

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Antiferromagnetic Coupling in (111)-Oriented Co/Pt Superlattices

K. LE DANG, P. VEILLET, C. CHAPPERT, R. F. C. FARROW, R. F. MARKS, D. WELLER and A. CEBOLLADA, *Phys. Rev. B*, 1994, 50, (1), 200–204

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

G. ZANGARI, B. BOZZINI, P. L. CAVALLOTTI, G. FONTANA, P. G. MAISTO and E. TERRENZIO, *J. Magn. & Magn. Mater.*, 1994, 133, (1–3), 511–515

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

S. LOGOTHETIDIS and N. K. FLEVARIS, *J. Appl. Phys.*, 1994, 75, (12), 7978–7982

The effect on the optical properties and electronic structure of Pd_n-Ni_n 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

S. Y. KWANG and J. B. WAGNER, *Solid State Ionics*, 1994, 69, (2), 107–115

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 dispersoid 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 UPd₂Al₃

N. SATO, Y. INADA, T. SAKON, K. IMAMURA, A. ISHIGURO, J. KIMURA, A. SAWADA, T. KOMATSUBARA, H. MATSUI and T. GOTO, *IEEE Trans. Magn.*, 1994, 30, (2), 1145–1147

Electrical resistivity, de Haas-van Alphen effect, specific heat and thermal expansion of UPd₂Al₃ are reported. The nominal composition was denoted by the formula UPd_{2+x}Al_{3-y}. Samples with composition UPd₂Al_{3.03} and UPd_{2.02}Al_{3.03} 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 UPd₂Al_{3.03}.

CHEMICAL COMPOUNDS

New Platinum(II) Complexes with Schiff Base Ligands

J. KUDUK-JAWORSKA, *Transition Met. Chem.*, 1994, 19, (3), 296–298

Neutral Pt complexes [PtABX₂], [PtD₂]X₂, [PtDX₂] and [Pt₂D₂Cl₂]Cl₂, where A, B = amines, D = Schiff bases, X = anionic ligand, were prepared. The reactions of [PtCl₄]²⁻ with Schiff bases gave chelates which further reacted yielding *cis*-co-ordinated mixed *N*-donor ligand complexes. Pt methylglyoxal Schiff bases may cross cell membranes without difficulty.

Preparation and Characterization of Rhodium C₆₀ Complexes [Rh(acac)(L)₂(C₆₀)] (L = py, 4-Mepy, 3,5-Me₂py)

Y. ISHII, H. HOSHI, Y. HAMADA and M. HIDAI, *Chem. Lett. Jpn.*, 1994, (4), 801–804

A series of new C₆₀ Rh complexes [Rh(acac)(L)₂(η²-C₆₀)] where L = pyridine, 4-methylpyridine, 3,5-dimethylpyridine, were prepared by the reaction of [Rh(acac)(C₂H₄)₂] with C₆₀ followed by treatment with pyridine or its derivatives. The molecular structure of [Rh(acac)(3,5-Me₂py)₂(η²-C₆₀)]·C₆H₆ was determined.

Reactions of RuClH(CO)(PPh₃)₃ with Allylic Amines: Insertions and an Unusual Carbon-Nitrogen Bond Cleavage of Allylic Amines

K. HIRAKI, T. MATSUNAGA and H. KAWANO, *Organometallics*, 1994, 13, (5), 1878–1885

The title hydrido-Ru(II) complex reacts with primary and secondary allylamines to give novel Ru(II) complexes Ru(CH₂CH₂CH₂NHR)Cl(CO)(PPh₃)₂, 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 (π-allyl)Ru(II) complexes.

Ruthenium Chromophores Containing Terpyridine and a Series of Polyazine Bridging Ligands

L. M. VOGLER, C. FRANCO, S. W. JONES and K. J. BREWER, *Inorg. Chim. Acta*, 1994, 221, (1-2), 55-59

Ru complexes $[\text{Ru}(\text{tpy})(\text{BL})\text{Cl}]^+$ 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 $[\text{Ru}(\text{tpy})(\text{BL})\text{Cl}]^+$ emitted in fluid at room temperature. The lowest energy adsorption was assigned as a $\text{Ru}(d\pi) \rightarrow \text{BL}(\pi^*)$ 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

P. OLIVI, L. O. S. BULHÕES, J.-M. LÉGER, F. HAHN, B. BEDEN and C. LAMY, *J. Electroanal. Chem.*, 1994, 370, (1-2), 241-249

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 CH_3OH 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

S. G. NEOPHYTIDES, D. TSIPLAKIDES, P. STONEHART, M. M. JAKSIC and C. G. VAYENAS, *Nature*, 1994, 370, (6484), 45-47

Studies of the oxidation of H_2 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_2 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

K.-I. TAKAMURA, H. HABAZAKI, A. KAWASHIMA, K. ASAMI and K. HASHIMOTO, *Mater. Sci. Eng.*, 1994, A181/A182, 1137-1140

The catalytic activity for the electro-oxidation of C_2H_4 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 Pb 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

H. A. GASTEIGER, N. MARKOVIC, P. N. ROSS and E. J. CAIRNS, *J. Electrochem. Soc.*, 1994, 141, (7), 1795-1803

The kinetics of CH_3OH electro-oxidation on well-characterised Pt-Ru alloy surfaces prepared in ultra-high vacuum, were measured in H_2SO_4 . The activity of Ru towards the dissociative adsorption of CH_3OH 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 HClO_4 and HCl Solutions

F. COLOM and M. J. GONZÁLEZ-TEJERA, *J. Appl. Electrochem.*, 1994, 24, (5), 426-433

The potentiostatic growth of the anodic film on Ru/Pt electrodes in HClO_4 , 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

A. S. ARICÒ, V. ANTONUCCI, N. GIORDANO, A. K. SHUKLA, M. K. RAVIKUMAR, A. ROY, S. R. BARMAN and D. D. SARMA, *J. Power Sources*, 1994, 50, (3), 295-309

Electro-oxidation of CH_3OH in H_2SO_4 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 CH_3OH 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 CH_3OH oxidation reaction.

Novel Semiconducting Ternary Compounds: $\text{Ir}_x\text{Ru}_{1-x}\text{S}_2$ ($0.005 < x < 0.5$) for Oxygen Evolution Electrocatalysis

H. COLELL, N. ALONSO-VANTE, C. FISCHER, P. BOGDANOFF, S. FIECHTER and H. TRIBUTSCH, *Electrochim. Acta*, 1994, 39, (11/12), 1607-1611

O_2 evolution occurred on degenerate $\text{Ir}_x\text{Ru}_{1-x}\text{S}_2$ 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 O_2 evolution occurred at an overpotential of 0.2 V, which is comparable to oxide electrodes. While O_2 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

C.-W. CHAN, L.-K. CHENG and C.-M. CHE, *Coord. Chem. Rev.*, 1994, 132, 87–97

The emission properties of the complexes [Pt(dppm)(5,6-Me₂phen)](ClO₄)₂ (1), [Pt(phen)(C≡CPh)₂], [Pt(5-Ph-phen)(CN)₂] (2) and [Pt(C[^]N[^]N-dpp)(NCCH₃)](ClO₄) were studied. The large percentage of metal-ligand charge transfer character was observed in the lowest excited states of these Pt(II) complexes. The ³MLCT excited state of Pt(II) is very electrophilic as shown by the large kinetic isotope effect observed in the quenching of the photoexcited (1) complex by cyclohexene and *d₆*-cyclohexene.

Pentane Carbonylation in the Photocatalytic System Bis(μ -chlorocarbonylrhodium)-Trimethylphosphine

N. K. KHANNANOV, G. N. MENCHIKOVA and E. H. GRIGORYAN, *Mendeleev Commun.*, 1994, (2), 39–40
The efficiency of the system containing Rh₂Cl₂(CO)₂ (1) and PMe₃ 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 PMe₃ in the ratio [P]:[Rh] = 3 and illuminating at $\lambda > 270$ nm. The characteristic feature of the system is the large concentration ($\cong 1$ mmol/dm³) of non-bonded phosphine in the solution.

Catalytic Effect of Rhodium(III) on the Chemiluminescence of Luminol in Reverse Micelles and Its Analytical Application

IMDADULLAH, T. FUJIWARA and T. KUMAMARU, *Anal. Chim. Acta*, 1994, 292, (1–2), 151–157

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

R. BAUER and H. A. F. WERNER, *Int. J. Hydrogen Energy*, 1994, 19, (6), 497–499

Mass-spectroscopy studies showed that H₂ which was produced in the presence of Na₂Rh(I)Cl(dpm)₃ catalyst (where dpm is diphenylphosphinobenzene-*m*-sulphonate) originated from H₂O and not ascorbic acid, as previously thought. The catalytic system containing Ru(bipy)₃²⁺, Rh(I)Cl(dpm)₃⁺ and ascorbic acid, irradiated at $\lambda > 400$ nm was highly active for photochemical reduction of H₂O giving a turnover number > 2000 in the presence of O₂. Rh(I)Cl(dpm)₃⁺ 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

H. SAKAGUCHI, T. NAGAMURA, T. L. PENNER and D. G. WHITTEN, *Thin Solid Films*, 1994, 244, (1–2), 947–950
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

B. HABA, K. SUGAI, Y. MORISHIGE and S. KISHIDA, *Appl. Surf. Sci.*, 1994, 79/80, 381–384

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 $\sim 30 \mu\Omega\text{cm}$ and good adhesion to the SiO₂ substrate. A highly selective, second-step Al-CVD gave resistivities of $\sim 6.5 \mu\Omega\text{cm}$ and 3000 Å thickness for a 7 min deposition.

Pyrophosphate Baths for Palladium-Nickel Alloy Coatings. Parts I and II

Z. RATAJEWICZ, C. SANELUTA and J. SAWA, *Plat. Surf. Finish.*, 1994, 81, (6), 89–90; (7), 60–62

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 Pt(110) Using Multiple Wave Number Photoelectron Diffraction Patterns

M. ZHARNIKOV, D. MEHL, M. WEINELT, P. ZEBISCH and H.-P. STEINRÜCK, *Surf. Sci.*, 1994, 312, (1/2), 82–96

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 Pt(110) surface from the Pt4f_{7/2} and 4f_{5/2} 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

H. I. GÖKÇEL and G. NISLI, *Anal. Chim. Acta*, 1994, 292, (1–2), 99–105

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^{-5} – 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 μ l were injected into the carrier stream of a phosphate buffer solution at pH 7. Periodate concentrations of 1.0×10^{-5} – 1.0×10^{-4} M could be detected at a throughput of 15–40 samples/h.

Amperometric Enzyme Electrodes for Substrates of Immobilized Pyranose Oxidase

M. PETRIVALSK, P. SKLÁDAL, L. MACHOLÁN and J. VOLC, *Collect. Czech. Chem. Commun.*, 1994, 59, (5), 1226–1234

Two kinds of glucose biosensors for the determination of pyranose oxidase substrates have been developed based on detection of evolving H_2O_2 on a Pt or platinised graphite electrode at +650 or +400 mV, respectively. The biosensors detect H_2O_2 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 by eliminating interference from D-glucose by an enzyme pre-membrane with immobilised hexokinase. The sensor is stable in basic borate.

Comparison and Analysis of Pd- and Pt-GaAs Schottky Diodes for Hydrogen Detection

W. P. KANG and Y. GÜRBÜZ, *J. Appl. Phys.*, 1994, 75, (12), 8175–8181

The H_2 -sensing behaviours of Pd- and Pt-GaAs Schottky diodes, fabricated on the same GaAs substrate, were compared and analysed as a function of H partial pressure and temperature by I - V and ΔI - t methods under steady-state and transient conditions. Adsorption activation energy of H and the heat of adsorption/ H_2 on the surface of Pd and Pt were studied and compared in both devices at 27–100°C. Pd-GaAs showed better performance for H_2 detection than Pt-GaAs under the same testing conditions.

Glucose Oxidation at Ruthenium Dioxide Based Electrodes

M. E. G. LYONS, C. A. FITZGERALD and M. R. SMYTH, *Analyst*, 1994, 119, (5), 855–861

The oxidation of glucose at RuO_2 -C paste composite electrodes in alkaline solution was examined. It is proposed that the catalytically active species are surface-bound oxy Ru groups which mediate substrate oxidation via a process of cyclic heterogeneous redox catalysis. The kinetics of glucose oxidation at RuO_2 -based composite materials are quite rapid, which suggests that conductive metallic oxides may be used for the direct amperometric determination of glucose.

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

I. KLIMANT, P. BELSER and O. S. WOLFBES, *Talanta*, 1994, 41, (6), 985–991

$Ru(II)$ diimine complexes with luminescence excitation maxima of 535–570 nm can be photoexcited by green LEDs and are found to be useful as luminescent O_2 probes. The probes were incorporated into organic polymers and the membranes were characterised with respect to O_2 sensitivity, luminescence intensity, response times and stability. The new probes can be used to optically sense O_2 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 Reforming Catalyst

F. LI, W. LU, G. WU and J. LI, *J. Alloys Compd.*, 1994, 207/208, 397–399

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 catalyst were studied using a poisoning method with CS_2 .

Hydrogen Recovery from Hydrogen Sulfide by Oxidation and by Decomposition

B. L. YANG and H. H. KUNG, *Ind. Eng. Chem. Res.*, 1994, 33, (5), 1090–1097

Selective oxidation of H_2S to H_2 and S oxides in a two-step process and the catalytic decomposition of H_2S were studied at 350–650°C for the recovery of H_2 from H_2S . Pt/ SiO_2 catalyst was effective in reacting with H_2S to produce H_2 and Pt sulphide at 500°C. The Pt was further treated with O_2 at 400°C to release S oxides and regenerate the Pt. Oxidation of SO_2 to SO_3 , retention of O by Pt, and adsorption of H_2S by SiO_2 also occurred and resulted in a minor loss in H_2 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

Z. ZHAN, I. MANNINGER, Z. PAÁL and D. BARTHOMEUF, *J. Catal.*, 1994, 147, (1), 333–341

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 C_6 -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

L. D. VOLKOVA, N. A. ZAKARINA, G. V. ARTYUKHINA and Y. G. KUL'EVSKAYA, *Mendeleev Commun.*, 1994, (2), 107–108

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 were 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

F. MERTENS and R. IMBIHL, *Nature*, 1994, 370, (6485), 124–126

A transition from elliptical to square-shaped concentric 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

S. R. KONUSPAEV, KH. N. ZHANBEKOV, T. S. IMANKULOV, R. K. NURBAEVA and K. SERGAZIEVA, *Kinet. Katal.*, 1994, 35, (1), 83–86

Hydrogenation of *p*-tert-butylphenol was studied over Ru/black or Ru catalysts supported on γ-Al₂O₃, SiO₂, TiO₂, sibunitite 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 Perovskites with Nominal Compositions La_{1-x}Sr_xAl_{1-2y}Cu_yRu_{1-y}O₃

M. SKOGLUNDH, L. LÖWENDAHL, K. JANSSON, L. DAHL and M. NYGREN, *Appl. Catal. B: Environ.*, 1994, 3, (4), 259–274

Ru oxide catalysts were prepared by impregnating Al₂O₃ washcoats with H₂O solutions containing La³⁺, Sr²⁺, Cu²⁺ and Ru³⁺ 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 333°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

K. HILL, B. GRUBER and K. J. WEESE, *Tetrahedron Lett.*, 1994, 35, (26), 4541–4542

A direct route for the telomerisation of butadiene with sucrose, catalysed by Pd(acac)₂ 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 mPas 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

T. HAYASHI, H. IWAMURA, Y. UOZUMI, Y. MATSUMOTO and F. OZAWA, *Synthesis*, 1994, (5), 526–532

(*R*)-(+)-3-Diphenylphosphino-3'-methoxy-4,4'-biphenanthryl (MOP-phen) was prepared with (-)-3,3'-dihydroxy-4,4'-biphenanthryl and used for the Pd catalysed asymmetric reduction of allylic esters with formic acid using Pd(OAc)₂-dppp, PdCl(η¹-1,1-dimethylallyl)((*R*)-MOP) and *trans*-PdCl₂((*R*)-MOP)₂ 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-1,1'-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

T. HIYAMA and Y. HATANAKA, *Pure Appl. Chem.*, 1994, 66, (7), 1471–1478

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 trifluorosilanes can produce the alkenyl, aryl or alkyl 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

M. YAMAGUCHI, K. OMATA and M. HIRAMA, *Tetrahedron Lett.*, 1994, 35, (31), 5689–5692

A mixture of HRh(CO)(PPh₃)₃ 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-Quinoline-carboxaldehyde by Rh(I)

C.-H. JUN, J.-S. HAN, J.-B. KANG and S.-I. KIM, *Bull. Korean Chem. Soc.*, 1994, 15, (3), 204–209

Stoichiometric ligand-promoted hydroacylation of styrene and 2,3,4,5,6-pentafluorostyrene with $[(C_8H_7)_2RhCl]_2$ 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 vinylcyclohexane in the presence of Wilkinson's complex, $(PPh_3)_3RhCl$, catalyst yielding 8-quinolinyls of 2-phenylethyl ketone, 2-pentafluorophenylethyl ketone and 2-cyclohexylethyl ketone.

Efficient and Selective Catalytic Dehydrogenation of Alkanes Using Rhodium(I) Arsine Complexes

J. A. MILLER and L. K. KNOX, *J. Chem. Soc., Chem. Commun.*, 1994, (12), 1449–1450

Arsine complexes of Rh(I), which are known to be relatively inactive homogeneous hydrogenation catalysts, efficiently catalysed the transfer dehydrogenation of alkanes in H_2 producing less 'direct hydrogenated' sacrificial olefins than similar phosphine-based Rh 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 $[RhCl(AsPh_3)_2]_2$ 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, $L_2RhSiMe_2Ph$ ($L = PMe_3$), can easily cleave C-F bonds in C_6F_6 and C_6F_5H , even for the latter in preference to the C_6F_5-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.

Hydroformylation of Alkenes and Alkynes Using a Heterobinuclear Rh-W Catalyst

R. S. DICKSON, T. DE SIMONE, E. M. CAMPI and W. R. JACKSON, *Inorg. Chim. Acta*, 1994, 220, (1–2), 187–192

Hydroformylation reactions of alkenes and alkynes were performed using the heteronuclear Rh-W catalysts, $(CO)_4W(\mu-PPh_2)_2RhH(CO)(PPh_3)$ (1) and $[Rh(OAc)_2]_2$ (2). The catalytic reaction of styrene using (1) gave a very high yield of the branched chain aldehyde containing only a trace of the straight chain isomer. Reaction of the alkenyl dithiane, $S(CH_2)_3SCH_2CH=CH_2$, with the (1) gave a higher ratio of linear to branched aldehydes than (2). Reaction of vinyl acetate with (1) gave a significant amount of linear aldehyde unlike (2), but reactions of allyl acetate gave similar products for both (1) and (2).

Direct Hydroesterification of Ethylene with Methyl Formate with the New System $RuCl_3-NR_2-NR_3$: an Example of Catalytic Activation of the CH Bond of Methyl Formate?

C. LEGRAND, Y. CASTANET, A. MORTREUX and F. PETIT, *J. Chem. Soc., Chem. Commun.*, 1994, (10), 1173–1174

A highly reactive system was obtained for direct hydroesterification of C_2H_4 with methyl formate in the presence of $RuCl_3-NR_2-NR_3$ 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, NH_4 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 Pyrroles with Perfluoroalkanesulfonyl Chloride Catalyzed by a Ruthenium(II) Phosphine Complex

N. KAMIGATA, T. OHTSUKA, M. YOSHIDA and T. SHIMIZU, *Synth. Commun.*, 1994, 24, (14), 2049–2055

Direct perfluoroalkylation of N-substituted pyrroles with tridecafluorohexanesulphonyl chloride catalysed by a Ru(II) phosphine complex proceeded regioselectively in high yield. After temporary protection of the N-H function of pyrrole by a trimethylsilyl or triisopropylsilyl group, perfluoroalkylation using perfluoroalkanesulphonyl chloride and dichlorotris(triphenylphosphine)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

J. ARAGANE, H. URUSHIBATA and T. MURAHASHI, *J. Electrochem. Soc.*, 1994, 141, (7), 1804–1808

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

K. ADACHI, S. IIDA and K. HAYASHI, *J. Mater. Res.*, 1994, 9, (7), 1866–1878

Diffusion behaviour of Ru ions in glass was studied in an interparticle glass matrix in RuO_2 -based thick film resistors. The dissolved Ru ions form clusters < 1 nm in size in low-Pb glasses, which condense into $Pb_2Ru_2O_{7-x}$ 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.