

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

On the Atomic Interdiffusion in Co/Pt Superlattices

X. YAN, T. EGAMI, E. E. MARINERO, R. F. C. FARROW and C. H. LEE, *J. Mater. Res.*, 1992, 7, (6), 1309–1312

XRD was performed on molecular beam epitaxially grown $\langle 111 \rangle$ and $\langle 001 \rangle$ oriented $\text{Co}(3 \text{ \AA})/\text{Pt}(18 \text{ \AA})$ superlattices, with the scattering vector Q covering a plane which included a major component perpendicular to, and a minor component parallel to the sample plane. The diffraction peaks of the superlattice had a large width parallel to the plane of the film, indicating strong in-plane disorder.

Properties of PTC Ceramics/Metal Sintered Compact

M. TAKADA, S. UMINO and K. HAYASHI, *J. Jpn. Inst. Met.*, 1992, 56, (3), 303–307

Mixtures of powders (Ba, Sr)(Ti, Sb) O_3 PTC ceramics and 0.5–11 vol.% Pt, Au or Ag powders were sintered at 1600 K for 3.6 ks in air and their properties were investigated. The specific resistivity increased at room temperature with increasing amount of metal, up to 10 vol.% for Pt, although the PTC characteristics remained for a small amount of metal. The thermal conductivity and fracture toughness were improved by ~ 1.6 and 1.9 times, respectively, by the addition of 10 vol.% Pt.

Dealloying Properties of Pt-NiCr Thin Films on Glass

C. R. WILLCOX, *Thin Solid Films*, 1992, 213, (1), 19–26
A dealloying reaction between sputter-deposited Pt and NiCr thin films on Pyrex glass was studied after annealing. Cubic Pt_3Cr and Ni_3Pt intermetallic phases emerged after annealing at 450°C, although no stability was observed at room temperature. The phases were no longer present at an anneal temperature of 700°C. There was complete dealloying of the NiCr film by the Pt, forming a tertiary alloy of Pt, Ni and Cr with an ordered f.c.t. structure.

Scaling of the Electrical Conductivity of Ultrathin Amorphous Palladium Films

Y. LIU, B. NEASE, K. A. MCGREER and A. M. GOLDMAN, *Europhys. Lett.*, 1992, 19, (5), 409–414

The temperature dependent electrical conductances of sets of ultrathin amorphous Pd films prepared by successive deposition in situ at low temperatures were found to scale over a range of conductances covering both the strongly and weakly localised regimes. The scaling parameter, which collapses the data onto a single curve, falls to zero as thickness or conductance increase. The scaling suggests a unified picture of the insulator-to-metal transition in two dimensions.

Diffusion of Pd Adatoms and Stability of Pd Overlayers on the (011) Surface of Pt

G. L. KELLOGG, *Phys. Rev. B*, 1992, 45, (24), 14354–14357

Field ion microscopy was used to examine the migration of Pd atoms and the stability of Pd overlayers on the (011) surface of Pt. Pd atoms migrated within the [011] surface channels at 207–235 K with an activation energy of 0.58 ± 0.05 eV. Cross-channel displacements are not seen. Clusters of Pd atoms on Pt(011) form stable (1 \times 1) structures at < 300 K and do not reconstruct to the “missing-row” structure. Pd adatoms deposited on top of (1 \times 1) overlayers diffused in channels at 167 K. Pd atom migration on a Pd overlayer occurs at much lower temperatures, near the centre of the plane.

Magnetic Properties of Multi-Layer Co/Pd Films

V. M. FEDOSYUK and G. V. MAKUTIN, *Fiz. Met. Metallov.*, 1992, (6), 70–74

Studies were performed of the magnetic properties of multilayer Co/Pd films of layer thickness ~ 8 –0.25 nm. There were intrinsic deposits with perpendicular magnetic anisotropy at the crystallographic surface and magnetostrictive anisotropic states. The occurrence of an induced magnetic moment on the magnetic Co/Pd layer was examined.

Permeability and Diffusivity of Hydrogen in Palladium-Rich Pd-Y(Gd)-Ag Ternary Alloys

Y. SAKAMOTO, F. L. CHEN, M. FURUKAWA and M. NOGUCHI, *J. Alloys Compd.*, 1992, 185, (2), 191–205
The permeabilities and diffusivities of H in $\text{Pd}_{100-x-y}(\text{Y}(\text{Gd}))_x\text{Ag}_y$ alloys, where $y = 0, 5, 10, 15, 20$ and 24 at.%, and x in at.% is the Y(Gd) content, fitting the condition $y + 3x = 24$, were measured as possible diffusion membranes for H purification at 523–673 K and input H pressures of 267–667 kPa. The $\text{Pd}_{95-x}(\text{Y}(\text{Ga}))_x\text{Ag}_5$ alloys with $x = 6.3$ were the most permeable to H, with permeability values a factor of 2–2.5 higher than those in Pd-24 at.% Ag alloy.

Schemes of the Phase Equilibria in the Quaternary System Palladium-Titanium-Cobalt-Nickel at 800°C

D. M. GERGAULOVA, M. V. RAEVSKAYA and A. L. TATARKINA, *Vestn. Moskov. Univ., Ser. Khim.*, 1992, 33, (3), 288–290

Studies of the system Pd-Ti-Co-Ni were performed at 800°C in the concentration range 0–25 at.% Ti. Physico-chemical interactions and structural diagrams of the phase equilibrium at 6, 10 and 25 at.% Ti were characterised.

Coherence of the Superconducting Wavefunction between the Heavy-Fermion Superconductor UPd₂Al₃ and Niobium

Y. HE, C. MUIRHEAD, A. BRADSHAW, J. S. ABELL, C. SCHANK, G. GEIBEL and F. STEGLICH, *Nature*, 1992, 357, (6375), 227-229

Quantum coherence of the superconducting wavefunction between superconductor Nb and heavy-fermion superconductor UPd₂Al₃ was demonstrated using a pointed rod of UPd₂Al₃ to bridge the gap in an almost closed Nb ring. Persistent currents in the composite ring and trapped flux, which was in discrete quantum states separated by the flux quantum $h/2e$, were observed.

Electrical and Magnetic Properties of U-X (X = Ru, Rh and Ir) Intermetallic Compounds

Y. ONUKI, S. W. YUN, I. UKON, A. KOBORI, I. UMEHARA, K. SATOH, T. FUKUHARA, H. SATO and S. TAKAYANAGI, *J. Phys. Soc. Jpn.*, 1992, 61, (5), 1751-1757

Magnetic and electrical properties of U-X intermetallic compounds, where X = Ru, Rh and Ir, were found from measuring electrical resistivity, Hall coefficient, thermoelectric power, specific heat, etc. Most U-Ru compounds, except U₃Ru₅, are Pauli-paramagnetic. U₃Ru₅ orders antiferromagnetically below 13 K. U₃Rh₅ and U₃Rh₄ are Curie-Weiss type paramagnetic compounds. URh orders ferromagnetically below 57 K, similar to UIr.

Photorefractive Properties of SBN:60 Systematically Doped with Rhodium

R. A. VAZQUEZ, R. R. NEURGAONKAR and M. D. EWBANK, *J. Opt. Soc. Am. B*, 1992, 9, (8), 1416-1427

Crystals of strontium barium niobate were grown and doped with 6 Rh concentrations from 0.015-0.2 wt.%. The results were analysed by net coupling, optimal gain conditions, etc. An effective coupling coefficient of almost 14/cm was observed in the 0.2 wt.% Rh doped sample for polarisation independent contradictory coupling. Two-beam coupling was enhanced by Rh doping throughout the visible spectrum.

CHEMICAL COMPOUNDS

Reversible Carbon Monoxide Addition to Sol-Gel Derived Composite Films Containing a Cationic Rhodium(I) Complex: Toward the Development of a New Class of Molecule-Based CO Sensors

J. I. DULEBOHN, S. C. HAEFNER, K. A. BERGLUND and K. R. DUNBAR, *Chem. Mater.*, 1992, 4, (3), 506-508

Synthesis and CO binding properties of Zr₂O₃ and TiO₂ glasses impregnated with a Rh ether-phosphine compound are reported. The complex [Rh(TMPP)₂(CO)]⁺ (TMPP = tris(2,4,6-trimethoxyphenyl)phosphine) reversibly bound CO within a glassy polymer matrix to form the dicarbonyl species [Rh(TMPP)₂(CO)₂]⁺.

Cs₄[IrO₄], a New Iridate with Planar Anion [IrO₄]⁴⁻

K. MADER and R. HOPPE, *Z. Anorg. Allg. Chem.*, 1992, 614, (8), 30-34

Structure studies of black single crystals of Cs₄[IrO₄] obtained by heating mixtures of CsO_{0.52} and IrO₂ at a molar ratio Cs:Ir = 4.30:1.00 at 740°C showed them to be monoclinic with a K₄[IrO₄]-type structure. The structure was determined by four circle diffractometer data.

Preparation and Crystal Structure of the Actinoid Ruthenium Phosphides ThRu₂P₂ and URu₂P₂

R. GLAUM, J. H. ALBERING, W. JEITSCHKO and L. BOONK, *J. Alloys Compd.*, 1992, 185, (2), 301-309

New compounds ThRu₂P₂ and URu₂P₂ were prepared by the reaction between the powders of elemental Th with RuP and a U-Ru alloy with elemental P, respectively, in a Sn flux. The compounds crystallised in the orthorhombic space group Pnma with the structure of both showing a tendency for higher co-ordination typical of intermetallic phases. The structures of ThRu₂P₂ and URu₂P₂ are discussed with other related compositions.

ELECTROCHEMISTRY

Oxidation of Formic Acid at Pt Bonded SPE Membrane Electrode

K. FUJIKAWA and K. TAKEYA, *Denki Kagaku*, 1992, 60, (6), 557-559

A solid polymer electrolyte (SPE) membrane electrode carrying Pt was studied for HCOOH vapour oxidation in a gas diffusion type cell. Reactant HCOOH vapour + Ar carrier gas was supplied to the Pt side of the electrode, while the SPE side was in contact with H₂ saturated 1M HClO₄ solution. Potential sweeps of 20 mV/s at 20°C were performed, and compared to those of CO oxidation on the same electrode. Current density at 0.9 V is larger by one or two orders at the Pt-SPE than at a Pt plate electrode, giving a current < a few mA/cm². A wide hysteresis loop is observed over the 0.25-1 V potential range, which is a broader range than for the Pt plate.

Study of Methanol Electrooxidation on Rh-Sn Oxide, Pt-Sn Oxide, and Ir-Sn Oxide in Comparison with that on the Pt Metals

A. ARAMATA, I. TOYOSHIMA and M. ENYO, *Electrochim. Acta*, 1992, 37, (8), 1317-1320

The catalytic activities of oxides of Rh-Sn, Ir-Sn and Pt-Sn were studied for the Sn oxide effect in comparison to those of the Pt metals and to each other. Sn oxide enhanced the catalytic activity of Pt-Sn oxide for MeOH electrooxidation with respect to Pt in acidic, but not alkaline solutions. Sn oxide had negative activity effect in Rh-Sn oxide and no effect in Ir-Sn oxide, with respect to Rh and Ir, respectively. This was linked to the presence or absence of redox coupling of the respective Pt group metal species.

Methanol Oxidation on Platinum-Tin Catalysts Dispersed on Poly(3-methyl)thiophene Conducting Polymer

S. SWATHIRAJAN and Y. M. MIKHAIL, *J. Electrochem. Soc.*, 1992, **139**, (8), 2105–2110

Studies of the effect of catalyst support and Pt loading on the electrochemical oxidation of MeOH were performed on Pt-Sn catalysts prepared by electrodeposition on poly(3-methyl)thiophene. Pt-Sn catalyst deposited in the H adsorption potential region showed an order of magnitude increase in surface area. The thickness and distribution of the catalyst layer in the conducting polymer support were estimated by Rutherford backscattering spectrometry. H oxidation was observed at Pt loadings as low as $20 \mu\text{g}/\text{cm}^2$.

Diffusion Rate of Deuterium in Pd during Cathodic Charging

T. MIZUNO, T. AKIMOTO, K. AZUMI and M. ENYO, *Denki Kagaku*, 1992, **60**, (5), 405–411

The absorption and release rates of D into or from Pd were measured during electrolysis in a closed cell. The difference in diffusion constants of the two states of D in Pd which were deduced from the diffusion behaviour, was two orders of magnitude — 10^{-6} and $10^{-8} \text{ cm}^2/\text{s}$, respectively, at room temperature.

Anodic Oxidation of Formic Acid at Nafion-Modified Palladium Electrocatalysts

M. MORITA, H. KIJIMA and Y. MATSUDA, *Denki Kagaku*, 1992, **60**, (6), 554–556

Results on the improved activities of Pd electrocatalysts deposited by RF sputtering on a Nafion-coated glassy C surface are reported for the anodic oxidation of HCOOH. Maximum electrode activity occurred for a 20 s sputtering time, which should give island-like Pd deposition. Larger amounts of Pd decreased the activity. The acidic properties of the thin Nafion film could contribute to the high activity of Pd/Nafion/GC. The Nafion coating was effective for both improved activity at $\leq 0.15 \text{ V}$ and suppressing the degradation of activity at $> 0.15 \text{ V}$.

Hydrogen and Oxygen Evolutions on Ru-Ir Binary Oxides

T.-C. WEN and C.-C. HU, *J. Electrochem. Soc.*, 1992, **139**, (8), 2158–2163

The electrocatalytic activities of Ir(Ru) mol% coating solutions on mixed Ru-Ir oxide electrodes, were compared for H_2 and O_2 evolution from 1N H_2SO_4 and 1N NaOH solutions. Maximum activity resulted from a coating solution with 60–80 mol% Ir. Pure RuO_2 coated electrode had a polycrystalline structure; its activity was worst for O_2 evolution in alkaline solutions, while its electrochemical behaviour for H_2 evolution was the same for acidic and basic solutions. The redox transition Ir(IV)/Ir(V) of the pure IrO_2 coated electrode strongly depended on pH; the rate determining step depended on current density (cd): at low cd H_2 desorption predominated, while at high cd H_2 adsorption predominated.

Water Oxidation at Polycrystalline OsX_2 Electrodes

T. SCHWARZLOSE, S. FIECHTER and W. JAEGERMANN, *Ber. Bunsenges. Phys. Chem.*, 1992, **96**, (7), 887–893
Polycrystalline OsX_2 powders, where X = S, Se or Te, have been synthesised, made into pressed electrode disks and electrochemically investigated for the oxidation of H_2O . OsS_2 was identified as O_2 evolution catalyst, whereas OsTe_2 was completely decomposed. The difference in catalytic behaviour is related to differences in the X-ray photoelectron valence band spectra and is discussed in terms of electronic states involved in charge transfer.

Electrochemical Reduction of Carbon Dioxide in Water: Analysis of Reaction Mechanism on Ruthenium-Titanium-Oxide

A. BANDI and H.-M. KÜHNE, *J. Electrochem. Soc.*, 1992, **139**, (6), 1605–1610

The kinetics of H_2 formation and CO_2 reduction were studied on mixed $\text{TiO}_2/\text{RuO}_2$ rotating disk electrodes prepared by thermal decomposition of the halides on Ti sheets. Current-voltage curves at pH = 4–7 showed a current-limiting behaviour at small overpotentials for H_2 evolution. The current efficiency for CO_2 reduction reaches a maximum under current-limiting conditions for H ion reduction, before a steep onset in H_2 evolution takes place, due to water reduction.

PHOTOCONVERSION

Solid State Photochemistry of $(\text{C}_8\text{H}_{12})\text{Pt}(\text{N}_3)_2$ as Thin Films on Si(111) Surfaces

D. G. BICKLEY, R. H. HILL and C. I. HORVATH, *J. Photochem. Photobiol. A: Chem.*, 1992, **67**, (2), 181–186

The solid state photochemistry of $(\text{COD})\text{Pt}(\text{N}_3)_2$ (1), where COD is 1,5-cyclooctadiene, has been investigated after deposition as a film on a Si(111) surface. Photolysis of a thin film of (1) initially lead to loss of a single azide radical and the formation of $(\text{COD})\text{Pt}(\text{N}_3)$; further photolysis lead to the loss of the remaining ligands. The final films were identified as 115 nm thick Pt films, with good adherence to the SiO_2 substrate.

Photocatalysis of Metal Clusters in Cages: Effective Photoactivation of the Water Gas Shift Reaction Catalysed on NaY Zeolite-Entrapped Pt_{12} and Pt, Carbonyl Clusters

R.-J. WANG, T. FUJIMOTO, T. SHIDO and M. ICHIKAWA, *J. Chem. Soc., Chem. Commun.*, 1992, (13), 962–963

Pt carbonyl clusters $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ ($n = 3, 4$) in NaY zeolite pores were catalytically active for the H_2O gas shift reaction at low temperatures, and were effective photocatalysts for this reaction with a large enhancement (~38 times) at 293 K, under Xe lamp illumination, compared to the dark reaction. The photoexcited Pt_{12} carbonyl anions may enhance H_2O oxidation to form an active intermediate “COOH” by nucleophilic attack of OH on the cluster carbonyls.

Palladium Catalysis of O₂ Reduction by Electrons Accumulated on TiO₂ Particles during Photoassisted Oxidation of Organic Compounds

C.-M. WANG, A. HELLER and H. GERISCHER, *J. Am. Chem. Soc.*, 1992, 114, (13), 5230-5234

Electrons accumulated on slurred TiO₂ particles during photoassisted oxidation of 1.6 M aqueous MeOH, and persisted there, for at least 1 min, even in O₂-saturated solutions. Incorporating Pd⁰ in the TiO₂ particles surface increased the quantum efficiency of the photoassisted oxidation of 10⁻² M aqueous 2,2-dichloropropionate 3 fold at 0.01 wt.% Pd and 7 fold at 2 wt.% Pd.

Ligand Macrocycle Effects on the Photophysical Properties of Rhodium(III) Complexes. A Detailed Investigation of *cis*- and *trans*-Dicyano(1,4,8,11-tetraazacyclotetradecane) rhodium(III) and Related Species

L. J. McCURE and P. C. FORD, *J. Phys. Chem.*, 1992, 96, (16), 6640-6650

Photophysical properties for the dicyano tetraaza-macrocycle Rh(III) complexes *trans*- and *cis*-Rh([14]aneN₄)(CN)₂⁺ and *trans*-Rh([15]aneN₄)(CN)₂⁺ (I, IV and II, respectively, [14]aneN₄ = 1,4,8,11-tetraazacyclotetradecane, [15]aneN₄ = 1,4,8,12-tetraazacyclopentadecane) and related compounds are described. I and II luminesced strongly in ambient temperature aqueous solutions, but (I) had an order of magnitude longer life.

Photochemical Behavior of Chlorocarbonylbis(triphenylphosphine)rhodium(I), ClRh(CO)P₂(P = PPh₃). Laser Flash Photolysis with Infrared Detection

S. OISHI and T. KAWASHIMA, *Chem. Lett. Jpn.*, 1992, (5), 747-750

Laser flash photolysis of ClRh(CO)P₂ with IR detection showed that CO was photoeliminated, rather than P. The generated ClRhP₂ reacted with the remaining ClRh(CO)P₂ to give a transient binuclear Rh carbonyl, which regenerated ClRh(CO)P₂ via the reaction with CO.

A Novel Photo-Induced Patterned Film Formation of Organic Pigments Using Tris(2,2'-bipyridine)ruthenium(II) and Surfactant with Ferrocenyl Moiety

H. MIZUNO, K. HOSHINO, J.-I. HANNA and H. KOKADO, *Chem. Lett. Jpn.*, 1992, (7), 751-754

When an acidic aqueous dispersion of an organic pigment containing a ferrocene attached surfactant, a Ru(bpy)₃²⁺ photocatalyst and a sacrificial agent, was illuminated at 450 nm through a masked In-Ti oxide-coated glass plate pigment layers were deposited onto unilluminated, but not illuminated, areas of the substrate. By this method, H₂Pc pigments (Pc = phthalocyanine) and other pigments: Cu phthalocyanines, halogenated Cu phthalocyanine (Pc Green) and perylene derivatives, were used for clear-cut patterns.

ELECTRODEPOSITION AND SURFACE COATINGS

Deposition and Characterization of Thin Electroless Palladium Films from Newly Developed Baths

M. L. CHOU, N. MANNING and H. CHEN, *Thin Solid Films*, 213, (1), 64-71

Pd films ~100 nm thick were deposited on activated hydrogenated amorphous Si by electroless deposition from hypophosphite based Pd-ammine baths. The baths were stable at 35-50°C operating temperatures. Active Pd aggregates have small irregularly shaped grains whose density and distribution depended on immersion time and substrate type. Higher coverage uniform, crack-free Pd films were obtained from NH₃-NH₄Cl, EDTA and TEA baths than from citrate baths.

Laser-Assisted Organometallic Chemical Vapor Deposition of Films of Rhodium and Iridium

J. S. COHAN, H. YUAN, R. S. WILLIAMS and J. I. ZINK, *Appl. Phys. Lett.*, 1992, 60, (11), 1402-1403

High purity Rh and Ir thin films with no C contamination detectable by XPS were deposited by UV irradiation of (η³-C₅H₅)₂M(C₂H₄)₂ (M is Rh or Ir) organic precursor in the presence of H₂. Wavelength dependence studies of the Rh compound precursor showed that only irradiation into the charge transfer band of the compound caused deposition.

APPARATUS AND TECHNIQUE

Amperometric Needle-Type Glucose Sensor Based on a Modified Platinum Electrode with Diminished Response to Interfering Materials

C.-Y. CHEN, M. GOTOH, H. MAKINO, Y.-C. SU, E. TAMIYA and I. KARUBE, *Anal. Chim. Acta*, 1992, 265, 5-14

A needle type glucose sensor for determining glucose in serum and whole blood samples, using Pt wire as the working electrode and a disposable hypodermic stainless-steel needle electroplated with Pt as the counter and reference electrode, was developed. The enzyme was immobilised by cross-linking with glutaraldehyde and photocross-linking of PVA-SbQ₂ (a poly(vinyl alcohol)), and the sensor showed good response, stability and reproducibility.

Development of SnO₂-Based Ethanol Gas Sensor

T. MAEKAWA, J. TAMAKI, N. MIURA, N. TAMAZOE and S. MATSUSHIMA, *Sens. Actuators B*, 1992, 9, (1), 63-69

The sensitivity and selectivity of SnO₂-based elements to EtOH vapour of 1000 ppm in air at 300°C were significantly improved by adding several basic oxides and then by loading the elements with Pt or Pd metals. The doubly promoted elements Pd(0.5 wt.%)-La₂O₃(5 wt.%)-SnO₂ and Pt(0.5 wt.%)-La₂O₃-SnO₂ showed excellent sensing properties to EtOH vapour in the range 100-1000 ppm at 300°C.

Applicability of Discontinuous Palladium Films as Strain Gauges

A. G. BISHAY, D. A. ABDELHADY and A. M. DARWISH, *J. Mater. Sci., Mater. Electron.*, 1992, 3, (3), 195–199

Discontinuous Pd films were prepared by evaporation and sublimation on glass substrates. The variation in DC resistance of the films with time was investigated in air at room temperature. Sublimed films had better stability than evaporated films. The piezoresistance of the discontinuous Pd films was measured at different strains and the gauge factor, ν , was deduced. Sublimed films had higher ν than evaporated films.

HETEROGENEOUS CATALYSIS

Catalytic Synthesis of C-Alkylimidazoles in the Presence of Pt/Al₂O₃ Catalysts

K. M. GITIS, G. E. NEUMOEVA, N. I. RAEVSKAYA, G. A. ARUTYUNYANTS and G. V. ISAGULYANTS, *Izv. Akad. Nauk Rossii, Ser. Khim.*, 1992, (4), 932–940

Studies of the synthesis of C-alkylimidazoles from 1,2-diamines and carboxylic acids in the presence of bifunctional Pt/Al₂O₃ showed a good yield of 2-alkyl- and 2,4-dialkylimidazoles, including those with long chain alkyls. The effect of the reaction temperature, space velocity of feed and H dilution on the yield of 2-methylimidazole was studied. The stability of Pt/Al₂O₃ in the reaction cycles with intermediate oxidative regeneration was studied.

The Influence of Pretreatment at Different Temperatures on the Surface Structure and Performance of Pt/Al₂O₃

Z. RUAN and Q. GAO, *J. Fuel Chem. Technol.*, 1992, 20, (2), 219–224

The effects on activity and selectivity of pretreatments at different temperatures in H₂ and N₂ and of thiophene poisoning, were examined on Pt/Al₂O₃ catalysts for reactions of C₆ alkanes with H₂. For high temperature treatment in H₂ the Pt particle sizes were unchanged, the surface atom ratios: Pt:Al, O:Al and C:Al were only slightly changed but hydrogenolysis of *n*-C₆ was drastically decreased. This decrease in activity also occurred after treatment at high temperature in N₂. For prepoisoning with thiophene the activity for *n*-C₆ was rapidly reduced.

Study of New Reforming Catalyst. Aromatization of C₆-C₈ Alkanes over Pt/BaKL Zeolite

J. DONG, C. JIN and Q. XU, *J. Fuel Chem. Technol.*, 1992, 20, (2), 124–130

The aromatisation performance of Pt/BaKL zeolite was studied in a continuous flow microreactor using C₆-C₈ alkanes as reactants. Pt particle size distribution on zeolite and the role of Pt were studied. Selectivity to aromatics of 90–95% was achieved at 95% conversion of *n*-C₆ over Pt/BaKL. Small amounts of cracking and isomerisation products were formed. Pt zeolite also acted as a mono-functional catalyst.

Kinetics of Reduction of Np(V) to Np(IV) by Platinum Black as Reduction Catalyst

T. NAKAMURA, M. TAKAHASHI, T. FUKASAWA and M. UTA-MURA, *J. Nucl. Sci. Technol.*, 1992, 29, (4), 393–395

The kinetics and mechanism of the reduction of Np(V) to Np(IV) by Pt black catalyst were studied to see if extraction of Np from high level radioactive liquid waste from spent fuel reprocessing was possible. Tests using HNO₃ solution containing hydroxylammonium (HA) nitrate with added Pt black and Np solution found that reduction of Np(V) did not occur without HA. Reduction of Np(V) by Pt group metals catalysts occurred without heat. The insoluble residue of spent fuel could act as catalyst since its main components are Pt group metals.

IR-Spectra of Catalysts and Adsorbed Molecules. Part 39. Acidic and Catalytic Properties of Pentasil Modified with Pt, Cr and Zn

L. I. LAFER, ZH. L. DYKH, T. V. VASINA, A. V. PREOBRAZHENSKII, O. V. BRAGIN and V. I. YAKERSON, *Izv. Akad. Nauk Rossii, Ser. Khim.*, 1992, (5), 1038–1042

Incorporating Pt into pentasil catalysts increased the concentration of L-centres by ~ twice without changing the number of B-centres. There was a maximum in B-centre concentration at 0.72 wt.% Cr in Pt-Cr catalysts. The B-centre concentration decreased in catalysts simultaneously promoted with Pt, Cr and Zn, while the L-centre concentration increased.

Regioselective Hydrogenation of Unsaturated Compounds Using Platinum-Zeolite Coupled with Organosilicon Alkoxide by CVD Method

H. KUNO, M. SHIBAGAKI, K. TAKAHASHI, I. HONDA and H. MATSUSHITA, *Bull. Chem. Soc. Jpn.*, 1992, 65, (5), 1240–1243

Regioselective hydrogenation of unsaturated compounds was performed by a Pt/zeolite catalyst coupled to an organosilicon alkoxide prepared by a CVD method. When a mixture of 1-nonene (1) and *trans*-4-nonene (2) was hydrogenated by this catalyst, the reaction rate of (1) was much greater than that of (2). Excellent selectivity was obtained when diphenyldiethoxysilane was the coupling reagent on the Pt/zeolite.

Catalytic Oxidation of Methane over Palladium Supported on Alumina. Influence of the Oxygen-to-Methane Ratio

N. MOUADDIB, C. FEUMI-JANTOU, E. GARBOWSKI and M. PRIMET, *Appl. Catal. A: Gen.*, 1992, 87, (1), 129–144

The oxidation of CH₄ over a Pd/Al₂O₃ catalyst was studied for O₂:CH₄ ratios of 4–0.66. After ageing under a mixture of the reactants at 600°C, an increase in catalytic activity was observed, independent of the O₂:CH₄ ratio, while the reaction selectivity depended on it. In O₂-deficient mixtures, the formation of CO was observed at conversion levels corresponding to the total O₂ consumed. Pd/Al₂O₃ was active in CH₄ steam reforming at moderate temperature.

Characteristics of Carbon-Supported Palladium Catalysts for Liquid-Phase Hydrogenation of Nitroaromatics

D. J. SUH, T.-J. PARK and S.-K. IHM, *Ind. Eng. Chem. Res.*, 1992, 31, (8), 1849–1856

The support and preparation of Pd/C catalysts were examined for dispersion, metal distribution and activity effects during liquid-phase hydrogenation of dinitrotoluene. Oxidation of the C support increased the number of surface O groups and enhanced Pd dispersion, but catalytic activity did not improve in proportion. In C-metal salt slurry, nuclei formation and growth by ion exchange and/or reduction were most important in determining the final state of catalysts prepared by alkali hydrolysis. Catalyst activity depended on metal location.

Metal-Support Interaction in Pd/CeO₂ Catalysts: Fourier-Transform Infrared Studies of the Effects of the Reduction Temperature and Metal Loading. Part I. Catalysts Prepared by the Microemulsion Technique

C. BINET, A. JADI, J.-C. LAVALLEY and M. BOUTONNET-KIZLING, *J. Chem. Soc., Faraday Trans.*, 1992, 88, (14), 2079–2084

A study of the effect of temperature of reduction by H₂ on Pd/CeO₂ catalysts on the accessibility of the Pd to CO adsorption showed that no adsorption occurred when the reduction temperature was > 673 K. The behaviour of catalysts with crystallites of the same morphology, was independent of Pd loading. The CO adsorbed could be completely recovered after oxidising the catalysts at 723 K followed by H₂ reduction at 423 K.

Catalytic Hydrodechlorination of 1,2-Dichloroethane and Trichloroethylene over Rh/SiO₂ Catalysts

J. W. BOZZELLI, Y.-M. CHEN and S. S. C. CHUANG, *Chem. Eng. Commun.*, 1992, 115, 1–11

Reactions of H₂ with 1,2-dichloroethane (1) and trichloroethylene (2) over Rh/SiO₂ catalysts at 365–553 K and 0.1 MPa produced HCl and C₂H₆. Selectivity for C₂H₆ increases with increasing temperature. Minor products are: C₂H₄, Cl for (1) and partially dechlorinated hydrocarbons for (2).

Novel Catalysts on Carbon Support Exhibiting Activity in Gas-Phase Ammonia Synthesis in the Absence of Specially Added Promoter

V. B. SHUR, S. M. YUNUSOV, V. K. PURI, H. MAHAPATRA, B. SEN, D. K. MUKERJEE, E. S. KALYUZHNYAYA, I. A. FOKINA, V. A. LIKHOLOBOV and M. E. VOL'PIN, *Izv. Akad. Nauk Rossii, Ser. Khim.*, 1992, (6), 1452–1453

Deposition of K₂[Ru₄(CO)₁₃] on the graphite-like "Sibunit" produced a system which catalysed gas-phase NH₃ synthesis at ≥ 250°C and atmospheric pressure without a promoter. The fastest synthesis was obtained at 350°C when the stationary NH₃ concentration in the gas stream reached ~77% relative to equilibrium value at 350°C and 90% at 400°C.

HOMOGENEOUS CATALYSIS

C-H Activation in Aqueous Medium. The Diverse Roles of Platinum(II) and Metallic Platinum in the Catalytic and Stoichiometric Oxidative Functionalization of Organic Substrates Including Alkanes

A. SEN, M. LIN, L.-C. KAO and A. C. HUTSON, *J. Am. Chem. Soc.*, 1992, 114, (16), 6385–6392

Studies of the oxidation of ethers, alcohols, esters and light alkanes by K₂PtCl₄ and Pt/O₂ in aqueous medium showed that unactivated C-H bonds were attacked and oxidised by Pt(II), whereas C-H bonds α to an O were activated and catalytically oxidised by metallic Pt in the presence of O₂. For example, Pt(II) oxidised ethane selectively to EtOH and ethylene glycol. In the presence of metallic Pt and O₂, further oxidation of the alcohol functionality occurred to generate the corresponding carboxylic acids.

Novel Synthesis of Indoles via Palladium-Catalyzed Reductive N-Heterocyclization of o-Nitrostyrene Derivatives

M. AKAZOME, T. KONDO and Y. WATANABE, *Chem. Lett. Jpn.*, 1992, (5), 769–772

Indole derivatives were prepared from the reductive N-heterocyclisation of o-nitrostyrene derivatives in the presence of a catalytic amount of PdCl₂(PPh₃)₂-SnCl₂ under a CO pressure of 20 kg/cm² at 100°C for 16 h. P ligands, such as triphenylphosphine and tributylphosphine, were also necessary for high catalytic activity. When o-nitrostilbene was used in the reaction, 2-phenylindole was formed in 75% yield.

Palladium-Catalyzed Formate-Nitrobenzene-Carbon Monoxide Reaction: Formation of Carbamate Ester

I. J. B. LIN and C.-S. CHANG, *J. Mol. Catal.*, 1992, 73, (2), 167–171

The catalyst PdCl₂(PPh₃)₂ together with OP(*n*-Bu)₃ and KBr, promoted the reaction of formate ester with nitrobenzene under CO pressure to produce good yields of *N*-phenylcarbamate. This new reaction did not involve the formation of aniline before the carbamate ester formation.

A New Synthesis of Trimethyl Aconitate by Palladium-Catalysed Triple Carbonylation of Propynyl Alcohol

B. GABRIELE, M. COSTA, G. SALERNO and G. P. CHIUSOLI, *J. Chem. Soc., Chem. Commun.*, 1992, (14), 1007–1008

Studies of a two-step Pd catalysed carbonylation consisting of an oxidative carbonylation of propynyl alcohol, followed by a substitutive carbonylation showed high yields of E and Z aconitic trimethyl esters. The first step occurred in MeOH at 20°C, 1.5 MPa of CO and 0.5 MPa of air under the catalytic action of Pd₂+KI or Pd/C+KI systems. The second step was catalysed by the ionic [Pd(thiourea)₄]I₂ complex at 40°C and 6.00 MPa of CO.

Palladium-Catalyzed Vinylation of Aryl Chlorides. Chelate Effect in Catalysis

Y. BEN-DAVID, M. PORTNOY, M. GOZIN and D. MILSTEIN, *Organometallics*, 1992, 11, (6), 1995–1996

A synthetically useful direct vinylation of aryl chloride, using Pd(OAc)₂ catalyst, was performed with the dippb ligand (dippb = 1,4-bis-(diisopropylphosphino)butane), which is specific for vinylation. This gives a reaction which tolerates various substituents and generally gives high yields.

Hydroformylation and Isomerization of Hex-1-ene Catalyzed by [Rh(acac)(CO)(PPh₃)]: Effect of Modifying Ligands

E. MIECZYNSKA, A. M. TRZECIAK and J. J. ZIÓLKOWSKI, *J. Mol. Catal.*, 1992, 73, (1), 1–8

Hex-1-ene hydroformylation performed in the presence of [Rh(acac)(CO)(PPh₃)] catalyst at 1 MPa and 353 K yielded 68% hex-2-ene and 20% aldehydes. IR studies showed the presence of [Rh₄(CO)₁₂] and [Rh₆(CO)₁₆] carbonyls in the post-reaction mixture which, when used as catalysts, yielded 70–90% hex-2-ene. Free triphenylphosphine increased the aldehyde yield to 80%.

Molecular Size Control of Rhodium Carbonyl Clusters Using Polystyrenes and Their Catalyst Function

K. KANEDA, K. FUJITA and T. IMANAKA, *Kagaku Kogaku Ronbunshu*, 1992, 18, (3), 338–345

The reaction of Ru₆(CO)₁₆ with aminated polymers, (prepared from chloromethylated PS with hydroxyl and ether functions), at 40°C under 6 atm of CO gave Rh₆ cluster anions, while a Rh₁₄ species was formed in the polymers at 100°C under 1 atm of CO. Treating the Rh₆ species with KOH gave Rh₇ species. Polymer-bound Rh₆ complexes were catalytically active for olefin hydroxymethylation. The Rh₁₄ species catalysed the deoxygenation of nitrobenzene to aniline by the water gas shift reaction.

Ruthenium-Catalysed Transfer Hydrogenation of Imines by Propan-2-ol

G.-Z. WANG and J.-E. BÄCKVALL, *J. Chem. Soc., Chem. Commun.*, 1992, (14), 980–982

Imines were readily transfer hydrogenated by propan-2-ol under mild reaction conditions in the presence of a catalytic amount of RuCl₂(PPh₃)₃ and base. The reactions were carried out in 15 ml propan-2-ol with a substrate:catalyst ratio of 200:1, using 13.8 mg of K₂CO₃ as base.

Ruthenium Catalysts of Liquid-Phase Hydrocracking of *n*-Alkanes

I. S. AKHREM, S. Z. BERNADYUK and M. E. VOL'PIN, *Izv. Akad. Nauk Rossii, Ser. Khim.*, 1992, (5), 1211–1213
Ru catalysts of higher activity than Ru powder were prepared by decomposition at 180–200°C of Ru₂(CO)₁₂, Ru₃(CO)₁₂ + *t*-Bu₂AlH at 5 MPa H₂ pressure and of (benzene)(cyclohexadiene-1,3)Ru at 20°C and 0.1 MPa H₂ pressure in the presence of alkanes.

Highly Active Coal Liquefaction Catalyst: Soluble Ruthenium Complexes as Catalyst Precursors

T. SUZUKI, H. YAMADA, K. YUNOKI and H. YAMAGUCHI, *Energy Fuels*, 1992, 6, (4), 352–356

Ru complexes: Ru₃(CO)₁₂, Ru(cyclooctadiene)(cyclooctatriene) and Ru(acetylacetonate) were examined as catalyst precursors for coal hydro-liquefaction in non-H donor solvent 1-methylnaphthalene. For Australian Yallourn brown coal, adding 0.02 wt.% Ru catalyst, gave 89.3% coal conversion and 45.9% oil yield, but with 0.07 wt.% Ru coal conversion was 96.5% and oil yield 57.8% at 673 K, under initial H pressure of 5.0 MPa. At 623 K the oil fraction dropped to 19.2% with 85.6% coal conversion.

Homogeneous Catalysis: A Ruthenium-Based Lewis-Acid Catalyst for the Diels-Alder Reaction

W. ODENKIRK, A. L. RHEINGOLD and B. BOSNICH, *J. Am. Chem. Soc.*, 1992, 114, (16), 6392–6398

A Ru based catalyst *trans*-[Ru(salen)(NO)(H₂O)]SbF₆, where salen is the *N,N'*-bis(salicylidene)ethylenediamine dianion ligand was used for the Diels-Alder reaction. At 1 mol.% loading, the catalyst accelerated the reaction by many orders of magnitude, often > 10⁵ over the corresponding thermal reaction. The binding of the Diels-Alder adduct of methacrolein and isoprene with the catalyst was also examined. Binding of the dienophile was stronger than that of the adduct.

FUEL CELLS

The Role of Hydrated Oxide Species on Platinum Electrocatalysts in the Methanol/Air Fuel Cell

L. D. BURKE and J. K. CASEY, *Electrochim. Acta*, 1992, 37, (10), 1817–1829

Thick deposits of incipient hydrated oxide species can be readily produced on Pt electrodes, in 3.0 M H₂SO₄ at 60°C, typical MeOH/air fuel cell conditions, by multicycling the electrode potential between suitable limits.

Influence of Electrode Properties on Water Management in a Solid Polymer Electrolyte Fuel Cell

P. STAITI, Z. POLTARZEWSKI, V. ALDERUCCI, G. MAGGIO, N. GIORDANO and A. FASULO, *J. Appl. Electrochem.*, 1992, 22, (7), 663–667

Water transport in a SPEFC having dual-layer electrodes with 0.5 mg/cm² Pt and 40% w/w PTFE as the catalyst layer, was regulated by varying the amount of hydrophobic polyfluoroethylenepropylene in the gas diffusion layer of the anode or by using C paper or C cloth substrates. C paper electrodes had low water transport giving higher ionic resistance, but C cloth electrodes performed better, due to greater H₂O penetration, not hindering the gas flow.

CHEMICAL TECHNOLOGY

Measurement of Diffusive and Surface Transport Resistances for Deuterium in Palladium-Coated Zirconium Membranes

R. E. BUXBAUM and P. C. HSU, *J. Nucl. Mater.*, 1992, 189, (2), 183–192

A Zr membrane with 2 μm Pd coating electrolessly plated on both sides, was tested for D through transport at 600–700 K and upstream D pressures of $2.7 \cdot 10^{-2}$ – $6.7 \cdot 10^{-4}$ Pa. At very low pressures, transport is limited by molecular adsorption on the Pd surface, whereas at higher upstream pressures Zr permeability limits transport.

A Membrane Reactor with Two Dispersion-Free Interfaces for Homogeneous Catalytic Reactions

S. CHEN, H. FAN and Y.-K. KAO, *Chem. Eng. J.*, 1992, 49, (1), 35–43

A two-bundle polypropylene hollow fibre membrane reactor, operating as a single-bundle and as a two-bundle membrane reactor, was used to study the use of multiple-membrane-bundle reactors for homogeneous catalysis, for example, in direct oxidation of ethylene to acetaldehyde in aqueous PdCl_2 - CuCl_2 solution. The two-bundle membrane reactor achieved higher conversions than a comparable single-bundle membrane reactor.

GLASS TECHNOLOGY

Processing of Bi-Sr-Ca-Cu-O Glasses Using Platinum and Alumina Crucibles

T. G. HOLESINGER, D. J. MILLER, S. FLESHLER and L. S. CHUMBLEY, *J. Mater. Res.*, 1992, 7, (8), 2035–2039

Reactions with Pt and Al_2O_3 crucibles were studied during preparation of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ “2212” glasses. With Al_2O_3 the glasses were completely homogeneous, free of secondary phases, but contained 2.26% Al in solution. After heat treatment, SrCaAlO_y particles formed mostly along grain boundaries of the 2212 superconducting phase. Contamination with Pt was < 0.02 at.%, and no Pt-containing secondary phases were found in samples.

ELECTRICAL AND ELECTRONIC ENGINEERING

Influence of the Electron Beam Evaporation Rate of Pt and the Semiconductor Carrier Density on the Characteristics of Pt/*n*-GaAs Schottky Contacts

G. MYBURG and F. D. AURET, *J. Appl. Phys.*, 1992, 71, (12), 6172–6176

Schottky barrier diodes (SBDs) were prepared on epitaxially grown *n*-GaAs substrates with different free carrier densities by e-beam evaporation of Pt. I/V measurements on Pt SBDs deposits with and without shielding the substrate from stray electrons during metallisation showed that shielding was essential for high quality devices.

Infrared Photoemission of Holes from Ultrathin (3–20 nm) Pt/Ir-Compound Silicide Films into Silicon

A. CZERNIK, H. PALM, W. CABANSKI, M. SCHULZ and U. SUCKOW, *Appl. Phys. A*, 1992, 55, (2), 180–191

The photoemissions of Schottky barrier IR detectors fabricated on PtSi, IrSi and compound silicide films were characterised at low temperatures, and compared to a Monte Carlo modelling of the emission process. The films are 3–20 nm thick and act as an electrode on *p*-type Si. The total yield for internal hole photoemission is 1% per incident photon for PtSi and 0.1% for IrSi at a wavelength of 4 μm . The cut-off wavelengths are 5.4 and 8.2 μm for PtSi and IrSi, respectively. The thinnest PtSi film (3.0 nm) had the greatest responsivity observed.

Investigation of Ruthenium Schottky Contacts to *n*-GaAs

K. PRASAD, *Appl. Phys. A*, 1992, 54, (6), 493–496

Ru evaporated onto *n*-GaAs to form Schottky contacts produced near ideal behaviour, with low current leakage and good stability on thermal ageing at $\leq 300^\circ\text{C}$. However, on ageing at $> 400^\circ\text{C}$ the diode rapidly deteriorates. A room temperature operating life of the order of 10^2 h was estimated.

TEMPERATURE MEASUREMENT

Thick Platinum Films as Low Temperature Thermometers

I. BAT'KO, M. SOMORA, D. VANICKY, K. FLACHBART, V. MATEJ and V. PAVLÍK, *Cryogenics*, 1992, 32, (7), 683–684

Resistance measurements of thick Pt films between 4.2 and 300 K are reported. The thick films were prepared by standard screen printing methods. Experimental data at 77–300 K were fitted to mathematical expressions, with an error in temperature $< 0.2\%$. Their properties and the ability to prepare even small thermometers on substrates ≤ 0.2 mm suggests a use as very low heat capacity sensors. This will enable production of small calorimeters or thermometers with short relaxation times for > 77 K.

MEDICAL USES

DNA Binding Properties of *cis*- $[\text{Pt}(\text{NH}_3)(\text{C}_6\text{H}_{11}\text{NH}_2)\text{Cl}_2]$, a Metabolite of an Orally Active Platinum Anticancer Drug

J. F. HARTWIG and S. J. LIPPARD, *J. Am. Chem. Soc.*, 1992, 114, (14), 5646–5654

The cyclohexyl substituent on the amine ligand in *cis*- $[\text{Pt}(\text{NH}_3)(\text{C}_6\text{H}_{11}\text{NH}_2)\text{Cl}_2]$ was found to have a profound effect on the selectivity for DNA binding sites and the ability of the resulting lesions to alter the processing of the damaged DNA. The results showed that the DNA adduct profile, and also the mechanism of activity, of the new class of orally active Pt complexes was similar to that of cisplatin.