

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Kerr Enhancement by Layer Modulation in Co/Pt Multilayers

K. YUSU, S. HASHIMOTO and K. INOMATA, *Jpn. J. Appl. Phys.*, 1992, 31, Pt. 1, (2B), 435-438

Layer modulated Co/Pt multilayers were studied to achieve perfect squareness for ultrathin films, even with a thickness ratio $t_{Co}/t_{Pt} = 1$, and to attain a large Kerr rotation angle. Good squareness of hysteresis was obtained by decreasing the number of repetitions n in $(5Pt/5Co)_n/100Pt$ multilayers. The $(5Pt/5Co)_2$ multilayers with good squareness were stacked through a Pt interlayer of various thicknesses, giving excellent magneto-optical properties. A Pt interlayer $> 30 \text{ \AA}$ gave characteristic hysteresis with good squareness.

Transformation of Platinum Carbonyl Clusters on Graphite under Laser Irradiation and Their Scanning Tunneling Microscopy Observation

T. FUJIMOTO, A. FUKUOKA and M. ICHIKAWA, *Chem. Mater.*, 1992, 4, (1), 104-107

STM images were obtained from an isolated aggregate of Pt carbonyl clusters $[\text{NEt}_4]_2[\text{Pt}_{12}(\text{CO})_{24}]$, which were adsorbed from the tetrahydrofuran solution onto the surface of a freshly cleaved highly oriented pyrolytic graphite under a N_2 atmosphere. The morphological changes of the surface bound Pt_{12} carbonyl clusters were observed under pulse laser irradiation resulting in the effective decarbonylation and fragmentation. The Pt_{12} carbonyl clusters were converted to a highly dispersed Pt microcrystalline.

Palladium-Zirconia Diffusion Bonds: Mechanical Properties and Interface Reactions

C.-D. QIN, N. A. JAMES and B. DERBY, *Acta Metall. Mater.*, 1992, 40, (5), 925-938

High strength and toughness diffusion bonds have been made using Pd foils between TZP zirconia blocks at temperatures $> 1000^\circ\text{C}$ only in vacuum. Bonds made at $< 1000^\circ\text{C}$ in vacuum and all air conditions had negligible strength. Strong bonds made in vacuum lost almost all their strength on annealing in air at $> 1000^\circ\text{C}$. Anneals in vacuum resulted in a decrease in bond strength, but with a much less marked effect. Pd-ZrO₂ interfaces have been characterised by TEM and a thin reaction zone identified, which contains Pd, Zr and O in ratio 30:52:18. Evidence for the presence of a liquid phase at the Pd-ZrO₂ interface during bonding is presented. The perfection of the bonded interface determines the strength and toughness of the bonds.

Anisotropy in a Heavy Fermion Superconductor: UPd_2Al_3

N. SATO, T. SAKON, N. TAKEDA, T. KOMATSUBARA, C. GEIBEL and F. STEGLICH, *J. Phys. Soc. Jpn.*, 1992, 61, (1), 32-34

The anisotropy of magnetisation, electrical resistivity and upper critical magnetic fields of UPd_2Al_3 are reported. The magnetisation curve in the antiferromagnetically ordered state shows large anisotropy, indicating that the sublattice moments lie in the basal hexagonal plane. The upper critical magnetic field was rather isotropic, whereas it was strongly anisotropic in UPt_3 , and the anisotropy in the magnetisation in the normal and antiferromagnetic state of UPd_2Al_3 was also larger.

Preparation of a Large $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ Single-Quasicrystal by the Czochralski Method and Its Electrical Resistivity

Y. YOKOYAMA, T. MIURA, A.-P. TSAI, A. INOUE and T. MASUMOTO, *Mater. Trans. JIM*, 1992, 33, (2), 97-101

A seed single-quasicrystal of AlPdMn was grown by the Czochralski method, after choosing a liquidus of composition $\text{I-Al}_{71.5}\text{Pd}_{19.7}\text{Mn}_{6.8}$ which equilibrates to the stoichiometric icosahedral(I) phase. The maximum size of the ingot reached was 10 mm in diameter and 50 mm long. The electrical resistivity of the crystal has a negative temperature dependence in the range 40-270 K, and has a maximum value of 65-107 $\mu\Omega\text{m}$ at $\sim 40 \text{ K}$.

Possible 4d Ferromagnetism of Rh and Ru Overlayers on a $\text{Ag}(001)$ Substrate

R. WU and A. J. FREEMAN, *Phys. Rev. B*, 1992, 45, (13), 7222-7228

The possibility of 4d ferromagnetism of Rh and Ru overlayers on a $\text{Ag}(001)$ substrate was studied using the full-potential linearised augmented-plane-wave method. The ferromagnetism of Rh/ $\text{Ag}(001)$ could be destroyed by an additional Ag layer whereas Ru/ $\text{Ag}(001)$ was predicted to be ferromagnetic with both a larger magnetic moment and larger magnetic energy even after being covered by a Ag layer.

Resistivity and Thermopower Studies in $\text{Ce}(\text{Ru}_{1-x}\text{Cu}_x)_2\text{Si}_2$ Systems

C. S. GARDE, J. RAY and G. CHANDRA, *Phys. Rev. B*, 1992, 45, (13), 7217-7221

Resistivity ρ and thermopower S studies at 1.7-300 K on $\text{Ce}(\text{Ru}_{1-x}\text{Cu}_x)_2\text{Si}_2$ alloys were performed. Variation of x provided a means for controlling the single-site and intersite coupling strengths and to check whether magnetic order developed in the limit of $x \rightarrow 0$ or 1. The ρ and S curves showed features that could be identified with the Kondo temperature.

Plasma Etching of RuO₂ Thin Films

S. SAITO and K. KURAMASU, *Jpn. J. Appl. Phys.*, 1992, 31, Pt. 1, (1), 135–138

The plasma etching of RuO₂ thin films was performed using CF₄ or O₂ plasma, and compared with sputter etching. O₂ plasma radicals, using ion impact, were more effective at etching than radicals from CF₄, and a higher etching rate and good selectivity were obtained. The plasma etching rate was higher than for sputter etching, giving fine patterns.

CHEMICAL COMPOUNDS

Ba₈Ru₃Ta₂O₁₈Br₂ — Synthesis and Structure Characterisation of a New Oxide-Bromide with Ruthenium

J. WILKENS and H. MÜLLER-BUSCHBAUM, *J. Alloys Compd.*, 1992, 182, (2), 265–270

A new compound Ba₈Ru₃Ta₂O₁₈Br₂ was prepared by a BaBr₂ flux. Crystal structure studies showed that it crystallises with rhombohedral symmetry, and lattice constants $a=5.981(1)$ Å and $c=60.79(2)$ Å; $Z=3$. It is described by a 24-layer structure of Ba²⁺/O²⁻ and Ba²⁺/Br⁻ with incorporated Ru⁴⁺ and Ta⁵⁺ ions forming (Ru,Ta)₂O₉ groups which are corner connected by RuO₆ octahedra.

ELECTROCHEMISTRY

Electro-oxidation of Methanol on Graphite-Supported Perovskite-Modified Pt Electrodes in Alkaline Solution

P. C. BISWAS and M. ENYO, *J. Electroanal. Chem. Interfacial Electrochem.*, 1992, 322, (1 and 2), 203–220

Graphite-supported perovskite-modified Pt electrodes showed much higher electrocatalytic activities than smooth Pt or graphite-supported Pt electrodes towards MeOH electro-oxidation in 1 M NaOH solution at 25°C with zero-current potential as low as 200 mV versus the reversible H electrode. The catalytic activities of the modified electrodes were very stable and remained unaffected towards the poisoning effect of CO. CO and MeOH could be oxidised simultaneously and MeOH oxidation was enhanced at high positive potentials by the presence of CO.

A Microelectrode Study of Oxygen Reduction at the Platinum/Recast-Nafion Film Interface

F. A. URIBE, T. E. SPRINGER and S. GOTTESFELD, *J. Electrochem. Soc.*, 1992, 139, (3), 765–773

The electrochemical reduction of O₂ at a Pt microelectrode under a range of humidification conditions and temperatures, in a cell containing a hydrated recast Nafion film as the only electrolyte is reported, the conditions being identical to those in a polymer electrolyte fuel cell. The interfacial rate of O₂ reduction near 0.9 V was similar for the Pt/recast ionomer interface and for Pt immersed in dilute aqueous acid solutions. A significant loss of O₂ reduction activity occurred when the recast ionomer electrolyte loses H₂O.

Ruthenium-Catalysed, Electrochemical Cleavage of Aryl Olefins for the Synthesis of Benzaldehydes

E. STECKHAN and C. KANDZIA, *Synlett*, 1992, (2), 139–140

A one-pot, one-step cleavage of electron-rich double bonds to the corresponding aldehydes, such as 3,4-methylenedioxy-1-(1-propenyl)benzene and related compounds, using a RuSiW₁₁O₃₉⁵⁻ catalyst in an electrochemical two-phase double mediator system or with stoichiometric regeneration is reported. Up to 200 turnovers of the catalyst could be obtained without any loss of activity of the system.

Formation of Hypochlorite, Chlorate and Oxygen during NaCl Electrolysis from Alkaline Solutions at an RuO₂/TiO₂ Anode

L. R. CZARNETZKI and L. J. J. JANSSEN, *J. Appl. Electrochem.*, 1992, 22, (4), 315–324

The current efficiency for hypochlorite, chlorate and O formation at a RuO₂/TiO₂ anode were determined under various conditions in order to optimise the electrolytic cell and electrolysis conditions for weak alkaline solutions of NaCl, for on-site disinfection. At 298 K, solution flow velocity of 0.075 m/s and high current density, hypochlorite formation was determined by mass transfer of chloride. The formation of chlorate is ascribed to the direct oxidation of chloride to chlorate and hypochlorite conversion.

PHOTOCONVERSION

Photodissociation and Photodesorption of O₂ Adsorbed on Pd(III)

E. HASSELBRINK, H. HIRAYAMA, A. DE MEIJERE, F. WEIK, M. WOLF and G. ERTL, *Surf. Sci.*, 1992, 269/270, (Part A), 235–246

The dynamics of the UV-photochemistry of molecularly adsorbed O on Pd(III) was studied using pulsed laser light at 3.9–6.4 eV photon energy. Upon UV-irradiation ($h\nu > 3.5$ eV) O₂ dissociates to form surface O and desorbs with translational energies exceeding the surface temperature. Displacement processes occurred causing conversion between molecular binding states and thermally accommodated desorption. All processes share a common dependence on photon energy in the form of an exponential rise by a factor of 35 between 3.9–6.4 eV.

Photochemistry of Adsorbed States of Diazirine on Pd(110)

S. SERGHINI MONIM and P. H. MCBREEN, *Chem. Phys. Lett.*, 1992, 192, (5, 6), 547–554

XPS studies of adsorbed states of diazirine on Pd(110) showed that it is possible to correlate the CN and NN photoinduced bond breaking processes in diazirine on Pd(110) with the initial different chemisorption state of the molecule. Photodissociation of π -chemisorbed diazirine results in NN bond cleavage.

Photoredox Properties of $[\text{Os}(\text{NH}_3)_4]^{3+}$ and Mechanism of Formation of $[\{\text{Os}(\text{NH}_3)_4(\text{CH}_3\text{CN})\}_2\text{N}_2]^{5+}$ through a Nitrido-Coupling Reaction

H.-W. LAM, C.-M. CHE and K.-Y. WONG, *J. Chem. Soc., Dalton Trans.*, 1992, (8), 1411–1416

The oxidation of $[\text{Os}(\text{NH}_3)_5\text{Cl}]^{2+}$ by Ce^{IV} in H_2O gave $[\text{Os}(\text{NH}_3)_4]^{3+}$ (1) quantitatively, and excitation of (1) in the solid state or in solution at 300–400 nm resulted in room-temperature photoluminescence. Photolysis of (1) in the presence of an electron donor in acetonitrile yielded the μ -dinitrogen product $[\{\text{Os}(\text{NH}_3)_4(\text{CH}_3\text{CN})\}_2\text{N}_2]^{5+}$ (2). Oxidation of (2) by Ce^{IV} in H_2O followed by precipitation with HCl gave the product $[\text{Os}(\text{NH}_3)_4]\text{Cl}_3$ in detectable yield.

pH Control of Photoreactivity of Ru(II) Pyridyltriazole Complexes: Photoinduced Linkage Isomerism and Photoanation

R. WANG, J. G. VOS, R. H. SCHMEHL and R. HAGE, *J. Am. Chem. Soc.*, 1992, 114, (6), 1964–1970

The photophysical and photochemical behaviour of mixed ligand complexes of Ru(II) with 3-(pyridin-2-yl)-1,2,4-triazole (HPTN) were studied in solutions of various acidities. Protonation of both the N-2 bound (HPTN-2) and the N-4 bound (HPTN-4) isomers of $[(\text{bpy})_2\text{Ru}(\text{HPTN})]^{2+}$ resulted in a decrease in the luminescence lifetime in solution and an increase in reactivity upon photolysis in CH_2Cl_2 . Photolysis of either protonated isomer in CH_2Cl_2 resulted in linkage isomerism.

ELECTRODEPOSITION AND SURFACE COATINGS

Studies of Palladium Electrodeposition from Baths Based on $\text{Pd}(\text{NH}_3)_2\text{X}_2$. Part II. $\text{X} = \text{Br}$ and $\text{X} = \text{NO}_2$

R. LE PENVEN, W. LEVASON and D. PLETCHER, *J. Appl. Electrochem.*, 1992, 22, (5), 421–424

The chemistry and electrochemistry of electroplating baths based on $\text{Pd}(\text{NH}_3)_2\text{Br}_2$ and $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ were studied and compared with that of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$. The electroactive species in all the baths was $\text{Pd}(\text{NH}_3)_4^{2+}$ but only in bromide electrolytes did Pd dissolve anodically.

Ultrahigh Vacuum Chemical Vapor Deposition of Rhodium Thin Films on Clean and TiO_2 -Covered Si(111)

J.-P. LU, P. W. CHU, R. RAJ and H. GYSLING, *Thin Solid Films*, 1992, 208, (2), 172–176

Thin film deposition by thermal decomposition of $\text{Rh}(\text{CO})_2(\text{C}_2\text{H}_5\text{O}_2)$ has been studied under UHV conditions. Thin films were deposited on clean Si(111)-(7 × 7) and TiO_2 -covered Si(111) substrates, and analysed. Rh films deposited at 200–500°C contain C and O impurities. The C and O incorporation is more severe in the initial deposition stage on a clean Si surface than on a growing surface.

APPARATUS AND TECHNIQUE

Use of the Electroreflectance Technique in Pt/GaAs Schottky Barrier Sensor Characterization

L. M. LECHUGA, G. ARMELLES, A. CALLE, D. GOLMAYO and F. BRIONES, *Sens. Actuators A*, 1992, 32, (1–3), 354–356

A new way to measure the gas sensitivity of a sensor based on a Pt/GaAs Schottky diode by measuring the electroreflectance spectra is reported. The electroreflectance spectra were obtained and analysed as a function of the device exposure to a H-containing atmosphere at different temperatures. The results obtained indicated that the H-induced modification of the spectra can be viewed as a barrier height lowering of about 0.2 eV.

Ammonia Sensitivity of Pt/GaAs Schottky Barrier Diodes. Improvement of the Sensor with an Organic Layer

L. M. LECHUGA, A. CALLE, D. GOLMAYO, F. BRIONES, J. DE ABAJO and J. G. DE LA CAMPA, *Sens. Actuators B*, 1992, 8, (3), 249–252

A sensor for the detection of NH_3 over a wide temperature range has been developed which utilises a Schottky barrier device Pt/*m*-GaAs with a porous discontinuous Pt film and a layer of polyetherimide. The organic layer increases the sensitivity of the device and may allow the sensor to be used in aqueous solution and with biological material. The detection limit of the device in synthetic air is 10 ppm of NH_3 .

Infrared Response of Pt/Si/ErSi_{1.7} Heterostructure: Tunable Internal Photoemission Sensor

L. PAHUN, Y. CAMPIDELLI, F. ARNAUD D'AVITAYA and P. A. BADOZ, *Appl. Phys. Lett.*, 1992, 60, (10), 1166–1168

An internal photoemission response of a Pt/Si/ErSi_{1.7} heterostructure is reported. With this device the photoresponse can be strongly modified when a bias of a few hundred mV is applied between the two metallic electrodes: the cutoff wavelength is shifted from 1.4 μm to >5 μm , and the quantum efficiency is increased up to 5% at a wavelength of 1.2 μm when a positive bias is applied to the front Pt electrode.

Efficient Palladium Isotope Chromatograph for Hydrogen (EPIC)

M. C. EMBURY, R. E. ELLEFSON, H. B. MELKE and W. M. RUTHERFORD, *Fusion Technol.*, 1992, 21, (2), 960–965

An apparatus was designed to separate a H flow into deuterium and protium, in an efficient Pd isotope chromatograph (EPIC), using 48 wt.% Pd deposited on Al_2O_3 packed into a column 6.8 mm i.d. × 910 mm long. Design modifications to permit operation with tritium, increased throughput and improved product purity are discussed.

Considerations of the pH Dependence of Hydrated Oxide Films Formed on Iridium by Voltammetric Cycling

M. L. HITCHMAN and S. RAMANATHAN, *Electroanalysis*, 1992, 4, (3), 291-297

The magnitude of the charge storage capacity attained by Ir oxide electrodes under potential cycling conditions is important for the ratio of protons to electrons participating in the potential-determining equilibria under zero current conditions. A model based on electron exchange between protons in solution and conductive sites on the hydrated oxide surface is proposed; electrochemical cycling of Ir can make simple, robust solid state pH electrodes.

Chemiluminescence Detection Using Regenerable Tris(2,2'-bipyridyl)ruthenium(II) Immobilized in Nafion

T. M. DOWNEY and T. A. NIEMAN, *Anal. Chem.*, 1992, 64, (3), 261-268

A detection method based on the electrogenerated chemiluminescence of tris(2,2'-bipyridine)Ru(II), (Ru(bpy)₃)²⁺, immobilised in a Nafion film coated on an electrode is described. The sensor is used in flow injection to determine oxalate, alkylamines and NADH. Detection limits are 1 μM, 10 nM and 1 μM, respectively, with working ranges extending over 4 decades in concentration. Sensitivity is constant over pH 3-10.

Determination of Nitrite Based on Medicated Oxidation at a Carbon Paste Electrode Modified with a Ruthenium Polymer

T. J. O'SHEA, D. LEECH, M. R. SMYTH and J. G. VOS, *Talanta*, 1992, 39, (4), 443-447

The mediated detection of nitrite by C paste electrodes modified with [Ru(bpy)₂(PVP)₁₀Cl]Cl is described. The Ru surface modifier substantially lowers the overpotential for nitrite oxidation, thus allowing its determination at a lower potential. Standard calibration curves yielded slopes of 0.3 μA/μM over the linear range 5 × 10⁻⁸ - 5 × 10⁻⁴ M nitrite, with a detection limit of 3 × 10⁻⁸ M (1.38 ppb).

HETEROGENEOUS CATALYSIS

Reforming of Pyrolysis Gasoline over Platinum-Alumina Catalysts Containing MFI Type Zeolites

K. MADHUSUDAN REDDY, S. K. POKHRIYAL, P. RATNASAMY and S. SIVASANKER, *Appl. Catal. A:Gen.*, 1992, 83, (1), 1-13

Reforming of pyrolysis gasoline was carried out over Pt/Al₂O₃ catalysts containing small amounts of pentasil zeolite of the MFI type. The addition of these zeolites lowered the coke deposition on the catalysts giving products almost free of aliphatics. The pressure was kept low enough to achieve a significant increase in the concentration of aromatics.

Change of the Valent State of Metals in the Film of the Pd-Pt/Al₂O₃ Catalyst during Heating in Air and Deep Methane Oxidation

S. V. BARAN, M. I. IVANOVSKAYA, G. A. BRANITSKII and V. M. PEROV, *Dokl. Akad. Nauk Belarusi*, 1992, 36, (1), 56-59

Studies of a mutual effect of Pt and Pd on the stability of their different valent states in bimetallic catalysts Pd-Pt/Al₂O₃ during heating in air and deep CH₄ oxidation at 600-700 K were performed on bimetallic Pd-Pt catalysts prepared by deposition of PdCl₂ and H₂PtCl₆ solutions on γ-Al₂O₃. In the reaction mixture CH₄-air at 600 K, the valent state of Pt changed from Pt⁰ to Pt²⁺ but in the presence of Pt oxidised forms, Pd⁺ stabilised the catalyst. Pd-Pt/Al₂O₃ catalyst showed high activity and stability.

Catalytic Etching of Pt/Rh Gauzes

J. M. HESS and J. PHILLIPS, *J. Catal.*, 1992, 136, (1), 149-160

Gauzes made of 90% wt.% Pt/10 wt.% Rh were catalytically etched in H₂/O₂ mixtures. The gauzes etched over exactly the same range of temperatures and gas stoichiometries as pure Pt. However, pure Rh etched in neither pure gases nor under reaction conditions. In a laminar flow type reactor weight loss in the gauzes was significant, indicating rapid etching, with smooth surfaces similar to those of untreated material. However, in an impinging jet reactor there was little weight loss, but the surfaces were partially covered by complex particle structures, 1-10 μm.

Hydrogen Formation in Propane Oxidation on Pt-Rh/CeO₂/Al₂O₃ Catalysts

J. BARBIER and D. DUPREZ, *Appl. Catal. A:Gen.*, 1992, 85, (1), 89-100

TPO of propane at 200-550°C was carried out on PtRh/CeO₂/Al₂O₃ catalysts with O-deficient C₃H₈/O₂ mixtures. At T < 330-350°C propane is oxidised exclusively into CO₂ and H₂O. At T > 350°C there are two distinct zones in the catalyst bed: total oxidation catalysed by Pt at the bed inlet and steam reforming catalysed by Rh in the outlet zone. Steam reforming is the slow step in forming H₂, and H₂O gas shift reaction is the fast reaction.

Synthesis of Liquid Hydrocarbons from CO and H₂ over Co-Ru and Co-Pd Catalysts Supported on Alumina

A. L. LAPIDUS, A. YU. KRYLOVA, M. P. KAPUR, E. V. LEONGARDT, A. B. FASTAN and S. D. MIKHAILENKO, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1992, (1), 60-64

Studies of the effect of additions of 0.1-0.5% Pd or Ru into 10% Co/Al₂O₃ catalyst on its activity and selectivity showed that bimetallic systems produced higher CO and C₅+ hydrocarbon yields. The Co-Ru catalysts were highly selective (< 80%) during the studied synthesis. When Pd or Ru were introduced into Co/Al₂O₃ catalysts, they allowed Co reduction at lower temperature and formation of Co aluminates.

Hydrogenation Activity of an Amorphous Pd-Zr Alloy Held in an Alumina Matrix

T. TAKAHASHI, K. ABE, T. KAI, H. KIMURA and T. MASUMOTO, *Can. J. Chem. Eng.*, 1992, 70, (1), 197-200

A catalyst of amorphous Pd-Zr alloy on an Al_2O_3 matrix was used to hydrogenate benzene, and its activity was compared to that of Pd-Zr cut into 1 mm fragments. The alloy fixed in Al_2O_3 had higher activity and also a smaller catalyst fouling rate than the alloy fragments. The Pd was considered to be well dispersed on the Zr oxide by the fixation of the amorphous alloy in the Al_2O_3 matrix.

Structure and Catalytic Activity of Metal Complexes Fixed on Supports. 5. Hydrodehalogenation of *p*-Bromotoluene with Chemically Bonded Hydrogen, Catalysed by Immobilised Rh(II) Complexes

V. I. ISAEVA, ZH. L. DYKH, L. I. LAFER, V. I. YAKERSON and V. Z. SHARF, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1992, (1), 65-71

Spectroscopic studies of the structure and activity of Rh(II) complexes with various ligands immobilised on γ -aminopropyl containing silicate gel (γ -AMPS) and on polymers containing 3(5)-methylpyrazole and imidazole groups showed a substitution of the ligands on amino groups of the support that occurred in acetonitrile and hexafluoroacetalacetate complexes. $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4]$ complex immobilised on γ -AMPS metal complexes showed the highest activity in hydrodehalogenation of *p*-bromotoluene via H transfer from NaBH_4 and propanol-2.

Preparation and Characterization of Chlorine-Free Ruthenium Catalysts and the Promoter Effect in Ammonia Synthesis. 1. An Alumina-Supported Ruthenium Catalyst. 2. A Lanthanide Oxide-Promoted Ru/ Al_2O_3 Catalyst. 3. A Magnesia-Supported Ruthenium Catalyst

S. MURATA and K.-I. AIKA; S. MURATA and K.-I. AIKA; K.-I. AIKA, T. TAKANO and S. MURATA, *J. Catal.*, 1992, 136, (1), 110-117; 118-125; 126-140

$\text{Ru}/\text{Al}_2\text{O}_3$ catalyst prepared from Cl-free Ru carbonyl was much more active for NH_3 synthesis under 1.01 bar $\text{N}_2 + 3\text{H}_2$ than that prepared from RuCl_3 . The high activity was related to the high dispersion and lack of Cl. Oxides and hydroxides of Cs, Rb and K ions were effective promoters. Synthesis rate was a maximum for Cs:Ru = 10. $\text{La}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$ and $\text{Sm}(\text{NO}_3)_3$ were more effective promoters of NH_3 synthesis than CsNO_3 . MgO , $\text{Na}_2\text{O-MgO}$ and $\text{Al}_2\text{O}_3\text{-MgO}$ supports were most effective for NH_3 synthesis using $\text{Ru}_3(\text{CO})_{12}$ as catalyst precursor, possibly due to high Ru dispersion. Alkali metal nitrates were the most effective promoters, and the synthesis rate was greatest when the Cs:Ru ratio was 1.0, where activity was 20 times as high as that without CsNO_3 , at 588 K.

HOMOGENEOUS CATALYSIS

Isomerization of Alkynemono-ols Catalyzed by Palladium(0) Complex and Diols

X. LU, J. JI, C. GUO and W. SHEN, *J. Organomet. Chem.*, 1992, 428, (1-2), 259-266

Studies of the isomerisation of various alkynemono-ols by $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3 + ^i\text{Pr}_3\text{P} + \text{HOCH}_2\text{CH}_2\text{OH}$ catalytic system in acetonitrile showed that it occurred under the milder reaction conditions of acetonitrile reflux temperature, when a catalytic amount of diols was added; α, β -unsaturated ketones were formed. $^1\text{H NMR}$ spectra showed the formation of two isomers, (*E*)- α, β -enones and β, γ -enones in the ratio of 4:1. This route gives a neutral, mild and convenient method for preparation of enones from the isomerisation of alkynemono-ols.

Synthesis of Sterically Hindered Biaryls via the Palladium-Catalyzed Cross-Coupling Reaction of Arylboronic Acids or Their Esters with Haloarenes

T. WATANABE, N. MIYaura and A. SUZUKI, *Synlett*, 1992, (3), 207-210

Sterically hindered arylboronic acids such as mesitylboronic acid were cross-coupled with 2-substituted haloarenes in high yields in the presence of $\text{Pd}(\text{PPh}_3)_4$ and aqueous $\text{Ba}(\text{OH})_2$ in 1,2-dimethoxyethane. An alternative method using esters of boronic acids and K_2PO_4 in dimethylformamide was also developed for the cross-coupling reaction of arylboronic acids which were sensitive to hydrolytic deboronation with aqueous base.

Rhodium(I) Complex-Catalyzed Hydro-silylation of Dimethyl Muconates

K. YAMAMOTO and T. Tabei, *J. Organomet. Chem.*, 1992, 428, (1-2), C1-C4

Complete regioselective 1,6-hydrosilylation of dimethyl *cis, cis*-muconate occurred by using trialkylsilanes in the presence of $\text{RhCl}(\text{PPh}_3)_3$ as a catalyst. The obtained functionalised ketene silyl acetal showed moderate electrophilic properties. Hydrosilylation of *trans, cis*-muconate resulted in a mixture of adducts but not a 1,6-adduct.

Direct Formation of Formic Acid from Carbon Dioxide and Dihydrogen Using the $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]_2\text{-Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ Catalyst System

E. GRAF and W. LEITNER, *J. Chem. Soc., Chem. Commun.*, 1992, (8), 623-624

Formic acid, isolable as Na formate from the reaction mixture, was produced directly from H_2 and CO_2 using a homogeneous catalyst system formed in situ from $[\{\text{Rh}(\text{cod})\text{Cl}\}_2]$ and $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$, with yields up to 1150 moles per mole of Rh. This in situ Rh catalytic system catalyses the reversible formation of formic acid from CO_2 and H_2 very efficiently, thus giving a way of activating CO_2 and/or storing H_2 .

Specifics of Dissolution of Gaseous Formaldehyde and Paraformaldehyde in Dimethylacetamide under Conditions of Their Hydroformylation on a Rhodium Catalyst

G. A. KORNEEVA, N. N. EZHOVA, E. V. SLIVINSKII and S. M. LOKTEV, *Neftekhimiya*, 1992, 32, (1), 43–48

Studies of some dependences of dissolution of gaseous formaldehyde and depolymerisation of paraformaldehyde in N,N'-dimethylacetamide were studied in a number of solutions during hydroformylation of CH₂O to glycol aldehyde in the presence of RhCl₃·4H₂O and RhCl(PPh₃)₃ catalysts. The rate of achieving the stationary state depended on the H₂O content in the solvent and on the presence and composition of Rh complexes in the solution.

[Rh(CO)₄]⁻, [Rh₃(CO)₁₅]⁻, and Bimetallic Clusters as Catalysts for the Carbonylation of Nitrobenzene to Methyl Phenylcarbamate

F. RAGAINI, S. CENINI, A. FUMAGALLI and C. CROTTI, *J. Organomet. Chem.*, 1992, 428, (3), 401–408

Bimetallic clusters of general formula [PPN]₂[MRh₂(CO)₁₅] (M = Ru, Os or Fe; PPN⁺ = (PPh₃)₃N⁺) are active catalysts in the presence of MeOH for the carbonylation of nitrobenzene to methyl phenylcarbamate, but the addition of bipy (2,2'-bipyridine) greatly improves both rates and selectivities. The monometallic cluster [Rh₃(CO)₁₅]⁻ was more active and selective, and the monomer [Rh(CO)₄]⁻ was even better.

Hydrodechlorination of Chloroaromatics: the Use of a Bifunctional Homogeneous Rhodium Catalyst for the Conversion of Chloroaromatics into Saturated Hydrocarbons

D. T. FERRUGHELLI and I. T. HORVÁTH, *J. Chem. Soc., Chem. Commun.*, 1992, (11), 806–807

The catalytic conversion of chloroaromatics into the corresponding saturated hydrocarbons was catalysed by a bifunctional homogeneous Rh catalyst system generated from [(C₅Me₅)RhCl₂]₂ in the presence of an excess of NEt₃ under 600 psi H₂ at 75°C.

Hydroformylation of Glucal Derivatives with Rhodium Catalysts. Crucial Influence of the Auxiliary Ligand Tri(ortho-tert-butylphenyl) Phosphite

A. POLO, E. FERNANDEZ, C. CLAVER and S. CASTILLON, *J. Chem. Soc., Chem. Commun.*, 1992, (8), 639–640

A Rh catalyst mediated hydroformylation of glucal derivatives was achieved in good yields and selectivities using [Rh₂{μ-S(CH₂)₃NMe₂]₂(cycloocta-1,5-diene)₂] and tris(ortho-tert-butylphenyl) phosphite as auxiliary ligands giving 2-formyl derivatives. The stereoselectivity of the reaction was determined by the stereochemistry of the allylic substituent when the formyl group entered at C 2.

The Osmium-Catalyzed Asymmetric Dihydroxylation: A New Ligand Class and a Process Improvement

K. B. SHARPLESS, W. AMBERG, Y. L. BENNANI, G. A. CRISPINO, J. HARTUNG, K.-S. JEONG, H.-L. KWONG, K. MORIKAWA, Z.-M. WANG, D. XU and X.-L. ZHANG, *J. Org. Chem.*, 1992, 57, (10), 2768–2771

The acceleration of osmate ester hydrolysis in the presence of organic sulphonamides and the discovery of a phthalazine class of ligands have led to a simple procedure for the Os-catalysed asymmetric dihydroxylation of olefins. This procedure is applicable to a wide range of olefinic substrates, and enantiomeric excesses > 90% for the resulting diols are obtained.

Ruthenium-Catalyzed Hydration of Nitriles and Transformation of δ-Keto Nitriles to Ene-Lactams

S.-I. MURAHASHI, S. SASAO, E. SAITO and T. NAOTA, *J. Org. Chem.*, 1992, 57, (9), 2521–2523

Hydration of nitriles and transformation of δ-keto nitriles to ene-lactams were performed efficiently by using RuH₂(PPh₃)₄(1) catalyst under mild conditions. In a typical case, the reaction of benzonitrile with 2 equiv. of H₂O in 1,2-dimethoxyethane in the presence of 3 mol% of (1) at 120°C gave benzamide in 93% yield after filtration over Florisil.

FUEL CELLS

Electrode Reaction at Fixed Platinum Film—Fixation of Platinum Film on Stabilized-Zirconia Electrolyte and Its Effect on the Electrode Performance of the Solid-Electrolyte Fuel Cell

N. NAKAGAWA, C. KURODA and M. ISHIDA, *J. Chem. Eng. Jpn.*, 1992, 25, (1), 55–61

Sputtered Pt electrodes were fixed on yttria stabilised zirconia, YSZ, electrolyte by covering the electrode with a porous ceramic layer, so that the Pt film was kept stable and the resistance of the electrodes was very small. The polarisation behaviour was examined. Cathodic current increased as the Pt thickness decreased and anodic current increased as the ceramic layer thickness decreased.

CHEMICAL TECHNOLOGY

Basic Experimental Study on Palladium Membrane Reactors

N. ITOH, W.-C. XU and K. HARAYA, *J. Membrane Sci.*, 1992, 66, (2+3), 149–155

Basic experiments on Pd membrane reactors, which use catalysts of 0.5 wt.% Pt on cylindrical Al₂O₃ pellets packed inside the membrane tube, were performed to explain the mechanism of H permeation through the membrane, and to find the effect of the membrane surface on dehydrogenation using cyclohexane dehydrogenation as a model reaction.

ELECTRICAL AND ELECTRONIC ENGINEERING

Quality Dependence of Pt-*n*-GaAs Schottky Diodes on the Defects Introduced during Electron Beam Deposition of Pt

F. D. AURET, G. MYBURG, H. W. KUNERT and W. O. BARNARD, *J. Vac. Sci. Technol. B*, 1992, 10, (2), 591–595

Current-voltage measurements performed on Pt Schottky barrier diodes (SBDs) deposited with and without shielding the *n*-GaAs substrate from stray electrons during electron beam metallisation showed that the use of a shield is essential if high quality devices have to be fabricated. The exposure of the semiconductor to stray electrons during metallisation caused non-ideal SBD properties.

Ballistic Electron Emission Microscopy Study of PtSi-*n*-Si(100) Schottky Diodes

P. NIEDERMANN, L. QUATTROPANI, K. SOLT, A. D. KENT and O. FISCHER, *J. Vac. Sci. Technol. B*, 1992, 10, (2), 580–585

Studies of PtSi-*n*-Si(100) Schottky contacts performed by BEEM for PtSi layers from 30–195 Å thick showed that Schottky barrier heights on the contacts followed mainly the values from the diode I-V characteristics. The ballistic transmission rate decreased with PtSi thickness and the average hot-electron mean free path in PtSi appeared to increase with thickness.

Shallow Ohmic Contact Formation by Sequential Deposition of Pd/AuGe/Ag/Au on GaAs and Rapid Thermal Annealing

L. ZHENG, *J. Appl. Phys.*, 1992, 71, (7), 3566–71

Shallow ohmic contacts to *n*-GaAs were prepared by sequential deposition of Pd/AuGe/Ag/Au and rapid thermal annealing at 450–500°C for 30 s. The metallisation showed good electrical properties with a contact resistivity of $2 \times 10^{-6} \Omega \text{ cm}^2$. Using Pd to replace Ni in the conventional Ni/AuGe/Ni/Au structure as the first layer considerably reduced contact resistivities and gave good substrate adherence.

The Si/Pd(Si,Ge) Ohmic Contact on *n*-GaAs

L. C. WANG, Y. Z. LI, M. KAPPES, S. S. LAU, D. M. HWANG, S. A. SCHWARZ and T. SANDS, *Appl. Phys. Lett.*, 1992, 60, (24), 3016–3018

A modified Si/Pd ohmic contact to *n*-GaAs of resistivity $2 \times 10^{-6} \Omega \text{ cm}^2$, has been developed, based on the solid-phase regrowth mechanism. A 15 Å layer of Ge or Si embedded in the Pd reduces the contact resistivity to $2-4 \times 10^{-7} \Omega \text{ cm}^2$ without loss of thermal stability. The reduction in the contact resistivity is explained by formation of a *n*⁺ GaAs surface layer via solid-phase regrowth. The modified contacts show uniform surface and interface morphologies, and contact resistivity stays in the mid- $10^{-6} \Omega \text{ cm}^2$ range after annealing at 400°C.

High-Reliability Interconnections for ULSI Using Al-Si-Pd-Nb/Mo Layered Films

J. ONUKI, Y. KOBUCHI, M. SUWA, M. KOIZUMI, D. S. GARDNER, H. SUZUKI and E. MINOWA, *IEEE Trans. Electron Devices*, 1992, 39, (6), 1322–1326

A new Al-Si-0.3 wt.% Pd-0.4 wt.% Nb alloy and a bilayered interconnection using this alloy with Mo were investigated for ULSI interconnections. The electromigration lifetime of the alloy was 5 times better than that of Al-Si-0.5 wt.% Cu. When the new alloy was layered with Mo the electromigration resistance improved considerably, as compared to Al-Si-Cu layered with high-resistivity metal.

MEDICAL USES

The Dialysis Electrode—A New Method for *in vivo* Monitoring

W. J. ALBERY, M. G. BOUTELLE and P. T. GALLEY, *J. Chem. Soc., Chem. Commun.*, 1992, (12), 900–901

The continuous measurement of neurotransmitter glutamate in the brain of a freely moving rat has been measured using an *in vivo* electrode. A working electrode of Teflon coated Pt wire with 4 mm Pt exposed at the end is inserted into the tip of a probe and the electrode is surrounded by a chosen enzyme, which is introduced by slow perfusion. The probe also contains a Ag/AgCl reference electrode.

Unwinding of Supercoiled DNA by Platinum-Ethidium and Related Complexes

M. V. KECK and S. J. LIPPARD, *J. Am. Chem. Soc.*, 1992, 114, (9), 3386–3390

A gel electrophoretic mobility shift assay was used to determine the unwinding of closed circular, supercoiled pUC 19 plasmid DNA induced by a variety of Pt complexes differing in their co-ordination mode to the double helix. Compounds included are the anti-cancer drug cisplatin and several of its analogues in which the organic intercalator ethidium is co-ordinated to Pt through an exocyclic amino group, and molecules in which 2 Pt centres are tethered by a polymethylene chain.

An Electrochemical Capillary Fill Device for the Analysis of Glucose Incorporating Glucose Oxidase and Ruthenium (III) Hexamine as Mediator

N. A. MORRIS, M. F. CARDOSI, B. J. BIRCH and A. P. F. TURNER, *Electroanalysis*, 1992, 4, (1), 1–9

A method for measuring glucose based on enzymic oxidation and thin-layer bulk electrolysis using Ru(III) hexamine as mediator is described. The analysis is carried out in the electrochemical capillary fill device where sample enters the cell by capillary action and freeze-dried assay components, such as glucose oxidase, Ru(III)hexamine and buffer salts, become solubilised and disperse throughout the cell.