis-adduct (1)(4-cp). In both cases x-interactions occurred between the Ru-Ru π* HOMO and the ligand x orbitals. TCNE and p-benzoquinone underwent redox reactions, with the latter giving the desired [1'][SQ-1] which was unstable and readily dissociated to give (1) and p-benzoquinone.

Preparation and Characterization of [HRu₃(CO)₆(PPh₃)₂BH₂] (x = 1–3) and the Oxidative Addition of a P-H Bond in [HRu₃(CO)₆(PPh₃)₂BH₂]


Mono-, di- and trisubstituted Ru products were prepared by the photolysis of [HRu₃(CO)₆BH₂] with PPh₃. The solid state structure of [HRu₃(CO)₆(PPh₃)₂BH₂]-CH₂NO₂ was confirmed and the substitution sites assigned. [HRu₃(CO)₆(PPh₃)₂BH₂] heated in cyclohexane undergoes oxidative addition of one P-H bond to form [H₂Ru₃(CO)₆(PPh₃)₂(P-PPh₂)BH₂].

Mixed Valence Properties of a New Binuclear Complex, [(edtaH)Ru₆M(NCp)₅(CN)],⁺ and Kinetic Studies of the Aqua Substitution Reaction in Ru₆(edta)(H₂O)⁺ by Ru(CN),⁺


The synthesis of an asymmetric mixed valence complex, K₄[(edtaH)Ru₆N(RuCN)₅(CN)],2H₂O, by the aqua substitution reaction of [Ru(edtaH)H₂O] with K₃[Ru(CN)] is reported. An associative mechanism for the substitution reaction with a second order rate constant of 13.8 ± 0.6 M⁻¹s⁻¹ at 25°C and pH = 5.0 was observed. The complex displayed a metal-to-metal charge transfer maximum at 682 nm in H₂O at 25°C.

ELECTROCHEMISTRY

Oxygen Electroreduction on Titanium-Supported Thin Pt Films in Alkaline Solution


The electrochemical reduction of O₂ at thin Pt films on Ti was studied in alkaline solution and the kinetics were shown to be qualitatively the same as at Pt/glassy C electrodes. Tafel plots showed a slope of -60 mV dec⁻¹ at low-, and -260 to -490 mV dec⁻¹ at high-current densities. The potential of the H₂ adsorption-desorption peaks and the Pt oxide reduction peak shifted towards positive potentials with increasing Pt film thickness in KOH and H₂SO₄.

Photoconvertion

Photoinduced Hydrogen Evolution by Using Platinum-Loaded Langmuir-Blodgett and Cast Films of Porphyrin


Pt-loaded Langmuir-Blodgett (1) and cast films (2) of a porphyrin have been prepared and steady photoinduced H₂ evolution observed from both films under steady state irradiation. The porphyrin turnover number in (1) and (2) reached 360 and 151, respectively, after 354 h irradiation and the rate of H₂ evolution was roughly twice as high on (2) as on (1).

Characterization of Excited Electronic and Vibrionic States of Platinum Metal Compounds with Chelate Ligands by Highly Frequency-Resolved and Time-Resolved Spectra


A comprehensive review is given of the lowest excited electronic states of triplet character and related vibronic properties of per-protonated, per-deuterated and partially deuterated [Pt(bpy)]⁺ [Rh(bpy)]⁺, [Ru(bpy)]⁺ and [Os(bpy)]⁺ based on highly frequency-resolved and time-resolved emission and excitation spectra. Data for other Ru and Pt complexes are given. The role of traps and sites is discussed in the context of high-resolution, site-selective, and line-narrowed spectra of chromophores doped into matrices. It is emphasised that chemical tunability may allow the controlled variation of physical properties. (321 Refs.)

Photochemistry of the IrCl₆²⁻ Complex in Methanol Matrices


The photochemistry of IrCl₆²⁻ in MeOH matrices frozen at 77 K was studied by ESR. Photo-reduction produced IrCl₅⁻ and a 'CH₂OH radical which gave rise to the radical complex, IrCl₄⁻, CH₂O ÷CH₂OH; this showed a maximum at 287 nm. When the matrix was heated at 115 K, this complex disappeared.
Dynamical Processes in the Lowest-Excited Triplet Metal-to-Ligand Charge Transfer States of Ruthenium and Osmium Diimine Complexes in Crystals


The lowest-excited states in Ru(II) and Os(II) diimine complexes, based on studies of their optical spectra in crystalline environments, are reviewed. The transferred charge in the lowest-excited triplet metal-to-ligand charge transfer states is localised on a single ligand in Ru(II) diimine complexes and the excitation exchange interaction between equivalent metal-ligand subunits is < 0.5 cm⁻¹. (70 Refs.)

Photocatalytic and Aerobic Oxidation of Saturated Alkanes by a Neutral Luminescent trans-dioxoosmium(VI) Complex [OsO₂(CN)₂(dpphen)]


A neutral trans-Os(VI) complex [OsO₂(CN)₂(dpphen)] (dpphen = 4,7-diphenyl-1,10-phenanthroline), which can mediate the photocatalytic oxidation of saturated alkanes in the presence of O₂, was emissive in the solid state and in solution at room temperature with emission occurring at 635 nm with an excited state lifetime of 0.95 μs in MeCN. Under UV-VIS irradiation, cyclohexane was oxidised to cyclohexanol and cyclohexanone with a turnover number of 16.

APPARATUS AND TECHNIQUE

Adsorptive Stripping Measurements of Chromium and Uranium at Iridium-Based Mercury Electrodes


Ir-based Hg electrodes are used for adsorptive stripping measurements of Cr and U in the presence of the DTPA and propyl gallate complexing agents. Detection limits of 0.4 μg l⁻¹ U and 0.5 μg l⁻¹ Cr were obtained after a 10 min adsorptive accumulation. This system is applicable to on-site measurements of trace U and Cr, such as in groundwater and soil samples. The electrodes are highly stable and contain less Hg than standard hanging Hg drop electrodes.

Sol-Gel Based Amperometric Biosensor Incorporating an Osmium Redox Polymer as Mediator for Detection of L-Lactate


A novel amperometric biosensor for the determination of lactate was made by immobilising lactate oxidase and the redox polymer [Os(bpy)₃(PVP)(Cl)]Cl onto the surface of a glassy C electrode, followed by coating with a sol-gel film derived from methyltriethoxysilane. Lactate was determined at 400 mV and the range of linear response, slope of linear response and detection limit were 0.1–9 mM, 1.02 μA mM⁻¹ and 0.05 mM, respectively.

HETEROGENEOUS CATALYSIS

Kinetics and Mechanism of the Reduction of NO by C₃H₆ over Pt/Al₂O₃, under Lean-Burn Conditions


The effects of temperature, contact time and reactant concentration on the lean deNOX reaction over Pt/Al₂O₃, using C₃H₆ as the reductant, were studied and a kinetic model developed. Adsorbed atomic O was the main species on the metal surface, inhibiting C₃H₆ oxidation by O₂ and facilitating the oxidation of NO to NO₂. The reaction rate was determined by dissociative chemisorption of C₃H₆, involving the breaking of a C-H bond. Possible mechanisms for the reduction of NO to N₂ and N,O are discussed.

Conversion of Canola Oil to Various Hydrocarbons over Pt/HZSM-5 Bifunctional Catalyst


The catalytic conversion of canola oil was studied over 0.5 wt. % Pt/HZSM-5 at atmospheric pressure in a fixed bed micro-reactor at 400–500°C. The gas yields were between 22 to 65 wt.% and higher in the presence of steam. The C₆ iso/mono-alkane ratios were higher, but the organic liquid product (OLP) yields were slightly lower, compared with pure HZSM-5 catalyst. The major components of OLP were aliphatic and aromatic hydrocarbons.

Reforming of Hexane with Pt/Zeolite Catalysts


The aromatisation and isomerisation of n-hexane were investigated over various zeolite-supported Pt catalysts. For Pt/K-β, Pt/K-mordenite and Pt/K-L, the addition of KCl increased the selectivity towards benzene formation and decreased selectivity towards hydroisomerisation. The treatment of Pt/K-FSM-16 with K₂CO₃ decreased the formation of cracking products and increased benzene selectivity. Above 623 K, Pt/H-FSM-16 and Pt/H-L catalysts showed lower cracking selectivity and higher isomerisation selectivity than Pt/H-β, with Pt/H-FSM-16 being more resistant to deactivation at high temperatures.

Catalytic Properties of Pt-Ge Intermetallic Compounds in the Hydrogenation of 1,3-Butadiene


The catalytic properties of Pt-Ge intermetallic compounds, Pt₆Ge, Pt₆Ge and Pt₆Ge were studied for the H₂-D₂ equilibration and the hydrogenation of 1,3-butadiene. These intermetallic compounds showed lower activity for H₂ dissociation than pure Pt which decreased with decreasing Pt content and resulted in low hydrogenation activity. A high selectivity for butenes resulted from the lower selectivity for butene hydrogenation than 1,3-butadiene hydrogenation.
A Highly Catalytic Bimetallic System for the Low-Temperature Selective Oxidation of Methane and Lower Alkanes with Dioxygen as the Oxidant


A bimetallic system consisting of a mixture of CuCl and metallic Pd in a 3:1 mixture of CF$_3$CO$_2$H and H$_2$O, in O$_2$ and CO, is highly catalytic for the low-temperature selective oxidation of CH$_4$, C$_2$H$_6$, and n-butane. CH$_4$ was selectively converted to MeOH at the rate of 119 min$^{-1}$ at 145–150°C. Both C-H and C-C cleavage products were observed for C$_3$H$_6$ and n-butane giving MeOH, EtOH and acetic acid.

Preparation, Characterisation and Catalytic Hydrogenation Properties of Palladium Supported on C$_x$


A C$_x$-supported Pd catalyst was prepared by reacting C$_x$ and Pd(OAc)$_2$(PPh$_3$)$_2$, in toluene to give the complex C$_x$[Pd(OAc)$_2$(PPh$_3$)$_2$], which was heated in H$_2$ at 523 K for 4 h. 1 mol% of the catalyst promoted hydrogenation of diphenylacetylene, phenylacetylene, cyclohexene and hex-1-ene to give 100% conversion to 1,2-diphenylethane, phenylethane, cyclohexane and hexane after 18, 13, 21 and 12 min, respectively. Similar hydrogenations over a Pd/active charcoal catalyst gave similar yields but took longer.

Oxidation of CO and Hydrocarbons on Palladium Zeolite Containing Catalysts


The effect of reaction conditions on the physico-chemical properties of a Pd/zeolite catalyst was studied during CO and hydrocarbon oxidation. When ≤ 30 wt.% of zeolite NaY was inserted into the matrix of amorphous alumino-silicate, highly stable zeolite granules were obtained. The optimum dispersion was obtained by depositing 15–30Å Pd particles on the support by calcination at 300°C followed by reduction in H$_2$ at 500°C. The activity of the catalyst decreased with the increase in acidity of the support, but the electron-deficiency increased due to adsorption changes.

Effect of Hydrogen Treatment of Active Carbon as a Support for Promoted Ruthenium Catalysts for Ammonia Synthesis


The treatment of active C with H$_2$ at 1073–1188 K for > 12 h leads to the elimination of surface impurities such as S, N, O and Cl. This treatment along with pre-reduction of the catalyst, was found to double or triple the activities of Cu$^{+}$-, Ba$^{2+}$- or Ce$^{3+}$-promoted Ru catalysts for NH$_3$ synthesis. When 2 mass% Ru-BaO/active C (Ba/Ru = 5) was used, the reaction gave 2 mmol NH$_3$ h$^{-1}$ g$^{-1}$ at 588 K under 1 atm. The activity increased with prolonged H$_2$ treatment of the active C.

HOMOGENEOUS CATALYSIS

A Novel Stereoselective and Catalytic C-C Coupling Reaction: Acetylene Dimerization Accompanied by Addition of Iodine to Yield (E,E)-1,4-diiodobuta-1,3-diene in the Pt$^{IV}$-I$_2$-MeOH System


The dimerisation of acetylene followed by addition of I$_2$ occurs at 30°C in a MeOH solution of NaI, Na$_2$PtCl$_4$, H$_2$O and I$_2$, to yield selectively (E,E)-1,4-diiodobuta-1,3-diene in virtually quantitative yield. A proposed mechanism involves the formation, via 2 triple bond iodoplatination steps, of an intermediate cis-divinyl Pt(IV) derivative followed by reductive elimination of the product.

Catalytic Colloidal Pd Dispersions in Water-Organic Solutions of Quaternary Ammonium Salt


Colloidal Pd, prepared in H$_2$O-organic microemulsions containing the cationic surfactant aliquat 336, was found to catalyse the transfer hydrogenolysis of p-bromotoluene with Na formate. Catalytic activity increased with a decrease in particle size. The particle size was controlled by the preparation conditions with coarser particles being formed at higher water contents and lower temperatures.

Novel Rhodium-Catalyzed Cyclic Carbonylation of 2-Phenylenylbenzoates Leading to Indeno[1,2-c]isocoumarin


The carbonylation of ethyl 2-phenylethynylbenzoate under H$_2$O-gas shift reaction conditions was catalysed by Rh$_6$(CO)$_{16}$ in the presence of PPh$_3$, Et$_3$N, CO and H$_2$O in 1,4-dioxane. The tetracyclic lactone, indeno[1,2-c]isocoumarin was the major product, derived from bond fission of the ester group and C-H bond activation of the phenyl group.

Liquid-Biphase Hydrogenolysis of Benzo[5]thiophene by Rhodium Catalyst


The catalytic activity of the zwitterionic complex [(sulphos)Rh(cod)] (sulphos = $-$O,S(C$_6$H$_5$)$_2$CH$_2$C($-$CH$_2$PPh$_3$)$_3$) for the hydrogenation and hydrogenolysis of benzo[5]thiophene was studied in either MeOH or liquid-biphase systems of MeOH or MeOH–H$_2$O and n-heptane. Under neutral conditions the selective hydrogenation proceeded slowly to give 2,3-dihydrobenzo[5]thiophene. In the presence of NaOH selective hydrogenolysis gave the 2-ethylthiophenol Na salt in < 5 h. This method can remove residual thiophenic contaminants from petroleum distillates.
Enantioselective Hydrogenation of Imines with Chiral (Phosphanodihydrooxazole)-iridium Catalysts


Cationic IrI complexes of chiral phosphanodihydrooxazoles were used for the enantioselective hydrogenation of prochiral N-alkyl and N-aryl imines. For N-aryl imines of acetophenone, enantiomeric excesses (ee) of ≤ 79 % were obtained. On hydrogenation of the N-phenyl imine of acetophenone, up to 89 % ee and turnovers numbers approaching 5000 were achieved with 0.1 mol% of catalyst.

Novel Ruthenium-Based Catalyst Systems for the Ring-Opening Metathesis Polymerization of Low-Strain Cyclic Olefins


Versatile and highly active catalyst systems for the ring-opening metathesis polymerisation of strained and low strain olefins were prepared from RuCl(arene)(PR)3 precursors after activation with (trimethylsilyl)diazomethane. Polymerisation of cyclooctene derivatives bearing acetal, ether, ester, epoxide, etc., functionalities gave polymers in good yields.

FUEL CELLS

Electrocatalytic Oxidation of Methanol on Platinum Nanoparticles Electrodeposited onto Porous Carbon Substrates


In order to enhance catalyst use on MeOH fuel cell electrodes, thin layers of various C powders and recast Nafion® were electrochemically plated with Pt. Both the Pt mass and specific activity for MeOH oxidation increased with the amount of surface oxides on the C support. It is concluded that the Pt activity for the MeOH oxidation is not directly related to particle size but to the fine structures of the Pt surface, which may depend on the Pt specific surface area, the nature of the substrate or preparation method of the catalyst.

ELECTRICAL AND ELECTRONIC ENGINEERING

Pd/Zn/Pd Ohmic Contacts to p-Type GaP


Low resistance ohmic contacts to Zn-doped p-type GaP were fabricated using an annealed Pd/Zn/Pd metallisation. After heating, the Pd/Zn/Pd multilayer structure had good ohmic characteristics. The quality of the ohmic layer depended on the time and temperature of alloying. When the surface hole concentration of the p-type GaP was 2 × 1018 cm−3, a specific contact resistance of 6 × 10−3 Ω cm2 was obtained at the optimum alloying temperature of 550°C and time of 3 minutes.

Comparison of Interfacial and Electronic Properties of Annealed Pd/SiC and Pd/SiO2/SiC Schottky Diode Sensors


The effects of placing a thin layer of SiO2 between the Pd and the SiC of Pd/SiC Schottky diodes used as H2 and hydrocarbon gas sensors were studied. The electrical response and interfacial properties of Pd/SiC (1) and Pd/SiO2/SiC (2) Schottky diodes were compared after annealing at 425°C for 140 h. The thin SiO2 layer decreased vertical interdiffusion and Pd,Si formation between the Pd and SiC, and formed a stable sharp (Pd+Pd,Si)/SiC interface. But, due to the SiO2 layer formation, further stabilisation is needed.

Conductive Powder Preparation and Electrical Properties of RuO2 Thick Film Resistors


Powder and electrical characteristics of thick film resistors (TFRs) using RuO2 powders were studied. The resistivity of TFRs decreased and the temperature coefficient of resistance (TCR) became more positive with decreasing crystalline size. TFRs having conductive powders of higher specific surface area at the same crystalline size showed lower resistivity and higher TCR values.

Characterization of a Sol-Gel Derived Pb(Zr, Ti)O3 Thin-Film Capacitor with Polycrystalline SrRuO3 Electrodes


Studies of a sol-gel derived Pb(Zr, Ti)O3 thin-film capacitor with polycrystalline top and bottom SrRuO3 electrodes showed the formation of Pb(Zr, Ti)O3, columnar grain thin-film with excellent crystallinity on the SrRuO3 substrate. SrRuO3/Pb(Zr, Ti)O3/SrRuO3 capacitors had good reversibility at an applied voltage of 3.0 V. The remanent polarisation density for 3.0 V was 14.3 μC cm−2; degradation was not observed.

MEDICAL USES

Room-Temperature Phosphorescent Palladium-Porphine Probe for DNA Determination


The room-temperature phosphorescence (RTP) enhancement of a Pd-TMPyP complex (1) (TMPyP = tetrakis(1-methyl-4-pyridyl)porphine) by DNA is reported. When bound to double-stranded DNA the complex (1) showed intense RTP and little reactivity to RNA, which allows the selective quantitative determination of DNA in the presence of RNA. The calibration graphs were linear up to 6 × 10−9 μM DNA with a detection limit of 5 × 10−9 μM.