

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Thermally Induced Structural Modification in Pt/C X-Ray Multilayer Mirrors Fabricated by Electron Beam Evaporation

G. S. LODHA, S. PANDITA, A. GUPTA, R. V. NANDEDKAR and K. YAMASHITA, *Appl. Phys.*, 1996, **A62**, (1), 29–32

The thermal stability of Pt/C multilayer mirrors with a bilayer spacing of 50 Å, fabricated in an UHV electron beam evaporator, was studied under vacuum annealing using X-ray reflectivity and XRD. At $\leq 450^\circ\text{C}$, the bilayer spacing increased monotonically giving a gradual increase in crystallite size and grain texture. At 500°C , multilayer reflection disappeared, the Pt crystallites grew rapidly and Pt in the [220]-plane had a strong texture.

Hydrogen-Induced Lattice Migration in Pd-Pt Alloys

H. NOH, J. D. CLEWLEY and T. B. FLANAGAN, *Scr. Metall. Mater.*, 1996, **34**, (4), 665–668

H_2 solubilities were determined in $\sim 100\ \mu\text{m}$ thick foils of Pd-Pt alloys under H_2 pressures of $\leq 100\ \text{MPa}$ at temperatures $\leq 873\ \text{K}$. Pd-Pt alloys do not segregate at higher temperatures when little H_2 dissolves; large amounts of H_2 are needed for segregation. The ternary (Pd + Pt + H) equilibrium causes a phase separation at $673\ \text{K}$. After H_2 removal at $\leq 673\ \text{K}$ and alloy cooling, metastable segregated Pd- and Pt-rich regions remain. Dissolved H_2 catalyses the return of the segregated alloy to the homogeneous state.

Properties and Interface Diffusion of Pd/Ni Composite Wire

Y. NING, H. DAI and F. WEN, *Precious Met. (China)*, 1995, **16**, (4), 25–30

Mechanical properties, interface diffusion and changes in Pd coating thickness were investigated in Pd/Ni composite wire. The thickness and weight percentage of the Pd coat were controllable on demand. The strength of the Pd/Ni composite wires, at ambient and high temperatures, is much higher than for pure Pd, and similar to that of Ni. The Ni diffusion rate from the interface to Pd is higher than that of Pd to Ni.

Magnetic Properties of $\text{U}(\text{Pd}_{1-x}\text{Fe}_x)_2\text{Ge}_2$

H. M. DUH, I. S. LYUBUTIN, I. M. JIANG, G. H. HWANG and K. D. LAIN, *J. Magn. & Magn. Mater.*, 1996, **153**, (1–2), 86–96

Solid solutions of $\text{U}(\text{Pd}_{1-x}\text{Fe}_x)_2\text{Ge}_2$ with a mixture of $3d$ and $4d$ transition elements in one lattice site were prepared. Even very small Pd doping in UFe_2Ge_2 and Fe doping in UPd_2Ge_2 changed the magnetic state of the compounds dramatically. Coexistence between the antiferromagnetic ordering and Pauli paramagnetism was observed over the range $0.1 \leq x \leq 0.9$.

Magnetism of Body-Centered Tetragonal $\text{FeRh}_{1-x}\text{Pd}_x$ Alloys. I. Magnetic Properties; II. Band Structure

S. YUASA, H. MIYAJIMA, Y. OTANI and A. SAKUMA; A. SAKUMA, S. YUASA, H. MIYAJIMA and Y. OTANI, *J. Phys. Soc. Jpn.*, 1995, **64**, (12), 4906–4913; 4914–4922

Crystalline structures and magnetic properties of the $\text{FeRh}_{1-x}\text{Pd}_x$ system were studied and first-principle spin-polarised band calculations were performed for the b.c.t. $\text{FeRh}_{1-x}\text{Pd}_x$ alloys with $x = 0, 0.5$ and 1 as a function of the axial ratio c/a . A new ferromagnetic phase of orthorhombic structure with space group C_{mmm} was found in the b.c.t. alloys with $x = 0.525 \sim 0.61$ below room temperature. At a constant c/a value, substituting Pd for Rh raised the Fermi energy level.

Magnetic Structure and Physical Properties of the Heavy Fermion UIr_2Si_2

A. VERNIÈRE, S. RAYMOND, J. X. BOUCHERLE, P. LEJAY, B. FAK, J. FLOUQUET and J. M. MIGNOT, *J. Magn. & Magn. Mater.*, 1996, **153**, (1–2), 55–62

Studies of the physical properties of a UIr_2Si_2 single crystal, which has CaBe_2Ge_2 -type structure and very high residual resistivity values at low temperature, indicated that UIr_2Si_2 is antiferromagnetic with $T_N = 6\ \text{K}$. A metamagnetic transition at a field of $1.5\ \text{T}$ and heavy-fermion characteristics with a linear specific heat coefficient of $\gamma \sim 300\ \text{mJ/mol K}^2$ were measured. The antiferromagnetic structure of UIr_2Si_2 was determined by neutron diffraction as (+, -, +, -).

Ruthenium and Sulphide Passivation of GaAs

S. T. ALI, S. GHOSH and D. N. BOSE, *Appl. Surf. Sci.*, 1996, **93**, (1), 37–43

The effectiveness of chemical surface treatment of GaAs using $(\text{NH}_4)_2\text{S}_{x_2}$, Na_2S and RuCl_3 was studied. Modification involved the removal of native oxides and the consequent formation of bonds with Ru or S. Ga atoms were bonded more strongly with Ru or S than As. This reduced the surface recombination velocity and increased the photoluminescence intensity. S and Ru can be used to passivate the GaAs surface.

Subsolidus Phase Equilibria in the RuO_2 - Bi_2O_3 - ZnO and RuO_2 - Al_2O_3 - ZnO Systems

M. HROVAT, S. BERNIK, J. HOLC and D. KOLAR, *J. Mater. Sci., Lett.*, 1996, **15**, (4), 336–338

Phase diagrams of the ternary systems RuO_2 - Bi_2O_3 - ZnO (I) and RuO_2 - Al_2O_3 - ZnO (II) were constructed and showed that the RuO_2 - ZnO system contained no binary compound or liquid phase (eutectic) at $< 1400^\circ\text{C}$, which is the temperature that RuO_2 decomposes to metallic Ru and O_2 . Tie lines within the phase diagrams are discussed. The microstructure of a sample of nominal composition $5\ \text{mol}\% \text{ZnO}/50\ \text{mol}\% \text{Bi}_2\text{O}_3/45\ \text{mol}\% \text{RuO}_2$, fired at 700°C , is shown.

Superconducting Properties of CeRu₂ Single Crystal

H. SUGAWARA, H. SATO, T. YAMAZAKI, N. KIMURA, R. SETTAI and Y. ONUKI, *J. Phys. Soc. Jpn.*, 1995, **64**, (12), 4849–4855

Lower and upper superconducting critical fields at 0 K, of 250–400 Oe and 74 kOe, respectively, were measured on single crystals of superconductor CeRu₂ grown by using a zone melting method. The upper critical field was slightly anisotropic, and was of size 64.8 kOe for the field along the <100> direction and 65.6 kOe along the <110> direction at 1.5 K. A characteristic feature of the superconducting mixed state was also observed.

CHEMICAL COMPOUNDS

Ternary Thallium Platinum and Thallium Palladium Chalcogenides Tl₂M₂X₆. Syntheses, Crystal Structures, and Bonding Relations

W. BRONGER and B. BONSMANN, *Z. Anorg. Allg. Chem.*, 1995, **621**, (12), 2083–2088

The compounds Tl₂Pt₂S₆, Tl₂Pt₂Se₆, Tl₂Pt₂Te₆ and Tl₂Pd₂Se₆ were fabricated by melting the elements or by the reaction of Tl carbonate, Pt group metal and chalcogen powders at 400–950°C. X-ray studies on single crystals and powders showed a new type of structure, which is a stacking variant of the known atomic arrangement of the alkaline metal Pt chalcogenides. The short distances in Tl–Pt and Tl–Pd indicate covalent bonds between the main group and the Pt group metal atoms.

Evidence for a Hydrogen Insertion Compound of Novel Palladium Incorporated Vanadyl Hydrogen Phosphates

A. DATTA and R. Y. KELKAR, *Chem. Commun.*, 1996, (1), 89–91

Pd was incorporated into the vanadyl H phosphate phase VOHPO₄·0.5H₂O in various ways depending on the medium used for preparation. In aqueous medium the incorporation of 0.61% Pd²⁺ changes the parent structure, so that Pd²⁺ ions appear to be located in the interlayer region. The relatively low reduction temperature of the incorporated Pd indicates it is located in the interlayer region. However, in an organic medium Pd is partially reduced to metal and partially introduced into the lattice of the parent compound.

Stable Carbonyl- and Thiocarbonylrhodium(I) Complexes Containing σ-Bonded Phenyl and Vinyl Groups as Ligands

R. WIEDEMANN, J. WOLF and H. WERNER, *Chem. Ber.*, 1996, **129**, (1), 29–31

Rh(I) phenyl and vinyl complexes, *trans*-[Rh(R)(CO)(P*i*Pr₃)₂] (1, 2) were prepared from the chloro derivative and Grignard reagents. The corresponding thiocarbonyl *trans*-[Rh(CH=CH₂)(CS)-(P*i*Pr₃)₂] was obtained from *trans*-[RhCl(CS)(P*i*Pr₃)₂] and CH₂=CHMgBr. The carbonyl complexes (1) and (2) are inert in the presence of CO and do not react by migratory insertion to give acyl Rh derivatives.

Synthesis of the First Bimetallic Ruthenium-Iridium Cluster

I. A. LOBANOVA, I. T. CHIZHEVSKII, P. V. PETROVSKII and V. I. BREGADZE, *Izv. Akad. Nauk Rosii, Ser. Khim.*, 1996, (1), 250–251

A new electron-deficient bimetallic cluster, (η⁴-C₈H₁₂)IrRu(μ-H)(PPh₃)₂(η³-C₂B₅H₁₁) was prepared by the reaction of *exo-nido*-5,6,10-[Cl(PPh₃)₂Ru]-5,6,10-(μ-H)₂-10-H-7,8-C₂B₅H₈ with dimeric or acetylacetonate complexes of Ir in the presence of KOH in EtOH at 22°C. Spectroscopic data are presented.

Formation of Ammonium Complexes during Interaction of Ruthenium Compounds with Hydrazine Chloride

YU. H. KUKUSHKIN, M. V. BAVINA and A. V. ZINCHENKO, *Zh. Obshch. Khim.*, 1995, **65**, (8), 1233–1235

The interaction of dimethylsulphoxide complexes [Ru(Me₂SO)₄Cl₂] (1) and RuCl₂·2 Me₂SO with N₂H₄·2HCl (2) produced ammonium Ru(III) compounds, [Ru(NH₃)₅Cl]Cl₂ and *fac*-[Ru(NH₃)₃Cl₃], depending on the length of heating. The interaction of RuCl₂·nH₂O with (2) resulted in the formation of isomeric compounds *mer*-[Ru(NH₃)₃Cl₃]. After a short heat treatment of (1) with (2), the Ru complex [Ru(Me₂SO)₂-(N₂H₅)Cl₃] was formed.

ELECTROCHEMISTRY

Oxygen Reduction on Well-Defined Platinum Nanoparticles inside Recast Ionomer

A. GAMEZ, D. RICHARD, P. GALLEZOT, F. GLOAGUEN, R. FAURE and R. DURAND, *Electrochim. Acta*, 1996, **41**, (2), 307–314

The effect of particle size on the catalytic activity of the O₂ reduction reaction at a Pt/recast ionomer interface was studied by TEM and H and CO electroadsorption, using porous graphite electrodes of well-defined geometry carrying well calibrated Pt particles. The catalytic powders were prepared by cationic exchange. For O reduction, the loss of catalytic activity with decreased Pt particle size is correlated with the stronger adsorption of oxygenated species under an inert atmosphere. No interparticle distance effects were seen, even for particles of 1.2 nm, 10 nm apart.

Electrocatalytic Activities of Graphite-Supported Platinum Electrodes for Methanol Electrooxidation

P. C. BISWAS, Y. NODASAKA and M. ENYO, *J. Appl. Electrochem.*, 1996, **26**, (1), 30–35

Electrooxidation of MeOH in 1 M NaOH at 30°C was studied on graphite-supported Pt electrodes prepared both in H₂ and in air at various temperatures. Heating in H₂ produced Pt of higher surface area with greater mass activity, than in air at a specific temperature. The electrodes had nearly the same specific activity as a smooth Pt electrode for MeOH electrooxidation regardless of the preparation conditions. The difference in mass activity is due to different surface areas resulting from different preparations. The first charge transfer process was the rate-determining step.

Pt-Base Electrodes and Effects on Phase Formations and Electrical Properties of High-Dielectric Thin Films

W.-J. LEE, Y.-M. KIM and H.-G. KIM, *Thin Solid Films*, 1995, **269**, (1-2), 75-79

Structures and properties of Pb(Zr, Ti)O₃, PZT, and (Ba, Sr)TiO₃, BST, thin films deposited on Pt/SiO₂/Si substrates by MOCVD and r.f. sputtering were studied. Pt films sputter-deposited at 400°C had perfect (111) preferred orientation and a dense surface. A 130 nm PZT film deposited on Pt at 400°C had dielectric constant, $\epsilon = 1300$ and remanent polarisation = 32 $\mu\text{C}/\text{cm}^2$; a 100 nm BST film had $\epsilon = 575$ and leakage current density at 2 V = 1.8×10^{-7} A/cm².

Oxygen Evolution and Hypochlorite Production on Ru-Pt Binary Oxides

C.-C. HU, C.-H. LEE and T.-C. WEN, *J. Appl. Electrochem.*, 1996, **26**, (1), 72-82

The effects of varying coating solutions on the OER and the hypochlorite production ability of Ru-Pt oxide electrodes were studied. Maximum apparent activity occurred for coatings of 60 and 20 mol.% Pt for the OER and the Cl evolution reaction, respectively. Freshly prepared electrodes had lower current efficiencies for hypochlorite production than those treated by repetitive cyclic voltammetry, but both types were stable in 0.5 M NaCl at 300 mA/cm² for a 480 h test.

Structural Effects in Electrocatalysis: Structural Oxidation of Carbon Monoxide on Pt₃Sn Single-Crystal Alloy Surfaces

H. A. GASTEIGER, N. M. MARKOVIC and P. N. ROSS, *Catal. Lett.*, 1996, **36**, (1, 2), 1-8

The electrochemical oxidation of CO and CO:H₂ mixtures in H₂SO₄ was studied on clean annealed and sputtered cleaned non-annealed (110) and (111) surfaces of single crystal Pt₃Sn. Annealed (111) and sputtered non-annealed (110) surfaces had very different activities. Relative to pure Pt surfaces, a potential shift > 0.5 V was observed for CO oxidation, which implies catalytic activity of four orders of magnitude higher. This high catalytic activity for the Pt₃Sn surface is attributed to a unique adsorbed CO state.

Reactivity of 17- and 19-Electron Organometallic Complexes. Formation of Bent Sandwich 19-Electron Radical Cation Complexes of Ruthenium and Osmium

S. V. KUKHARENKO, V. V. STRELETS, L. I. DENISOVICH, M. G. PETERLEITNER, A. Z. KREIDLIN, A. R. KUDINOV and M. I. RYBINSKAYA, *Izv. Akad. Nauk, Ser. Khim.*, 1995, (12), 2394-2399

The redox behaviour of sandwich indenyl complexes ($\eta^5\text{-C}_6\text{H}_7$)ML, M = Ru or Os, L = $\eta^5\text{-C}_6\text{H}_7$, etc., was studied by cyclic voltammetry at a Pt electrode at -85 to 20°C and by controlled potential electrolysis. The complexes underwent reversible one-electron oxidation to the corresponding radical cations. A fast interaction of the 17-electron radical cations with nucleophiles yielded bent sandwich 19-electron radical cations $[(\eta^5\text{-C}_6\text{H}_7)\text{M}(\text{L})(\text{Nu})]^+$, Nu = Cl⁻, MeCN, etc.

High Sensitivity of Electron Transfer Rates within Nafion Coatings Saturated with Os(bpy)₃²⁺ to the Extent of Hydration of the Coating

M. SHI and F. C. ANSON, *J. Electrochem. Soc.*, 1995, **142**, (12), 4205-4214

Hydration effects on Nafion coatings on glassy C disk electrodes showed that when only one electroactive counterion is present in the coating the electrochemical response is enhanced. Nafion coatings fully saturated with Os(bpy)₃²⁺ but containing little H₂O had Nafionate salt properties; these are low ionic and electronic conductance and a high affinity for H₂O, which occurs when some of the Os(bpy)₃²⁺ counterions are ejected from the coating allowing H₂O to enter. Hydrated and unhydrated coatings are compared.

Electrooxidative Fission of Carbon-Carbon Double Bond in a K₂OsO₂(OH)₄/HIO₄ Double Mediator System

H. TANAKA, R. KIKUCHI, M. BABA and S. TORII, *Bull. Chem. Soc. Jpn.*, 1995, **68**, (10), 2989-2992

Electrooxidative C-C double bond fission of olefins occurred in the presence of catalytic amounts of K osmate and periodic acid. Corresponding carbonyl compounds were produced in moderate to good yields, when the turnover number of periodic acid reached ~ 3. The oxidative fission occurred by dihydroxylation of olefins followed by glycol cleavage. High selectivity to ketones showed that the regeneration of periodic species can occur in this electrooxidative media.

Surface Characterization of RuO₂-SnO₂ Coated Titanium Electrodes

M. ITO, Y. MURAKAMI, H. KAJI, K. YAHIKOZAWA and Y. TAKASU, *J. Electrochem. Soc.*, 1996, **143**, (1), 32-36

Studies of the morphology of RuO₂-SnO₂ coatings supported on Ti showed that Ru is segregated in island-like deposits for RuO₂-rich electrodes (1). For SnO₂-rich electrodes, where Sn is localised in the macroscopically flat plane of ultrafine particles, Ru was segregated along cracks. The ultrafine particles on the SnO₂-rich electrodes were smaller than those found for (1) and contributed to the large active surface area of the electrode. Only particles < 10 nm will give more active electrodes.

PHOTOCONVERSION

Effect of *n*-Si on the Photocatalytic Production of Hydrogen by Pt-Loaded CdS and CdS/ZnS Catalyst

G. C. DE, A. M. ROY and S. S. BHATTACHARYA, *Int. J. Hydrogen Energy*, 1996, **21**, (1), 19-23

Studies of H₂ production on illuminated CdS suspensions in Na₂S/Na₂SO₃ solution showed that the maximum rate occurred with a photocatalyst of 1.5 wt.% Pt/CdS/*n*-Si (6-7 wt.%)/ZnS in a 1.5:1 weight ratio. An increased H₂ rate was achieved by incorporating P-doped *n*-type Si in CdS. Combining small-bandgap semiconductor particles and larger-bandgap semiconductor particles increases photocatalytic efficiency.

Rigid Multinuclear Arrays Assembled Around Platinum Centres

A. HARRIMAN, M. HISSLER, R. ZIESSLER, A. DE CIAN and J. FISHER, *J. Chem. Soc., Dalton Trans.*, 1995, (24), 4067–4080

A series of *cis*- and *trans*-Pt(II) acetylide complexes of type $[Pt^II(PBu^u)_2L_2]$ where L = 2,2'-bipyridin-4-ylethynyl or 2,2':6',2''-terpyridin-4'-yl-ethynyl or -butadiynyl, were prepared and their photophysical properties were measured at 293 and 77 K. The peripheral metal complexes of these Pt^{II} systems have relatively long-lived excited triplet states, and could function as effective photosensitisers. Photons collected by the central Pt^{II} site are quantitatively transferred to the terminal metal complexes. The Pt^{II} centre thus acts as a light-harvesting antenna, for near-UV light.

Photoreactions of Metal Complexes with DNA, Especially Those Involving a Primary Photo-Electron Transfer

A. KIRSCH-DE MESMAEKER, J.-P. LECOMTE and J. M. KELLY, *Topics Current Chem.*, 1996, 177, 25–76

Photochemical reactions induced by Ru(II), Rh(III) and Co(III) polypyridyl complexes, porphyrins and uranyl ions with DNA are reviewed. Electron transfer reactions are examined. Evidence for direct oxidation of the DNA bases, production of DNA-damaging reactive species, direct H abstraction from the DNA ribose and formation of adducts between the metal complex and DNA is provided. The use of metal complexes as photoprobes for studying nucleic acids and photo-therapeutic applications is discussed.

APPARATUS AND TECHNIQUE

Development of a Micro Glucose Sensor Using an Electrodeposited Platinum Black with Mechanical Stability

S. IKEDA, H. WATANABE and I. IGARASHI, *Denki Kagaku*, 1995, 63, (12), 1138–1140

A glucose sensor has been fabricated from a Pt wire, sealed in the capillary of a 23-gauge needle with epoxy resin and electrodeposited with stable Pt black by ultrasonic irradiation from a solution containing $H_2PtCl_6 \cdot 6H_2O$. The sensor responds to glucose concentration of ≤ 50 mg/dl within a few minutes and its output current varies with O_2 partial pressure. The sensor can be implanted via a semipermeable membrane.

In-situ Modification of the NO_x Sensitivity of Thin Discontinuous Platinum Films as Gates of Chemical Sensors

J. ZUBKANS, A. L. SPETZ, H. SUNDGREN, F. WINQUIST, J. KLEPERIS, A. LUSIS and I. LUNDSTRÖM, *Thin Solid Films*, 1995, 268, (1–2), 140–143

A sensor of improved NO_x sensitivity, optimum at $\sim 125^\circ C$, was obtained by modifying a thin discontinuous Pt gate MOSFET with NH_3 at $150^\circ C$ for 10 min. NO_x exposure increases the threshold voltage but exposure to H_2 , NH_3 , alcohols and unsaturated hydrocarbons decreases it. The sensor was stable to NO_x for one month without more NH_3 treatment.

Voltresistometry of Noble Metals and Extension of Measuring Capability of the Contact Electroresistance Method by Using Iridium Reference Electrodes

V. A. MARICHEV and L. A. CHARNY, *Surf. Sci.*, 1996, 347, (1/2), 228–236

The potential dependence of the contact electroresistance (CER) of Pt, Ir, Ag and Au was studied in borate buffer solutions of pH 1–14. It has the lowest CER by 3–14 m Ω and can be used as the reference electrode for measuring high CER values of the oxides of metals, such as Ti, Zr and Cr. The CER of oxidised metal surfaces was non-ohmic. Thus, a new method is proposed for an in situ evaluation of the specific area of defects in oxide films on metals.

HETEROGENEOUS CATALYSIS

Adsorbate-Assisted NO Decomposition in NO Reduction by C₃H₆ over Pt/Al₂O₃ Catalysts under Lean-Burn Conditions

R. BURCH and T. C. WATLING, *Catal. Lett.*, 1996, 37, (1–2), 51–55

The rates and product selectivities of the C_3H_6 -NO- O_2 (1) and NO- H_2 reactions over a Pt/Al₂O₃ catalyst, and of the NO decomposition over the reduced catalyst were compared at $240^\circ C$. The NO decomposition rate over reduced catalyst was 7 times greater than the NO decomposition rate in reaction (1). The (extrapolated) rate of the NO- H_2 reaction at $240^\circ C$ was $\sim 10^4$ times faster than the rate of the NO decomposition. NO decomposition may be assisted by H_{ads} .

Nitric Oxide and Carbon Monoxide Adsorption on Lanthana-Supported Platinum and Rhodium Catalysts

H. CORDATOS and R. J. GORTE, *Appl. Catal. B: Environ.*, 1995, 7, (1–2), 33–48

CO and NO adsorption studies by TPD on model Rh/lanthana and Pt/lanthana catalysts showed that the lanthana surface can be reduced in CO by forming the carbonate which decomposes at > 650 K. The reduced lanthana has similar adsorption and decomposition properties for NO as those seen for Pt and Rh. Adding Pt and Rh promotes the CO reduction of the lanthana surface, possibly by migration of the O from the lanthana to the metal surfaces.

Control of the Efficiency of Low-Percentage Pt-Cu/Al₂O₃ Catalysts in the Activation of C-H and C-C Bonds in Light Alkanes

D. B. FURMAN and A. P. BARKOVA, *Kinet. Katal.*, 1995, 36, (6), 878–882

The effects of preliminary preheating $Cu(NO_3)_2/Al_2O_3$ on Pt metal deposition and on C-H and C-C bond activation by Pt-Cu/Al₂O₃ catalysts were studied in ethane and propane. Treating $Cu(NO_3)_2/Al_2O_3$ in H_2 at 300 – $900^\circ C$ produced catalysts which activate the ethane C-H bond, and form C_2H_4 selectively in 92–85% yield. Preliminary heat treating the support in air gave catalysts which activate the C-C ethane bond, and form CH_4 selectively in $> 60\%$ yield.

Stationary Kinetics of Essential Reactions on Automobile Exhaust Pt-Rh/Al₂O₃ Catalyst

P. MANNILA, T. SALMI, H. HAARIO, M. LUOMA, M. HÄRKÖNEN and J. SOHLO, *Appl. Catal. B: Environ.*, 1996, 7, (3–4), 179–198

Oxidation and reduction reactions of three-way catalysts were studied over CeO₂-promoted Pt-Rh/Al₂O₃ at 100–400°C. The concentrations of CO, CO₂, total hydrocarbons, NO/NO_x and O₂ at the monolith outlet were measured for different gas feeds. When H₂O was present, oxidation reactions were enhanced at low temperatures, while the H₂O-gas shift reaction and steam reforming occurred at higher temperatures.

Aromatics Reduction over Supported Platinum Catalysts. 2. Improvement in Sulfur Resistance by Addition of Palladium to Supported Platinum Catalysts

T.-B. LIN, C.-A. JAN and J.-R. CHANG, *Ind. Eng. Chem. Res.*, 1995, 34, (12), 4284–4289

Effects on the S resistance of a supported Pt catalyst on adding Co, Mo, Ni, Re, Ag and Pd, were studied by accelerated ageing reactions on tetralin hydrogenation with 1000 ppm S at 280°C, 380 psig and H₂:oil = 2.7. Pd-Pt had the highest S resistance. Pd-Pt had the best catalytic performance for aromatic reduction, hydrodesulphurisation and hydrodenitrogenation of diesel. Pd-Pt bimetallic interactions lower the Pt electron density and inhibit H₂S adsorption.

Surface Structure Change of a [Pt₄(μ-CH₃COO)₈]/SiO₂ Catalyst Active for the Decomposition of Formic Acid

W.-J. CHUN, K. TOMISHIGE, M. HAMAKADO, Y. IWASAWA and K. ASAKURA, *J. Chem. Soc., Faraday Trans.*, 1995, 91, (22), 4161–4170

Studies of catalytic properties of Pt₄-cluster/SiO₂ (1) prepared from the [Pt₄(μ-CH₃COO)₈] cluster showed that it is highly active for HCOOH decomposition giving 100% selectivity to CO₂ and H₂, compared with the Pt-particle/SiO₂ catalyst, which also gives CO and H₂O. Reaction on (1) involved: an induction period; a slow reaction period; a catalytic high-rate reaction period; and deactivation. The surface structure of (1) changed from tetramer to dimer during induction, then to monomers which were active for catalysis.

Effects of Barium on NO_x Reduction Activities of Palladium Three-Way Catalyst

H. SHINJOH, K. YOKOTA, H. DOI, M. SUGIURA and S. MATSUURA, *Nippon Kagaku Kaishi*, 1995, (10), 779–788

Three-way automotive Pd/γ-Al₂O₃ catalyst modified with Ba was studied by NO_x reduction using simulated exhaust gases, reaction gas chemisorption, H₂O gas shift reaction, etc. A big improvement in the NO_x reduction activity was seen at 100–500°C on adding Ba, under stoichiometric simulated exhaust gas (1) and under reduction conditions for the simulated exhaust gas (2). Under (1) NO was selectively reduced, rather than O₂. Under (2), suppression of chemisorbed hydrocarbons allowed smooth NO_x reduction.

Effect of Ceria Structure on Oxygen Migration for Rh/Ceria Catalysts

H. CORDATOS, T. BUNLUESIN, J. STUBENRAUCH, J. M. VOHS and R. J. GORTE, *J. Phys. Chem.*, 1996, 100, (2), 785–789

The adsorption and reaction properties of Rh particles supported on a CeO₂(100) surface and on polycrystalline CeO₂ film annealed at low (970 K) and high (1720 K) temperatures were studied. Significant growth of the CeO₂ crystallite size and change in the surface morphology upon high-temperature annealing was found. High-temperature annealed CeO₂ single crystals and polycrystalline films are relatively inert, but CO adsorbed on Rh/small CeO₂ crystallites can be oxidised by CeO₂. Thus, loss of O₂ storage capacity in automotive catalysts may be due to changes in the CeO₂ morphology and crystallite size.

Propionitrile Formation from Ethene and Ammonia over Rh/Y-Zeolite

N. TAKAHASHI, H. SAKAGAMI, T. KAMISHIMA, S. AZUMA and T. MATSUDA, *Catal. Lett.*, 1996, 36, (3, 4), 241–244

Rh-Y zeolite catalyst was found to be very effective for C₂H₅CN formation from C₂H₄ and NH₃. The catalyst was more active and selective than other transition metals supported on Y-zeolites. The reaction between C₂H₄ and HCN is proposed as a reaction route for C₂H₅CN formation.

One-Step Preparation of Highly Dispersed Supported Rhodium Catalysts by Low-Temperature Organometallic Chemical Vapor Deposition

P. SERP, R. FEURER, R. MORANCHO and P. KALCK, *J. Catal.*, 1995, 157, (2), 294–300

A new method for preparing supported Rh catalysts using organometallic CVD, and contacting a Rh complex vapour with SiO₂ in a fluidised bed reactor at 50–100 Torr, is described. Adding small amounts of H₂ allows Rh deposition at low temperature (100°C). Three Rh precursors, [Rh(μ-Cl)(CO)₂]₂, [Rh(η³-C₃H₅)₃] and [Rh(acac)(CO)₂], were used. Small aggregates of 1–2 nm with high dispersions of 0.95–0.70 were obtained. Rh(0) was detected on the surface, and Rh(I) and Rh(II) centres were found near the interface, covalently bound to the support. The catalyst showed greater hydrogenation activity than its counterpart prepared by conventional impregnation.

Ethanol Synthesis from Carbon Dioxide on TiO₂-Supported [Rh₁₀Se] Catalyst

H. KURAKATA, Y. IZUMI and K.-I. AIKA, *Chem. Commun.*, 1996, (3), 389–390

An efficient synthesis of EtOH from CO₂/H₂ over TiO₂-supported [Rh₁₀Se] clusters prepared from [Rh₁₀Se(CO)₂₂]²⁺ is reported. Promoter effects of the interstitial Se inside the [Rh₁₀] framework are discussed. [Rh₁₀Se]/TiO₂ converted CO₂ into EtOH faster, 60 × 10⁻³ mol/h/g cat., and more selectively, ~83%, than other supported Rh clusters or [Rh₁₀Se] clusters on other inorganic oxides. This may be due to effects from interstitial Se and the [Rh₁₀Se]/TiO₂ interface.

Redox and Carbonylation Chemistry of Iridium Species in the Channels of H-ZSM-5 Zeolite

T. V. VOSKOBOJNIKOV, E. S. SHPIRO, H. LANDMESSER, N. I. JAEGER and G. SCHULZ-EKLOFF, *J. Mol. Catal. A: Chem.*, 1996, **104**, (3), 299–309

Reduction of Ir/H-ZSM-5 by H₂ yields Ir⁰ clusters with a large positive XPS shift and an upward IR shift of linearly bonded CO, which suggest a strong electron deficiency. Ir clusters (< 1 nm) can be rapidly reoxidised by the highly acidic hydroxyls with subsequent formation of Ir⁺(CO)₂ gem-dicarbonyl even with residual CO. Displacement of NH₃ ligands which were co-ordinated to unreduced Ir³⁺ cations formed Ir³⁺(CO)₂. This species is reduced stepwise to Ir⁺(CO)₂ and Ir⁰-CO via the H₂O-gas shift reaction.

Preparation of Ruthenium-Containing Polycarbonate Films and the Chemistry of Ruthenium in Polycarbonate

I.-W. SHIM, W.-S. OH, H.-C. JEONG and W.-K. SEOK, *Macromolecules*, 1996, **29**, (4), 1099–1104

RuCl₃·3H₂O complexes were incorporated into polycarbonate (PC) using solvent. Interactions with CO, O₂, H₂ etc., effects of the Ru complexes and thermal properties of PC were studied in films. Catalytic activities were observed in various gas phase reactions under relatively mild conditions, such as NO reduction, H₂O-gas shift reaction, etc.

HOMOGENEOUS CATALYSIS

Polyketone Polymers Prepared Using a Palladium/Alumoxane Catalyst System

Y. KOIDE and A. R. BARRON, *Macromolecules*, 1996, **29**, (4), 1110–1118

The Pd-catalysed copolymerisation of CO and ethylene to give polyketone polymers was achieved using either (dppp)Pd(OAc)₂ or (dppp)Pd[C(O)Bu]Cl in the presence of a *tert*-butyl alumoxane as a co-catalyst. The polymers were alternating ethylene/CO and had high molecular weights. No furanisation or cross-linking was found. The crystal structure of these polymers was that of the α -phase polyketone. The increased densities of these polyketones is due to a decrease in the interchain packing distances.

Unprecedented Intra- and Intermolecular Palladium-Catalyzed Coupling Reactions with Methylene-cyclopropane-Type Tetrasubstituted Alkenes

S. BRÄSE and A. DE MEIJERE, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, (22), 2545–2547

A cascade of reactions consisting of a Heck coupling, cyclopropyl ring-opening and a domino Diels-Alder reaction proceeded in a one-pot synthesis in the presence of Pd(OAc)₂. The Pd-catalysed coupling of bicyclopropylidene with vinyl iodide gave dendralene, even in the presence of dienophile, which then reacted with R¹ = H, CO₂Me or R₂ = CO₂Me to yield bisadducts. Carbopalladation of the tetrasubstituted alkene proceeds faster than the Heck reaction with the dienophile.

A New, Highly Selective, Water-Soluble Rhodium Catalyst for Methyl Acrylate Hydroformylation

G. FREMY, Y. CASTANET, R. GRZYBEK, E. MONFLIER, A. MORTREUX, A. M. TRZECIAK and J. J. ZIOLKOWSKI, *J. Organomet. Chem.*, 1995, **505**, (1), 11–16

Hydroformylation of methylacrylate to α -aldehyde was achieved in a two-phase system in the presence of two new H₂O-soluble Rh phosphine PNS and PC catalysts, prepared by reacting [Rh(acac)(CO)₂] with various H₂O-soluble monodentate phosphines, such as Ph₂PCH₂CH(COOLi)(CH₂COOLi) (PC), Ph₂PCH₂-CH₂CONHC(CH₃)₂CH₂SO₃Li (PNS), P(CH₂)_n-C₆H₄SO₃Na₃, etc. High yields and selectivities of α -aldehyde were obtained.

Substrate Selective Catalysis by Rhodium Metallohosts

H. K. A. C. COOLEN, J. A. M. MEEUWIS, P. W. N. M. VAN LEEUWEN and R. J. M. NOLTE, *J. Am. Chem. Soc.*, 1995, **117**, (48), 11906–11913

A new supramolecular catalyst, consisting of a basket-shaped molecule with a catalytically active Rh(I) complex attached, is described. It functions according to the principles of enzymatic catalysis. The catalyst selectively hydrogenates and isomerises allyl-substituted dihydroxyarene substrates bound in its cavity. The rate-limiting component of these catalysts is the metal centre and the process sequence there.

Ligand Effects in the Catalytic Hydrogenation of Carbon Dioxide to Formic Acid Using in situ Catalysts Formed from [Co(dppp)Rh(μ -Cl)]₂ and Monodentate and Bidentate Phosphorus Ligands

E. GRAF and W. LEITNER, *Chem. Ber.*, 1996, **129**, (1), 91–96

Highly active catalysts for the hydrogenation of CO₂ to formic acid in DMSO/NEt₃ were formed in situ from [Co(dppp)Rh(μ -Cl)]₂ and various monodentate or bidentate ligands with P as the donor atom. Formic acid concentrations of $\leq 2.3 \pm 0.2$ mol/l were obtained in < 6 h at ambient temperature under a total initial pressure of 40 atm by using Rh concentrations of 5×10^{-3} mol/l. With bidentate ligand R₂P(CH₂)_nPR₂ the chain length *n* determines the activity of the catalysts.

Ligand-Induced Selectivity in the Rhodium(II)-Catalyzed Reactions of α -Diazo Carbonyl Compounds

A. PADWA, D. J. AUSTIN and S. F. HORNBuckle, *J. Org. Chem.*, 1996, **61**, (1), 63–72

The reaction of 3-allyl-2,5-diazopentanedione and 3-butenyl-2,5-diazopentanedione with traces of a Rh(II) catalyst in methylene chloride at room temperature gave products with internal trapping of a carbonyl ylide as well as intermolecular cyclopropanation. When the catalyst was changed from Rh₂(OAc)₄ to Rh₂(cap)₄ to Rh₂(tfa)₄, a significant change occurred in the product distribution. With Rh₂(tfa)₄, an unexpected regiochemical crossover occurred in cycloaddition, due to complexation of the metal with the dipole.

Homogeneous Hydrogenation of Carbon Dioxide to Methanol Catalyzed by Ruthenium Cluster Anions in the Presence of Halide Anions

K.-I. TOMINAGA, Y. SASAKI, T. WATANABE and M. SAITO, *Bull. Chem. Soc. Jpn.*, 1995, **68**, (10), 2837–2842

Detailed catalytic and mechanistic studies showed the first formation of MeOH, together with CH₄, by homogeneous hydrogenation of CO₂ using a system consisting of Ru₃(CO)₁₂ and alkaline iodides in *N*-methylpyrrolidone solution at 240°C. The successive formation of CO, MeOH, and then CH₄ was indicated. An overall reaction mechanism is proposed.

Coupling H₂ to Electron Transfer with a 17-Electron Heterobimetallic Hydride: A "Redox Switch" Model for the H₂-Activating Center of Hydrogenase

R. T. HEMBRE, J. S. MCQUEEN and V. W. DAY, *J. Am. Chem. Soc.*, 1996, **118**, (4), 798–803

The preparation of a meta-stable heterobimetallic mixed-valence ion, [Fe(II),Ru(III)], formed by one-electron oxidation of Cp*(dppf)RuH (1), where dppf = 1,1'-bis(diphenylphosphino)ferrocene and Cp* = pentamethylcyclopentadienide, is reported. Cyclic voltammetry of (1) showed that there was great stability for one-electron oxidation. Two reversible oxidations at +0.073 and +0.541 V and a quasireversible oxidation at +0.975 V (vs NHE) appeared and were assigned to Ru(III/II), Ru(IV/III) and Fe(III/II), respectively. Compound (1) is the first homogeneous catalyst to reduce methyl viologen with H₂.

Amino Alcohol Effects on the Ruthenium(II)-Catalysed Asymmetric Transfer Hydrogenation of Ketones in Propan-2-ol

J. TAKEHARA, S. HASHIGUCHI, A. FUJII, S.-I. INOUE, T. IKARIYA and R. NOYORI, *Chem. Commun.*, 1996, (2), 233–234

A Ru(II) complex, generated in situ from [$\{\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)_2\}$], (1*S*, 2*S*)-2-methylamino-1,2-diphenylethanol and KOH was found to be an efficient catalyst for asymmetric transfer hydrogenation of acetophenone derivatives in propan-2-ol. The catalyst had high reactivity at room temperature. (*S*)-enriched alcohols in $\leq 92\%$ ee and in $> 90\%$ yield are produced.

FUEL CELLS

A New Fuel Cell Electrocatalyst Based on Highly Porous Carbonized Polyacrylonitrile Foam with Very Low Platinum Loading

S. YE, A. K. VIJH and L. H. DAO, *J. Electrochem. Soc.*, 1996, **143**, (1), L7–L9

A carbonised polyacrylonitrile (PAN) microcellular material of high porosity with incorporated Pt loading of $\sim 13 \mu\text{g}/\text{cm}^2$ was prepared, characterised and used as the electrode material for O₂ reduction. It has excellent electrocatalytic activity which is attributed to the highly homogeneous distribution of the small Pt particles in the carbonised PAN foam surface.

Improved Pt Alloy Catalysts for Fuel Cells

A. FREUND, J. LANG, T. LEHMANN and K. A. STARZ, *Catal. Today*, 1996, **27**, (1–2), 279–283

Electrode catalysts, Pt-Co-Cr/C black, with increased activity and stability for the O₂ reduction reaction in phosphoric acid fuel cells were developed by co-precipitation of the corresponding metal nitrates. A tetragonal ordered structure was formed at $> 873 \text{ K}$. This method will allow preparation of more efficient catalysts of small Pt-Co-Cr alloy particle size.

CORROSION PROTECTION

Effect of Mo and Pd on Corrosion Resistance of V-Free Titanium Alloys for Medical Implants

Y. OKAZAKI, K. KYO, Y. ITO and T. TATEISHI, *J. Jpn. Inst. Met.*, 1995, **59**, (10), 1061–1069

The corrosion resistance of Ti-15%Zr-4%Nb-4%Ta-0.2%Pd-0.2%O-0.05%N and Ti-15%Sn-4%Nb-2%Ta-0.2%Pd-0.2%O alloys, for medical implants, were compared with pure Ti Grade 2 alloys, Ti-6%Al-4%V ELI (Extra low interstitial), etc., by anodic polarisation and immersion testing at 310 K in various pseudo saline solutions. The rate of Ti ion released by Ti alloys in a deaerated 5% HCl solution decreased with increasing Zr, Nb, Ta and Pd contents.

ELECTRICAL AND ELECTRONIC ENGINEERING

Improved *p*-Channel InAlAs/GaAsSb HIGFET Using Ti/Pt/Au Ohmic Contacts to Beryllium Implanted GaAsSb

K. G. MERKEL, C. L. A. CERNY, V. M. BRIGHT, F. L. SCHUERMEYER, T. P. MONAHAN, R. T. LAREAU, R. KASPI and A. K. RAI, *Solid-State Electron.*, 1996, **39**, (2), 179–191

Ti/Pt/Au metallisation produces an extremely low contact resistance on Be implanted GaAs_{1-x}Sb_x. The contact is thermally stable at 250°C for $\sim 500 \text{ h}$ and can withstand thermal cycling to 450°C. The use of Ti/Pt/Au as the source, drain and gate metallisation produced a single, conventional metallisation for the In_{0.52}Al_{0.48}As/GaAs_{0.51}Sb_{0.49} *p*-HIGFET, which is improved with respect to ohmic contact reliability, etc. Using Be implantation with Ti/Pt/Au metallisation directly enhances future device designs.

Bias and Thickness Dependence of the Infra-Red PtSi/*p*-Si Schottky Diode Studied by Internal Photoemission

V. W. L. CHIN, J. W. V. STOREY and M. A. GREEN, *Solid-State Electron.*, 1996, **39**, (2), 277–280

IR PtSi/*p*-Si diodes with different metal thicknesses were studied at $\sim 80 \text{ K}$ by internal photoemission as a function of reverse bias. The zero-bias barrier height of PtSi/*p*-Si was found to increase only marginally with metal thickness. The main lowering of the Schottky barrier height is at low to moderate electric fields. The carrier mean free path in Si decreased with an increase in the semiconductor acceptor density.