ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES

Antiferromagnetic Coupling in (111)- Oriented Co/Pt Superlattices
Antiferromagnetic (AF) coupling in molecular beam epitaxy grown (111)-oriented Co/Pt superlattices (1) was studied using NMR and low-temperature magnetisation. Spin-echo spectra and magnetisation results showed AF interlayer coupling in (1) with a Pt layer thickness of 18 Å. The coupling energy per unit area was ≤1 erg/cm². The structure of the Co films is mainly h.c.p. The model of separate regions of local interlayer AF coupling of different strengths was confirmed.

Coercivity and Microstructure in Co-Pt and Co-Pd Thin Films
Thin films of Co-Pt and Co-Pd were electrodeposited from alkaline baths based on Co amino-citrate and amino-nitrite complexes of the noble metal. Soft Co-Pd alloy films with coercivities of 3 kA/m were obtained. Co-Pt films had high coercivities ≤200 kA/m and high squareness. Ferromagnetism was found in Co-Pd alloy layers with low Co contents, below the known ferromagnetic limit for bulk samples.

Optical and Electronic Properties Modifications in Pd-Ni Multilayers
The effect on the optical properties and electronic structure of Pdₙ-Ni multilayers of the modulation period of ≤20 monolayers, was studied in the energy region 1.6-9.5 eV. A broad structure around 4.6 eV depended strongly on (m+n) whereas the plasma energy depended on both Pd-layer thickness m and modulation period. At 7 eV more features occurred in the dielectric function spectra, depending on m.

Electrical Transport and Impedance Spectra in NiO-Pd Composites
Transport properties of NiO-Pd composites were studied by measuring AC electrical conductivity at 700-1200°C in pure O₂, air and Ar. The electrical conductivity of the Pd-dispersed NiO composites under partial O₂ pressure decreased at first but then began to increase as a function of the volume fraction of dispersed Pd particles. The overall resistivity of the composites was affected by both the bulk and the boundary effects, in contrast to that of the undoped poly-NiO.

Magnetic, Electrical and Thermal Properties of Heavy Fermion Superconductor UPd₃Al₃
Electrical resistivity, de Haas-van Alphen effect, specific heat and thermal expansion of UPd₃Al₃ are reported. The nominal composition was denoted by the formula UPd₃₋ₓAlₓ₋₃. Samples with composition UPd₃Al₁₋ₓ and UPd₃₋ₓAl₁₋ₓ revealed de Haas-van Alphen oscillations of the magnetic susceptibility. An anomaly was observed in the superconducting phase in the temperature dependence of the specific heat and thermal expansion of UPd₃Al₁₋ₓ.

CHEMICAL COMPOUNDS

New Platinum(II) Complexes with Schiff Base Ligands
Neutral Pt complexes [PtABX₃], [PtDX₃], [PtDX₃] and [PtD₃Cl₃]Cl, where A, B = amines, D = Schiff bases, X = anionic ligand, were prepared. The reactions of [PtCl₃] with Schiff bases gave chelates which further reacted yielding cis-coordinated mixed N-donor ligand complexes. Pt methylglyoxal Schiff bases may cross cell membranes without difficulty.

Preparation and Characterization of Rhodium C₂₈ Complexes [Rh(acac)(L)ₓ(Cₜₒ)] (L = py, 4-Mepy, 3,5-Me₂py)
A series of new C₂₈ Rh complexes [Rh(acac)(L)ₓ(Cₜₒ)] where L = pyridine, 4-methylpyridine, 3,5-dimethylpyridine, were prepared by the reaction of [Rh(acac)(Cₜₒ)], with Cₜₒ followed by treatment with pyridine or its derivatives. The molecular structure of [Rh(acac)(3,5-Me₂py)(Cₜₒ)].C₂₈ was determined.

Reactions of RuHCl(CO)(PPh₃)₂ with Allylic Amines: Insertions and an Unusual Carbon-Nitrogen Bond Cleavage of Allylic Amines
The title hydrido-Ru(II) complex reacts with primary and secondary allylamines to give novel Ru(II) complexes Ru(III) with HC₅H₅, CH₅H₄CH₂NHRCl(CO)(PPh₃), R = H, CH₃, CH₂CH = CH₂ and the corresponding enamines. These reactions result in the insertion of the allylic function into the Ru-H bond to yield the 5-membered aminopropyl chelate complexes. Tertiary allylic amines react with the hydrido complex to give the corresponding (α-allyl)Ru(II) complexes.
Ruthenium Chromophores Containing Terpyridine and a Series of Polyazine Bridging Ligands


Ru complexes [Ru(tpy)(BL)Cl]+ containing the tridentate ligand tpy, where tpy = 2,2',6,2'-terpyridine and BL = bridging ligand, were synthesised and characterised. The attached bidentate bridging ligands were 2,3-bis(2-pyridyl)pyrazine, 2,3-bis(2-pyridyl)quinoxaline and 2,3-bis(2-pyridyl)benzoquinoxaline. All the [Ru(tpy)(BL)Cl]+ emitted in fluid at room temperature. The lowest energy adsorption was assigned as a Ru(ads)→BL(π*) transition. These Ru(tpy) compounds can be utilised for multimetallic systems capable of intramolecular electron transfer.

ELECTROCHEMISTRY

New Results in the Electro-oxidation of Formaldehyde on a Platinum Electrode in an Acid Medium


Studies of the oxidation of HCHO in perchloric acid on Pt electrodes showed the formation of a strongly bonded layer due to the hydration-dehydration equilibrium of HCHO. The presence of CH₂OH in HCHO solutions as stabiliser increases the rate of CO formation. Three structures were found for the adsorbed CO: the linearly bonded, bridge-bonded and multibonded forms. The adsorbed CO is responsible for blocking the surface, preventing the adsorption of reactive species.

Electrochemical Enhancement of a Catalytic Reaction in Aqueous Solution


Studies of the oxidation of H on a Pt/graphite electrode immersed in aqueous KOH solution showed that the application of a positive potential of 1-2 V to the Pt electrode increases the rate of H oxidation by up to 500%. It is suggested that hydroxide ions are acting as promoters, with each ion supplied to the catalyst causing the oxidation of up to 20 H atoms.

Amorphous Ni-Nb-Pt Alloy Catalysts for Electro-oxidation of Ethylene


The catalytic activity for the electro-oxidation of C₂H₄ on HF-treated amorphous Ni-40Nb-xM-(1-x)Pt alloys was greatly increased after partial substitution (0.2 at. % M) of Pt by Sn or Ru. Additions of Mo and Mn slightly enhanced the activity, but W and Pd additions were ineffective. The highest activity was for Sn-containing alloy with Pt:Sn ratio of ~ 1:1. The binding energies of Pt 4f and Sn 3d electrons were independent of the Sn content of the alloy and the potential.

Temperature-Dependent Methanol Electro-oxidation on Well-Characterized Pt-Ru Alloys


The kinetics of CH₃OH electro-oxidation on well-characterized Pt-Ru alloy surfaces prepared in ultra-high vacuum, were measured in H₂SO₄. The activity of Ru towards the dissociative adsorption of CH₃OH was a strong function of temperature. The optimum Ru surface concentration increased with increasing temperature, from ~10 at. % Ru at 25°C to ~30 at. % Ru at 60°C, and the apparent activation energies were consistent with this.

Anodic Film Growth on Ru/Pt Electrodes in HClO₄ and HCl Solutions


The potentiostatic growth of the anodic film on Ru/Pt electrodes in HClO₄, formed by a voltammetric run in the potential range of 0-1.1 V vs. SCE proceeded through the formation of two layers of different reduction reversibility at potentials below 500 mV vs. SCE. The outer layer grows more rapidly than the inner layer, up to 3 O monolayers in 7h. In HCl solution, Cl⁻ adsorption inhibits the formation of the anodic layer, decreasing its growth rate but reaching no limiting thickness for 7h. When held at potentials of >650 mV, the initially homogeneous film converts into a bilayer where the outer layer becomes hardly reducible.

Methanol Oxidation on Carbon-Supported Platinum-Tin Electrodes in Sulfuric Acid


Electro-oxidation of CH₃OH in H₂SO₄ was studied on C-supported electrodes containing highly dispersed Pt-Sn bimetallic electrocatalyst which was prepared by an in situ potentiometric-characterisation route. The (3:2)Pt-Sn/C electrodes displayed the highest catalytic activity towards the electro-oxidation of CH₃OH giving maximum charge transfer from Sn to Pt. It is suggested that the charge transfer within this catalyst, together with the partial scavenging of oxidic impurities from Pt sites, are determining factors for the observed synergistic promotion of the CH₃OH oxidation reaction.

Novel Semiconducting Ternary Compounds: Ir,Ru,Sn (0.005 < x < 0.5) for Oxygen Evolution Electrocatalysis


O₂ evolution occurred on degenerate Ir,Ru,Sn semiconductor electrodes. The Tafel slope showed a positive linear variation at 180-300 mV/dec with increasing Ir content of 0.5-50%. A higher Tafel slope and O₂ evolution occurred at an overpotential of 0.2 V, which is comparable to oxide electrodes. While O₂ evolves at low overpotentials, the higher Tafel slopes were due to a potential loss in the degenerate semiconductor.
PHOTOCONVERSION

Luminescent Donor-Acceptor Platinum(II) Complexes
The emission properties of the complexes \([\text{Pt}(dpp)(5,6-\text{Me}-\text{phen})(\text{CN})_2] \) (C104) were studied. The large percentage of metal-ligand charge transfer character was observed in the lowest excited states of these Pt(II) complexes. The MLCT excited state of Pto is very effective observed in the quenching of the photoexcited system.

Pentane Carbonylation in the Photocatalytic System Bis(\(\mu\)-chlorocarbonylrhodium)-Trimethylphosphine
The efficiency of the system containing RhCl(\((\text{CO})_2\) (I) and PMe, in different ratios was studied during pentane carbonylation at an initial CO partial pressure of 60 Torr. A very effective photocatalytic system for pentane carbonylation was obtained with efficiency 20 times higher than that of other known systems, by mixing (1) and PMe, in the ratio [P]:[Rh] = 3 and illuminating at \(\lambda > 270 \text{ nm}\). The characteristic feature of the system is the large concentration (\(\approx 1 \text{mmol/dm}^3\)) of non-bonded phosphine in the solution.

Catalytic Effect of Rhodium(III) on the Chemiluminescence of Luminol in Reverse Micelles and Its Analytical Application
Using Rh(III) catalyst resulted in an increase in the chemiluminescence (CL) of luminol, even in the absence of K periodate, both in an aqueous basic buffer solution and in a reverse micellar medium of cetyltrimethylammonium chloride in chloroform-cyclohexane. The CL emission intensity decreased greatly when O2 was excluded from the reaction. The Rh(III)-catalysed CL emission from luminol oxidation by O2 in a reverse micellar medium was used to quantify Rh(III) in samples after liquid-liquid extraction.

Investigations on a Homogeneous Wilkinson’s Catalyst for the Water Photolysis
Mass-spectroscopy studies showed that H2 which was produced in the presence of Na,Rh(II)Cl(dpm), catalyst (where dpm is diphenylphosphinobenzene-\(m\)-sulphonate) originated from H2O and not ascorbic acid, as previously thought. The catalytic system containing Ru(bipy), Rh(II)Cl(dpm), and ascorbic acid, irradiated at \(\lambda > 400 \text{ nm}\) was highly active for photochemical reduction of H2O giving a turnover number > 2000 in the presence of O2. Rh(II)Cl(dpm), acts both as an electron relay and as a catalyst.

Ultrafast Optical Modulation of Quadratic Non-Linearity from an Ru(II)-bipyridine Complex in Langmuir-Blodgett Assemblies
Alternate Langmuir-Blodgett (LB) films consisting of a Ru(II)-bipyridine complex and ammonium amphiphiles show a strong second-harmonic generation (SHG) on irradiation with nanosecond Nd-doped YAG 1064 nm laser pulses. The switching time for the optical modulation of SHG was determined to be < 2 ps from a sub-ps dye laser pump-probe SHG study. The mechanism for the optical modulation of SHG is ascribed to a change in the molecular hyperpolarisability of the Ru complex on going from the ground state to the excited state.

ELECTRODEPOSITION AND SURFACE COATINGS

Large Scale Two-Step Selective Aluminum CVD on Laser Patterned Palladium Lines
A maskless 2-step technology is described for writing Pd lines directly by laser onto a large uniform deposition of PdAc from acetone solution. The Pd lines are well resolved with good resistivity ~ 30 \(\mu\)\Omega cm and good adhesion to the SiO2 substrate. A highly selective, second-step Al-CVD gave resistivities of ~ 6.5 \(\mu\)\Omega cm and 3000 A thickness for a 7 min deposition.

Pyrophosphate Baths for Palladium-Nickel Alloy Coatings. Parts I and II
Concentration ranges of Na pyrophosphate for the primary bath used for Pd-Ni alloy coatings have been studied. Coating was carried out using a Pt sheet as an insoluble anode with the anode to cathode area ratio of 2 : 1. The operating conditions were selected with respect to repeatable deposition of 15–20% Ni-Pd alloy coatings. Plating solutions containing Na pyrophosphate, Pd and Ni compounds, can be used to deposit Pd-Ni alloy without using NH3.

APPARATUS AND TECHNIQUE

Holographic Reconstruction of P1(110) Using Multiple Wave Number Photoelectron Diffraction Patterns
The single wave number reconstruction and the multiple wave number phased sum reconstruction algorithms were used to obtain a 3D real space image of the P(110) surface from the Pt4f and 4f2 photoelectron diffraction patterns (holograms) for six kinetic energies at 120–370 eV. The image quality depends on the photoelectron kinetic energy. The best quality reconstructed images were observed for single energy reconstruction at a kinetic energy of ~370 eV.
Static and Flow-Injection Voltammetric Determination of Periodate by Reduction at a Rotating Platinum Wire Electrode


The behaviour of periodate at a rotating Pt wire electrode was studied as a function of pH and concentration of periodate in two systems and a method for periodate determination was developed. In the static system, 4.0 × 10⁻⁴–4.2 × 10⁻⁴ M periodate could be determined in the cell in a pH 7–7.5 phosphate buffer. In the flow-injection system periodate solutions of 20–100 μl were injected into the carrier stream of a phosphate buffer solution at pH 7. Periodate concentrations of 1.0 × 10⁻¹–1.0 × 10⁻² M could be detected at a throughput of 15–40 samples/h.

Amperometric Enzyme Electrodes for Substrates of Immobilized Pyranose Oxidase


Two kinds of glucose biosensors for the determination of pyranose oxidase substrates have been developed based on detection of evolving H₂O₂ on a Pt or platinnised graphite electrode at +650 or +400 mV, respectively. The biosensors detect H₂O₂ produced by pyranose oxidase bonded on an activated nylon net with about the same sensitivity to D-glucose as a similar sensor containing glucose oxidase. The lower selectivity allowed determination of saccharides, which are more difficult to detect, over a wide concentration range. The biosensors were compared in both devices at 330–570 nm for aqueous samples.

Novel Metal-Organic Ruthenium(II) Diimine Complexes for Use as Longwave Excitable Luminescent Oxygen Probes

J. KLMANT, P. BIELER and O. S. WOLFBREIE, Talanta, 1994, 41, (6), 985–991

Ru(II) diimine complexes with luminescence excitation maxims of 535–570 nm can be photoexcited by green LEDs and are found to be useful as luminescent O₂ probes. The probes were incorporated into organic polymers and the membranes were characterised with respect to O₂ sensitivity, luminescence intensity, response times and stability. The new probes can be used to optically sense O₂ over partial pressures of 0–200 Torr, with response times of ~1 min for aqueous samples but seconds for gaseous samples.

HETEROGENEOUS CATALYSIS

A Study of Platinum-Dysprosium-KL Zeolite Refining Catalyst


The effect of Dy on the surface behaviour and catalytic properties of Pt-KL zeolite catalyst was studied in a pulsed micro-catalytic reactor. Pt-Dy-KL zeolite catalyst containing 0.1–0.5 wt. % Dy displayed higher activity for the aromatisation of either n-hexane or methylcyclopentane than unmodified Pt-KL catalyst. The stabilities of the Pt-KL and Pt-Dy-KL catalysts were studied using a poisoning method with Cs₂S.

Hydrogen Recovery from Hydrogen Sulfide by Oxidation and by Decomposition


Selective oxidation of H₂S to H₂ and S oxides in a two-step process and the catalytic decomposition of H₂S were studied at 350–650°C for the recovery of H₂ from H₂S. Pt/SiO₂ catalyst was effective in reacting with H₂S to produce H₂ and Pt sulphide at 500°C. The Pt was further treated with O₂ at 400°C to release S oxides and regenerate the Pt. Oxidation of SO₂ to SO₃, retention of O₂ by Pt, and adsorption of H₂S by SiO₂ also occurred and resulted in a minor loss in H₂ yield. It is suggested that H losses can be minimised by choice of operating conditions.

Reactions of n-Hexane over Pt-Zeolite Catalysts of Different Acidity


Pt/HY, Pt/NaHY, Pt/NaY and Pt/NaX catalysts, which are in order of decreasing acidity and increasing basicity, were tested at 603 K in n-hexane conversion as a model reaction. The acidic Pt/HY and Pt/NaHY catalysts were more active by ~ an order of magnitude than the two non-acidic catalysts. They produced mainly skeletal isomers, fragments, etc., whereas over Pt/NaY and Pt/NaX catalysts, metal catalysed C₆ cyclic isomerisation, ring closure and aromatisation prevailed. Pt/NaY showed a great aromatisation selectivity which can be attributed to the interaction of basic centres of the framework with the Pt particles.
Adsorption and Structural Properties of Heteropolyacid-Modified Pd/Al₂O₃ Catalysts: Effects on Hydrogenation Activity


The correlation between the adsorption properties of modified Pd + HPA/Al₂O₃ catalysts (HPA are heteropolyacids) and their activity in the hydrogenation of C-C and C=C bonds in but-2-yne-1,4-diol and oct-1-ene was studied. The modification of Pd/Al₂O₃ catalysts by HPA increases the number of adsorption sites by 2.5–3 times. The initial dimensions of the Pd particles were 30–70 Å and did not change, even after treatment at 973 K.

Square Chemical Waves in the Catalytic Reaction NO + H₂ on a Rhodium(110) Surface


A transition from elliptical to square-shaped chemical waves in the catalytic reaction of NO and H₂ on a Rh(110) surface is reported. The origin of the square pattern is attributed to a state-dependent anisotropy, which is an anisotropy that varies along the wave profile as changes in the adsorbate coverage generate different reconstructions of the substrate structure. This interplay between diffusional anisotropy and the state of the system may be general, causing new varieties of oscillatory patterning.

Stereoselective Hydrogenation of Alkylphenols. II. Hydrogenation of p-tert-Butylphenol over Ruthenium Catalysts


Hydrogenation of p-tert-butylphenol was studied over Ru or Ru catalysts supported on γ-Al₂O₃, SiO₂, TiO₂, sibunit and MgO. Two simultaneous reactions were observed over Ru: black hydrogenation of p-tert-butylphenol and isomerisation of cis-4-tert-butylcyclohexanol to trans-4-tert-butylcyclohexanol. Isomerisation was strongly suppressed over the Pt/support catalyst. Effects of solvents, pH and H₂ pressure on stereoselectivity of hydrogenation were also studied.

Characterization and Catalytic Properties of Peroxovskites with Nominal Compositions La₋ₓSr₋ₓAl₋ₙ₋₁₋ₓCu₋ₓRu₋ₓOₓ


Ru oxide catalysts were prepared by impregnating Al₂O₃ washcoats with H₂O solutions containing La⁺⁺, Sr⁺⁺, Cu⁺⁺ and Ru⁺⁺ ions followed by calcination at 900°C. A perovskite phase of the nominal title composition was prevalent in samples with increasing Ru and Sr contents. The presence of Ru and Sr retarded the formation of La₂CuO₄ and promoted the formation of the perovskite phase. The light-off temperatures for NO reduction decreased from 534 to 335°C for the catalyst without Sr and with Ru.

HOMOGENEOUS CATALYSIS

Palladium Catalyzed Telomerization of Butadiene with Sucrose: A Highly Efficient Approach to Novel Sucrose Ethers


A direct route for the telomerisation of butadiene with sucrose, catalysed by Pd(acac), and Ph₃P ligand is reported. The reaction yielded the corresponding sucrose octadienyl ethers at high turnover numbers of 40,000. The products were clear, almost colourless liquids with a viscosity of 1500–2000 mPa*s at 25°C and insoluble in H₂O. The products are potential emulsifiers and defoaming agents.

A New Optically Active Monodentate Phosphine Ligand, (R)-(+)-3-Diphenylphosphino-3'-methoxy-4,4'-biphenanthryl (MOP-phen): Preparation and Use for Palladium-Catalyzed Asymmetric Reduction of Allylic Esters with Formic Acid


(−-)(R)-(+)-3-Diphenylphosphino-3'-methoxy-4,4'-biphenanthryl (MOP-phen) was prepared with (−)-3,3'-dihydroxy-4,4'-biphenanthryl and used for the Pd catalyst asymmetric reduction of allylic esters with formic acid using Pd(OAc)₂-dppp, PdCl₂(n-1,1-dimethylallyl)((R)-MOP) and trans-PdCl₂((R)-MOP) catalysts. The Pd-catalysed reaction yielded active olefins of ≤ 85 ee with monodentate optically active phosphine which was a more enantioselective ligand than (R)-(+)-2-diphenylphosphino-2'-methoxy-1'-binaphthyl, (MOP). The absolute configuration of (+)-(MOP-phen) was determined to be R.

Palladium-Catalyzed Cross-Coupling Reaction of Organometalloids through Activation with Fluoride Ion


A transient pentaco-ordinate silicate produced by activation of organosilicon compounds with fluoride ion was found to be capable of transmetalation with a catalytic organo-Pd complex in a cross-coupling reaction. Mono-, di- or triflorosilanes can produce the alkene, aryl or alkylic group, respectively. The reaction which was highly chemo- and stereoselective, was successfully applied to synthesise HMG-CoA reductase inhibitor NK-104 and functionalised biaryls for liquid crystals.

Rhodium-Catalyzed Cross Coupling of Unactivated Allenes and 1-Alkynes


A mixture of HRh(CO)(PPh₃) and Et₃P catalysed the cross-coupling reaction of unactivated allenes and 1-alkynes. C-C bond formation occurred regioselectively at the 2-position of allenes giving conjugated endo-(E)-enynes in high yields and selectivities. Added PEt₃ improves the regio- and stereoselectivity.
Catalytic and Stoichiometric Hydroacylation of Olefin Derivatives with 8-Quinolinecarboxaldehyde by Rh(I)


Stoichiometric ligand-promoted hydroacylation of styrene and 2,3,4,5,6-pentafluorostyrene with [(C₅H₅)₂RhCl], resulted in a mixture of branched and linear alkyl ketones. Catalytic hydroacylation was obtained by the reaction of 8-quinolinecarboxaldehyde and vinyl derivatives, such as the above and vinylacetate obtained by the reaction of 8-quinolinecarboxaldehyde by Rh(I) compounds. The Rh arsine catalysts were highly active in systems using simple alk-1-enes as sacrificial olefins than similar phosphine-based catalysts, efficiently catalysing the transfer dehydrogenation of alkanes in H₂ producing less 'direct hydrogenation' sacrificial olefins than similar phosphine-based compounds. The Rh arsine catalysts were highly active in systems using simple alk-1-enes as sacrificial H acceptors. A heterogeneous arsine-based Rh catalyst which was synthesised by covalently grafting [RhCl(AsPh₃)], onto polystyrene beads also promoted the transfer dehydrogenation of alkanes.

Catalytic Activation of Carbon-Fluorine Bonds by a Soluble Transition Metal Complex

M. AIZENBERG and D. MILSTEIN, Science, 1994, 265, (5170), 359–361

Homogeneous catalytic activation of strong C-F bonds was achieved by Rh complex catalysts under mild conditions. Rh(I) silyls, L₄RhSiMe₃Ph (L = PMe₃), can easily cleave C-F bonds in C₂F₆ and C₃F₇ even for the latter in preference to C₂F₆-H bond. The catalytic chemo- and regioselective reactions between polyfluorobenzenes and hydrosilanes result in substitution of F atoms by H. The catalytic cycles have high selectivity.

Direct Hydroesterification of Ethylene with Methyl Formate with the New System RuCl₃·NRₓ·I-NRₓ: An Example of Catalytic Activation of the CH Bond of Methyl Formate?


A highly reactive system was obtained for direct hydroesterification of C₂H₄ with methyl formate in the presence of RuCl₃·NRₓ·I-NRₓ·combined catalyst (where R = alkyl or aryl) using dimethylformamide as a solvent, in the absence of CO. The ratio of 1:2:5 for the Ru salt, NH₂ iodide and amine is particularly efficient, giving a turnover frequency of up to 2000/h. The excellent reactivity obtained was due to a direct activation of methylformate.

A Novel Perfluoroalkylation of Pyroles with Perfluoroalkanesulfonyl Chloride Catalyzed by a Ruthenium(II) Phosphine Complex


Direct perfluoroalkylation of N-substituted pyroles with tridecafluorohexanesulphonyl chloride catalysed by a Ru(II) phosphine complex proceeded regioselectively in high yield. After temporary protection of the N-H function by a trimethylsilyl or triisopropylsilyl group, perfluoroalkylation using perfluoroalkanesulphonyl chloride and dichlorotris(triphénylphosphine)Ru(II), followed by desilylation, was found to be an excellent method for the regioselective synthesis of 2- and 3-perfluoroalkylpyrroles.

FUEL CELLS

Evaluation of an Effective Platinum Metal Surface Area in a Phosphoric Acid Fuel Cell


The effective Pt metal surface area in a real phosphoric acid fuel cell (PAFC) was evaluated by a new method, using in situ cyclic voltammetry. The electrochemical Pt surface area of a PAFC under real operational conditions was ~25 m²/g which was due to the isolation of the Pt particles from a C support.

ELECTRICAL AND ELECTRONIC ENGINEERING

Ruthenium Clusters in Lead-Borosilicate Glass in Thick Film Resistors


Diffusion behaviour of Ru ions in glass was studied in an interparticle glass matrix in RuOₓ-based thick film resistors. The dissolved Ru ions form clusters < 1nm in size in low-Pb glasses, which condense into Pb₄Ru₃O₁₀· crystallites in high-Pb glasses. A typical distance between Ru clusters in low-Pb glasses was 2–4 nm, which shows that the electrical conduction in TFR is sustained by the Ru crystallites in the glass.