

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Formation of Thin Films of Platinum, Palladium, and Mixed Platinum:Palladium Nanocrystallites by the Langmuir Monolayer Technique

F. C. MELDRUM, N. A. KOTOV and J. H. FENDLER, *Chem. Mater.*, 1995, 7, (6), 1112-1116

Chloroform solutions of colloidal Pt, Pd and mixed Pt:Pd = 1:1 particles prepared by solvent extraction were dispersed on a H₂O subphase in a Langmuir trough to generate particulate films 30 Å thick. A great amount of the stabiliser was incorporated in the films, thus preventing a completely close-packed arrangement of the metal particles.

Structural Investigation of Bimetallic Rh-Pt Nanoparticles through X-Ray Absorption Spectroscopy

L. E. ALEANDRI, H. BÖNNEMANN, D. J. JONES, J. RICHTER and J. ROZIÈRE, *J. Mater. Chem.*, 1995, 5, (5), 749-752
EXAFS studies of an isolated Rh-Pt colloid, Rh_{0.44}Pt_{0.56}, showed mixed-metal shells, with the environment around the Rh absorber consisting of 3.5 Rh atoms at a distance of 2.72 Å and 4.7 Pt atoms at 2.74 Å, and around the Pt absorber 3.6 Rh at 2.72 Å and 8.3 Pt atoms at 2.75 Å. The average co-ordination number was lower than the 12 expected for a f.c.c. structure. The system is best described as a nanoparticulate Rh-Pt alloy, surface rich in Rh.

Solid-State Reaction in Pd/ZnSe Thin Film Contacts

K. J. DUXSTAD, E. E. HALLER, K. M. YU, E. D. BOURRET, J. M. WALKER, X. W. LIN and J. WASHBURN, *Appl. Phys. Lett.*, 1995, 67, (7), 947-949

Solid-state reactions in Pd thin film contacts on ZnSe initiated at the Pd/ZnSe interface by thermal annealing at 200°C, formed a tetragonal ternary phase Pd_{5.7}ZnSe which had highly oriented grains and was stable up to an annealing temperature of 400°C. The Pd/ZnSe interface was thermally more stable than the corresponding Pd/GaAs and Pd/Si structures. Pd/semiconductor interfacial phenomena were studied.

Observation of Internal Structures of Martensites of Fe-Rh Alloys

N. TAKAHARA, M. TAKAHASHI and R. OSHIMA, *J. Jpn. Inst. Met.*, 1995, 59, (6), 599-606

Internal structures of the martensites of Fe-5 at.% Rh and Fe-25 at.% Rh (1) were examined by XRD, optical microscopy and TEM. Both alloys showed surface reliefs, which result from martensite transformation. The martensites are of a dislocated lath type. In (1) alloy twinning shear is associated with the lattice invariant shear of the transformation.

Structure of Two-Dimensional Conductor of Sr₂RhO₄

M. ITOH, T. SHIMURA, Y. INAGUMA and Y. MORII, *J. Solid State Chem.*, 1995, 118, (1), 206-209

The structure of the two-dimensional conductor Sr₂RhO₄ was refined by powder X-ray diffraction at room temperature. Sr₂RhO₄ crystallises with the symmetry of space group *I4₁/acd*, isostructural with Sr₂IrO₄, and the lattice parameter *a* = 0.54516(1) and *c* = 2.57539(4) nm. The structural data were similar to those for semiconducting and antiferromagnetic Sr₂IrO₄.

CHEMICAL COMPOUNDS

First Octahedral Platinum Cluster: Structure as a Function of Electron Count in Pt₆ Clusters

L. HAO, G. J. SPIVAK, J. XIAO, J. J. VITTAL and R. J. PUDDPHATT, *J. Am. Chem. Soc.*, 1995, 117, (26), 7011-7012

Two new types of Pt₆ clusters, interconvertible by the gain or loss of two electrons, and one having octahedral stereochemistry, are reported. The dark red-purple, air-sensitive cluster [Pt₆(μ-CO)₆(μ-dppm)₃] (dppm = Ph₂PCH₂PPh₂) (1) was prepared by reduction of [PtCl₂(SMe₂)₂] and [PtCl₂(dppm)] with NaBH₄ under CO, in high yield. (1) has two Pt₃(μ-CO)₃ triangles bridged by 3 μ-dppm ligands, with D_{3h} symmetry and is easily oxidised to give the cluster cation [Pt₆(CO)₆(μ-dppm)₃]²⁺ with terminal carbonyl ligands.

Reductive Reactions in Synthesis of Low-Valence Platinum and Palladium Complexes

N. YU. KOZITSYNA and I. I. MOISEEV, *Usp. Khim.*, 1995, 64, (1), 51-65

The use of reductive reactions of Pt(II) and Pd(II) complexes in the synthesis of complexes containing the metals in low-valence states (0 ≤ *n* ≤ 2) with π-acceptor ligands: phosphines, phosphides, phenanthroline and dipyriddy is discussed. Transformation of *tert*-phosphine ligands with a reductive agent and X-ray data for the mono- and polynuclear complexes of Pt and Pd in low oxidation states are reviewed. (138 Refs.)

Synthesis of Large Palladium Clusters. The Preparation of Pd₃₈(CO)₂₈(PR₃)₁₂ (R = Et, Buⁿ) and Pd₃₄(CO)₂₄(PET₃)₁₂

E. G. MEDNIKOV and N. I. KANTEEVA, *Izv. Akad. Nauk Rosii, Ser. Khim.*, 1995, (1), 167-170

The Pd₃₈(CO)₂₈L₁₂ cluster (L = PET₃) was prepared by reacting Pd₁₀(CO)₁₂L₆ with CF₃COOH-Me₃NO, CF₃COOH-H₂O₂, and Pd(OAc)₂-Me₃NO and Pd₂(dba)₃ mixture (dba = dibenzylidenacetone). Tri-*n*-butylphosphine Pd₃₈(CO)₂₈(PBu₃)₁₂ was synthesised by the reaction of Pd₁₀(CO)₁₄(PBu₃)₄ with Me₃NO. The reaction of Pd₄(CO)₅L₄ with Pd₂(dba)₃ yielded clusters Pd₃₄(CO)₂₄L₁₂ and Pd₁₀(CO)₁₁L₆.

One-Pot Synthesis and X-Ray Studies on Cyclic Oligobipyridines and One of Their Dinuclear Ruthenium Complexes

C. KAES, M. W. HOSSEINI, R. RUPPERT, A. DE CIAN and J. FISCHER, *J. Chem. Soc., Chem. Commun.*, 1995, (14), 1445-1446

A one-pot synthesis of three new macrocycles containing two, three or four 2,2'-bipyridine units is described. A homodinuclear Ru^{II} complex was prepared in almost quantitative yield by reacting one of the macrocycles with 2 equiv. of Ru(bipy)₂Cl₂ in a butanol-H₂O solution. Precipitation of the PF₆ salt from an aqueous solution gave the pure complex as a mixture of diastereoisomers. The X-ray structure of one of the diastereoisomers of the dinuclear Ru complex shows two metal centres held in close proximity.

Chiral [Ru(pp)₂(CO)₂]²⁺ Species (pp = Bidentate Polypyridyl Ligand) and Their Use in the Stereoselective Synthesis of Ligand-Bridged Dinuclear Complexes

T. J. RUTHERFORD, M. G. QUAGLIOTTO and F. R. KEENE, *Inorg. Chem.*, 1995, 34, (15), 3857-3858

The decarbonylation of chiral [Ru(pp)₂(CO)₂]²⁺ (pp = bidentate polypyridyl ligands) in the presence of excess pp showed stereoretention in the [Ru(pp)₃]²⁺ product. Under the same conditions, its reaction with chiral [Ru(pp)₂(BL)]²⁺ centres (pp and pp' may or may not be identical; BL = bridging ligand) allows the synthesis of specific diastereoisomeric forms of the dinuclear species [(pp)₂Ru(BL)Ru(pp')]⁴⁺.

ELECTROCHEMISTRY

Methanol Oxidation at Electrochemically Oriented Platinum Electrodes in Acidic Medium

A. A. EL-SHAFAEI, *J. Phys. Chem. (München)*, 1995, 190, (II), 231-239

Methanol oxidation was studied as a structure sensitive process on different Pt surfaces: polycrystalline Pt and reproducibly prepared electrochemically oriented Pt surfaces. The fabrication of Pt surfaces with preferred orientations or different surface concentrations of low index planes depends on the electrochemical treatment. Bulk MeOH oxidation depended both on the predomination of one low index plane and on the ratio of the surface planes.

Contribution to the Interpretation of the Multistep Cathodic Reduction of Oxygen at the Pt/Zirconia Base Electrolyte Interface at High Temperature

G. B. BARBI, *Ber. Bunsenges. Phys. Chem.*, 1995, 99, (5), 741-748

The multistep cathodic reduction of O₂ molecules at high temperatures at the porous Pt/Y₂O₃ stabilised ZrO₂ solid electrolyte interface was analysed by steady state polarisation. For very thin and porous layers and O₂ mixtures of ≥ 1% O₂, the rate of the overall process was controlled by the electrode/electrolyte interfacial diffusion of neutral and/or single ionised atoms.

Attempts to Modify an Electrode with a Conducting Platinum Cluster Compound

L. XU, F. LI and S. DONG, *Electroanalysis*, 1995, 7, (8), 734-737

A conducting Pt cluster compound K_{1.64}Pt(C₂O₄)₂ was electrochemically synthesised on a glassy C electrode through the electro-oxidation of K₂Pt(C₂O₄)₂ in an aqueous medium using single potential step and cyclic voltammetry methods. The excellent conductivity of the fibrous material that grew on the electrode was observed voltammetrically. Each conducting fibre in contact with the electrode could act as an ultramicroelectrode, and the electrode behaviour changed from a plain to an ultramicroelectrode array.

Absorption-Desorption of Deuterium at Pd95%-Rh5% Alloy. I: Environment and Temperature Effects

G. MENGOLI, M. FABRIZIO, C. MANDUCHI, E. MILLI and G. ZANNONI, *J. Electroanal. Chem.*, 1995, 390, (1-2), 135-142

The gas phase and electrolytic loading of 5%Rh-Pd alloy with D₂ were studied. Gas loading was performed isochorically under 900 mbar D₂, by decreasing the temperature from 900 to 20°C. The absorption was measured at 20°C when the [D]:[Me] ratio exceeded the typical value for pure Pd. Electrolytic insertions of D₂ were carried out potentiostatically in alkaline D₂O electrolytes, giving maximum [D]:[Me] ratios at 25°C, while at 90°C alloy deuterides of large [D]:[Me] ratio were obtained.

A Novel Ru(VII)/Ru(IV) Mediator System for Electrooxidation of Primary and Secondary Alcohols, Leading to Aldehydes and Ketones

S. TORII and A. YOSHIDA, *Chem. Lett.*, 1995, (5), 369-370

A soluble Ru(VII)/Ru(IV) redox system in MeCN/H₂O-Bu₄NOH-(Pt/Pt) was found to be a mild oxidising system for the electrochemical conversion of primary and secondary alcohols into their corresponding aldehydes and ketones under basic conditions. Direct evidence on the working of the Ru(VII)/Ru(IV) redox as a mediator system was obtained from UV spectroscopy.

PHOTOCONVERSION

Acid-Base Behavior of the Ground and Excited States of Platinum(II) Complexes of Quinoxaline-2,3-dithiolate

S. D. CUMMINGS and R. EISENBERG, *Inorg. Chem.*, 1995, 34, (13), 3396-3403

Studies of the pH-dependent absorption and emission behaviour of Pt(qdt)₂²⁺ (1) and Pt(phen)(qdt) (2) (qdt = quinoxaline-2,3-dithiolate and phen = 1,10-phenanthroline) showed pH-dependent changes in both their charge-transfer absorption and emission spectra, which were attributed to protonation of the qdt ligand at the imine N. For (1), single protonation leads to a large red shift (2582/cm), but for (2) the lowest-energy excited state involves charge transfer from an orbital of Pt(d)/S(p) to a phen π* orbital.

Electronic Spectra and Photochemistry of Trichlorostannyl Complexes of Ruthenium(II) and Osmium(II)

V. PAWLOWSKI, H. KUNKELY and A. VOGLER, *Inorg. Chim. Acta*, 1995, **234**, (1-2), 55-60

The absorption spectra and photochemistry of $[M(\text{SnCl}_3)_3]^+$, $[M(\text{SnCl}_3)_2\text{Cl}]^+$ and $[M(\text{SnCl}_3)_2\text{AN}]^+$, where M = Ru, Os; AN = acetonitrile, in acetonitrile were studied. It is suggested that the lowest energy transitions are largely of the intraligand type. The photolysis in acetonitrile leads to substitutions of SnCl_3 or in the case of $[\text{Ru}(\text{SnCl}_3)_3]^+$ to a ligand fragmentation as primary photoreactions. $[M(\text{SnCl}_3)_2(\text{AN})_2]^2$ was the terminal product of all the photoreactions.

Ruthenium(II) tris-(2,2'-bipyridine)-Specific Extrinsic Lyoluminescences of X-ray Irradiation Colored and Electrolytically Colored Alkali Halides

S. KULMALA, A. HAKANEN, P. RAERINNE, A. KULMALA and K. HAAPAKKA, *Anal. Chim. Acta*, 1995, **309**, (1-3), 197-210

Short-lived solid/solution interfaces, which are sufficiently energetic to initiate the radiative ³MLCT-based transition lyoluminescence (LL) of Ru(II) tris-(2,2'-bipyridine)chelate can be produced on dissolving X-ray irradiation coloured or electrolytically coloured alkali halides in H₂O. Using Ru(bpy)₃²⁺ as a model lyoluminophore, the basis of using LL as a new analytical tool is discussed. The extrinsic LL of F-coloured alkali halides allows detection of luminescent compounds at trace levels in aqueous solutions.

Control of Photosubstitution in Dinuclear Ruthenium Polypyridyl Complexes by Choice of Bridging Ligand

H. P. HUGHES and J. G. VOS, *Inorg. Chem.*, 1995, **34**, (15), 4001-4003

Photolysis of $[(\text{Ru}(\text{bpy})_2)_2(\text{bpzt})]^{3+}$ (Hbpzt is 3,5-bis(pyrazin-2-yl)-1,2,4-triazole) resulted in a unique labilisation of the metal moiety bound to the triazole N4 site. This is contrary to results obtained for the analogous compound based on the 3,5-bis(pyridin-2-yl)-1,2,4-triazole ligand for which both the N1 and N4 sites were subject to photochemical substitution. This is explained by changes in the rate of relaxation to the lowest excited state, due to the different natures of the luminescent properties in these complexes.

ELECTRODEPOSITION AND SURFACE COATINGS

Rhodium Plating

R. J. MORRISSEY, *Plat. Surf. Finish.*, 1995, **82**, (8), 69
Rh can be evaporated under vacuum, but is mostly electrodeposited. Electroplating solutions for Rh are highly acidic, and are usually based on the sulphate or phosphate. For decorative applications, Rh plating solutions contain ~ 2 g/l Rh and ~ 20 ml/l concentrated H₂SO₄, at 1-5 A/dm² and at 40-45°C. Rh can be plated from molten cyanide systems to a thickness of > 100 μm. Rh deposits are non-toxic and hypoallergenic.

APPARATUS AND TECHNIQUE

Calorimetric Measurement of the Energy Difference between Two Solid Surface Phases

Y. Y. YEO, C. E. WARTNABY and D. A. KING, *Science*, 1995, **268**, (5218), 1731-1732

The energy difference between two solid surface structures was measured using a single-crystal surface calorimeter which is a clean Pt{100} surface reconstructed to a stable phase where the surface layer of Pt atoms has a quasi-hexagonal structure. By comparing the heats of adsorption of CO and C₂H₄ on this stable Pt{100}-hex phase with those on a metastable Pt{100}-(1 × 1) surface, the energy difference between the two clean phases was measured as 20 ± 3 and 25 ± 3 kJ/mole of surface Pt atoms.

Platinum/Glassy Carbon Electrode as Detector for Liquid Chromatographic Determination of Hydroxyl-Containing Compounds

I. G. CASELLA, *Anal. Chim. Acta*, 1995, **331**, (1), 37-46
A Pt-modified glassy C electrode (CME) was studied as an amperometric detector for mono- and polyhydric compounds in flowing streams, including liquid chromatography. The Pt-CME showed good sensitivity and time stability. The electrode response was stable showing a signal loss of < 5% after 8 h trials.

Morphologic and Spectroscopic Characterization of Porous Pt/GaAs Schottky Diodes by Scanning Tunnelling Microscopy

J. MASÓ, N. BARNIOL, F. PÉREZ-MURANO and X. AYMERICH, *Thin Solid Films*, 1995, **261**, (1-2), 299-306

The porous character of the Pt film of Pt/GaAs Schottky diodes used as NH₃ gas sensors was studied using STM. Electrical measurements were also performed in very localised regions of the surface. The diameter of the Pt grains of the porous film was found to depend on its thickness.

Tunable, Long-Wavelength PtSi/SiGe/Si Schottky Diode Infrared Detectors

J. R. JIMENEZ, X. XIAO, J. C. STURM and P. W. PELLEGRINI, *Appl. Phys. Lett.*, 1995, **67**, (4), 506-508

The fabrication is reported of p-type PtSi/SiGe/Si Schottky diodes with barrier heights (from photoreponse) that are lowered (relative to PtSi/Si) and are highly dependent on the applied bias. Variability in barrier height was obtained by using the SiGe/Si valence band offset as an additional barrier close to the PtSi/SiGe Schottky barrier. The total effective barrier can then be altered by adjusting the applied reverse bias.

Study of the Adsorptive Voltammetric Behavior of the Rh^{III}-5-Br-PADAP Complex

C. WANG, C. HONG and H. LI, *Electroanalysis*, 1995, **7**, (8), 759-762

The adsorptive voltammetric behaviour of the Rh^{III}-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol complex was studied by linear scan in a solution of NaOAc, HOAc and ethanol. This method provides sensitive selective adsorptive stripping voltammetry for the detection of 7.8 × 10⁻⁹ - 9.7 × 10⁻⁷ mol/l traces of Rh.

Novel Thick-Film pH Sensors Based on Ruthenium Dioxide-Glass Composites

H. N. MCMURRAY, P. DOUGLAS and D. ABBOT, *Sens. Actuators B*, 1995, 28, (1), 9–15

Composite electrodes comprising thick films of $30 \pm 10 \mu\text{m}$ RuO_2 -glass composite on a Pyrex substrate were made and showed a near Nernstian dependence of potential on pH in aqueous buffer at pH 2–12 and at a RuO_2 :Pb borosilicate glass ratio of 1:1. The electrodes displayed a maximum hysteresis of 30 mV and a response time of ~ 90 s. The electrodes are porous and the response time increased with the RuO_2 :Pb borosilicate glass ratio in the composite.

HETEROGENEOUS CATALYSIS

A Novel Aminoalcohol Modifier for the Enantioselective Hydrogenation of Ethyl Pyruvate on Pt/Alumina

B. MINDER, T. MALLAT, A. BAIKER, G. WANG, T. HEINZ and A. PFALTZ, *J. Catal.*, 1995, 154, (2), 371–378

A chiral modifier, (*R*)-2-(1-pyrrolidinyl)-1-(1-naphthyl)ethanol (PNE) was prepared and tested in the enantioselective hydrogenation of ethyl pyruvate over $\text{Pt}/\text{Al}_2\text{O}_3$. An enantiomeric excess in (*R*)-ethyl lactate of $\leq 75\%$ was obtained. The optimum reaction conditions were 1–10 bar H_2 pressure, 0–25°C and a catalyst loading ≥ 15 g/l. The efficiency of PNE was shown by the very low modifier:reactant molar ratio, 1:30,000, to obtain maximum enantioselectivity.

Structural Characterization of a Model Catalyst: $\text{Pt}/\text{Al}_2\text{O}_3/\text{NiAl}(110)$

T. BERTRAMS, F. WINKELMANN, T. UTTICH, H.-J. FREUND and H. NEDDERMEYER, *Surf. Sci.*, 1995, 331–333, (Part B), 1515–1519

The condensation of Pt was studied on clean $\text{NiAl}(110)$ and on a thin ordered Al_2O_3 film grown on $\text{NiAl}(110)$. On $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ and up to a coverage of one monolayer, Pt forms highly dispersed two-dimensional islands with an average diameter of 10–30 Å whose density increased with coverage. For higher Pt coverage the formation of three-dimensional Pt clusters was observed. Annealing of the Pt-covered surface led to Pt diffusion into the oxide film. On $\text{NiAl}(110)$ and up to 1 monolayer, 2-dimensional growth of Pt with constant island density was observed.

The Positive Effect of Hydrogen on the Reaction of Nitric Oxide with Carbon Monoxide over Platinum and Rhodium Catalysts

R. DÜMPPELMANN, N. W. CANT and D. L. TRIMM, *Catal. Lett.*, 1995, 32, (3, 4), 357–369

The effect of adding 330–4930 ppm H_2 to a reaction mixture of NO and CO over Pt and Rh catalysts was studied at 200–250°C. The addition of H_2 results in a large increase in the conversion of both NO and CO. The equation for the reaction accounts for the 50–100% of CO_2 formed with $\text{Pt}/\text{Al}_2\text{O}_3$ and the 20–50% with $\text{Rh}/\text{Al}_2\text{O}_3$. The process arises by formation of isocyanic acid on the metal followed by hydrolysis to CO_2 and NH_3 on the support.

Naphthalene Hydrogenation over $\text{Pt}/\text{Al}_2\text{O}_3$ Catalyst in a Trickle Bed Reactor

T.-C. HUANG and B.-C. KANG, *Ind. Eng. Chem. Res.*, 1995, 34, (7), 2349–2357

Naphthalene dissolved in different volatile solvents was hydrogenated over $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst in a trickle bed reactor. The activity and selectivity were studied with various H_2 and feed flow rates at 513 K and 5.17 MPa. The activity of naphthalene hydrogenation increased with increasing wetting efficiency, and the selectivity of *cis*-decalin decreased with increasing solvent volatility.

Hydrogenation of Oxygen-Containing Acyclic Compounds Using Finely Dispersed Catalysts Based on Platinum Group Metals

T. N. ANTONOVA, A. A. KUNITSKII, E. M. CHABUTKINA, G. N. KOSHEL', A. L. SOKOLOV and S. P. KOROVINA, *Neftekhimiya*, 1995, 35, (1), 49–55

Studies of the hydrogenation of the double bonds in 5,6-epoxy-*cis*-cyclooctene, 5-cyclooctene-1,2-diol and the reduction of aqueous cyclooctylhydroperoxide were performed using finely dispersed Pt group metal catalysts, such as 3–5%Pt/C, 1–5%Pd/C and 2–5%Rh/C. These finely dispersed catalysts were highly effective in producing cycloalkanol and cycloalkanone.

Vapour-Phase Hydrodehalogenation of Chlorobenzene over Platinum/H-BEA Zeolite

E. J. CREYGHTON, M. H. W. BURGERS, J. C. JANSEN and H. VAN BEKKUM, *Appl. Catal. A: Gen.*, 1995, 128, (2), 275–288

Studies of Pt/H-BEA zeolite and $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts during the vapour-phase hydrodehalogenation of chlorobenzene showed them to be highly active in the hydrogenolysis of the C-halogen bond. Deactivation of Pt/H-BEA is due to acid catalysed oligomerisation reactions and coke formation. Coke formation diminished and catalyst stability improved by replacement of Brønsted acid sites in the Pt catalyst by Na ions.

Skeletal Reactions on *n*-Hexane over Pt-NaY, Pt/SiO₂, HY, and Mixed Pt/SiO₂ + HY Catalysts

Z. PAÁL, Z. ZHAN, I. MANNINGER and W. M. H. SACHTLER, *J. Catal.*, 1995, 155, (1), 43–51

The activity and selectivity of three 8%Pt/NaY catalysts calcined at 633, 723 and 823 K were studied with *n*-hexane as the model reactant at 603 K and subatmospheric pressure. The activity of all the Pt/NaY catalysts was superior to that of EUROPT-1 and they deactivated more slowly. The sample calcined at 633 K had the highest dispersion and the highest aromatisation selectivity.

First Heck Reactions of Aryldiazonium Salts Using Heterogeneous Catalysts

M. BELLER and K. KÜHLEIN, *Synlett*, 1995, (5), 441–442

A very simple and practical Heck reaction of diazonium salts and acrylic acid esters, based on heterogeneous Pd catalysts supported on C, Al_2O_3 , SiO_2 and BaSO_4 has been developed. Cinnamic acid esters were obtained under very mild conditions in good to excellent yields. No addition of a base or of phosphane ligands was needed for good conversion.

High Activity of CO Oxidation over Nanocrystalline CuO-Pd/ γ -Al₂O₃ Catalysts Prepared by the γ -Radiation Method

Y. ZHU, P. LIN, Y. QIAN, S. YU, Z. CHEN and M. ZHANG, *Chin. J. Chem. Phys.*, 1995, 8, (3), 274–278

The nanocrystalline CuO (8 wt.%, 12 nm)-Pd (0.5 wt.%, 10 nm)/ γ -Al₂O₃ catalyst prepared by the γ -radiation method was very active in CO oxidation reactions. It started operating at 110°C; its light-off temperature was 145°C and 100% CO conversion was obtained at 148°C. The catalyst showed thermal stability in its activity after thermal treatment at \leq 750°C.

Structure and State of Surface of Aluminopalladium Catalysts from bis(π -Allyl Palladium Chloride)

N. V. PERKAS, G. D. ZAKUMBAEVA and T. D. LEVINTOVA, *Neftekhimiya*, 1995, 35, (2), 141–147

Studies of the Pd/ γ -Al₂O₃ catalyst prepared by reducing (C₃H₅PdCl)₂ with N₂H₄·H₂O on γ -Al₂O₃ in aqueous ethanol solution, followed by drying in alcohol, showed the formation of highly dispersed Pd on the surface of the support. The active phase was of zero-valence order, containing low-valent ionic Pd forms, which were stabilised by organic ligands. The catalyst was highly reactive in liquid-phase hydrogenation.

Palladium-Ceria Catalysts: Reversibility of Hydrogen Chemisorption and Redox Phenomena

A. BENSALÉM, F. BOZON-VERDURAZ and V. PERRICHON, *J. Chem. Soc., Faraday Trans.*, 1995, 91, (14), 2185–2189

Studies of the H₂ interaction with Pd/CeO₂ catalysts showed that the ratio H_{irr} : Pd_{total}, H_{irr} = irreversibly adsorbed H, is 2.5–3.5. This is due to H spillover from Pd to CeO₂. The uptake of H by CeO₂ resulted in its complete surface reduction at room temperature, while bulk reduction started at 473 K. The reoxidation ratio depended on the outgassing temperature.

Catalytic Decomposition of N₂O over Rhodium-Loaded Metal Oxides

J. OI, A. OBUCHI, A. OGATA, H. YAGITA, G. R. BAMWENDA and K. MIZUNO, *Chem. Lett. Jpn.*, 1995, (6), 453–454
Studies of catalytic decomposition of N₂O to N₂ and O₂ on Rh-loaded metal oxide catalysts showed that Rh/ZnO had the highest activity. An air-pretreated 0.5 wt.% Rh/ZnO catalyst was the most active, giving a reaction rate of 4.0 \times 10⁴ μ mol (N₂O)/gh under 950 ppm of N₂O and 5% of O₂ at 300°C.

Selective Hydrogenation over Ruthenium Catalysts

P. KLUSON and L. CERVENY, *Appl. Catal. A: Gen.*, 1995, 128, (1), 13–31

A review is given of the preparation, characterisation and activities of Ru catalysts used in the selective hydrogenation of carbonyl groups in the vicinity of conjugated or isolated double bonds, for the production of α,β -unsaturated alcohols. The effects of promoters, particle size, inorganic and organic modifiers, and catalyst supports are discussed. (137 Refs.)

HOMOGENEOUS CATALYSIS

Palladium-Catalyzed Stereoselective Allylaminocyclization and 1,3-Butadien-2-ylaminocyclization of Allenyl Tosylcarbamates

M. KIMURA, S. TANAKA and Y. TAMARU, *J. Org. Chem.*, 1995, 60, (12), 3764–3772

Pd catalysts, PdCl₂(PhCN)₂ or Pd₂(dba)₃·CHCl₃ (dba = dibenzylideneacetone) catalysed an allylaminocyclisation of 2,3-butadienyl tosylcarbamates (1) with allylic chlorides in the presence of Et₃N or K₂CO₃ base in THF at room temperature to give selectively *trans*-4,5-disubstituted 2-oxazolidinones in good yields. Under similar conditions, Pd(PPh₃)₄ catalysed an N-allylation of (1). In the absence of an allylic chloride, Pd(PPh₃)₄ and PdCl₂(PhCN)₂ catalyse a formal dimerisation of (1) to give C₄-triene-substituted 2-oxazolidinones in moderate to good yields.

Asymmetric Hydrosilylation of 1-Alkenes Catalyzed by Palladium-MOP

Y. UOZUMI, K. KITAYAMA, T. HAYASHI, K. YANAGI and E. FUKUYO, *Bull. Chem. Soc. Jpn.*, 1995, 68, (3), 713–722

Asymmetric hydrosilylation of 1-alkenes with trichlorosilane at 40°C in the presence of 1 \times 10⁻³ or 1 \times 10⁻⁴ molar amounts of Pd-MOP catalyst proceeded with good regioselectivity and with high enantioselectivity to give high yields of 2-(trichlorosilyl)alkanes. The catalyst was prepared in situ from [PdCl-(η^3 -C₃H₅)₂] and (*S*)-2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl ((*S*)-MeO-MOP). Oxidation of the C-Si bond gave optically active 2-alkanols (87–97% ee).

Stereoselective Addition of Carboxylic Acids to Electron Deficient Acetylenes Catalyzed by the PdMo₃S₄ Cubane-Type Cluster

T. WAKABAYASHI, Y. ISHII, T. MURATA, Y. MIZOBE and M. HIDAI, *Tetrahedron Lett.*, 1995, 36, (31), 5585–5588

The mixed-metal sulphide cubane-type cluster complex [PdMo₃S₄(tacn)₂Cl][PF₆]₂ (tacn = 1,4,7-triazacyclononane) was found to be a highly efficient and selective catalyst for the addition of carboxylic acids to acetylenes with electron-withdrawing groups. The corresponding *trans* addition products were exclusively obtained in good yields under mild conditions in the presence of a catalytic amount of triethylamine.

Rhodium(I)- and Palladium(0)-Catalyzed Carbonylation of Triarylbismuthines with Carbon Monoxide via a Possible Oxidative Addition of a Carbon-Bismuth Bond to Rhodium(I) and Palladium(0)

C. S. CHO, Y. YOSHIMORI and S. UEMURA, *Bull. Chem. Soc. Jpn.*, 1995, 68, (3), 950–957

Triarylbismuthines reacted with CO at atmospheric pressure in acetonitrile at 25°C in the presence of a catalytic amount of a Rh compound, such as [RhCl(CO)₂]₂, RhCl₃·3H₂O and [RhCl(COD)]₂, where COD is cyclooctadiene, to give high yields of the corresponding diaryl ketones and methyl esters. With MeOH solvent, methyl benzoates are also produced. Oxidative addition of a C-Bi bond to Rh(I) and Pd(0) is the major step in the carbonylations.

Transformations of Formaldehyde and Glycolaldehyde during Rhodium-Catalysed Hydroformylation of Formaldehyde

N. N. EZHOVA, G. A. KORNEEVA, E. V. SLIVINSKII and R. A. ARONOVICH, *Izv. Akad. Nauk Rosii, Ser. Khim.*, 1995, (1), 75–78

The hydroformylation of formaldehyde to glycolaldehyde (GA) catalysed by $\text{RhCl}(\text{PPh}_3)_3$, $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{RhCl}_2 + \text{PPh}_3$ system in *N,N*-dimethylacetamide was studied. The hydroformylation was accompanied by the Kannizzaro-Tishchenko reaction, hydrogenation of CH_2O to MeOH, condensation of CH_2O with GA to polyoxaldehydes $\text{C}_3\text{--C}_6$ and dimerisation of GA. The formation of polyoxaldehydes was the predominant side reaction, probably preceded by GA co-ordination with a Rh atom. $\text{RhCl}_2 + \text{PPh}_3$ catalyst gave the best results for CH_2O hydroformylation. At the substrate conversion to 62–67%, the selectivity for GA formation was 96% and the yield was 60–65%.

Strong Electronic Effects on Enantioselectivity in Rhodium-Catalysed Hydroborations with Novel Pyrazole-Containing Ferrocenyl Ligands

A. SCHNYDER, L. HINTERMANN and A. TOGNI, *Angew. Chem., Int. Ed. Engl.*, 1995, 34, (8), 931–932

Studies of the Rh catalysed hydroboration of styrene with catecholborane using $[\text{Rh}(\text{cod})_2]\text{BF}_4$ catalyst (cod=cyclooctadiene) showed the highest enantioselectivity yet for a hydroboration (98% ee) obtained with the pyrazolyl-containing ferrocenyl ligand containing Me, H and 4- $\text{CF}_3\text{C}_6\text{H}_4$. The effect of the substituents on both the pyrazolyl and phosphano fragments was studied, and the results were interpreted in terms of the varying electronic asymmetry they produce at the metal centre.

Optically Active Bis(oxazoliny)pyridine (Pybox) Rhodium Complexes: Asymmetric Hydrosilylation of Ketones

H. NISHIYAMA and K. ITOH, *J. Synth. Org. Chem. Jpn.*, 1995, 53, (6), 500–508

Optically active bis(oxazoliny)pyridine (Pybox) was developed as a chiral N ligand for asymmetric hydrosilylation of ketones. Pybox reacted with RhCl_2 in ethanol solution to give a stable $\text{RhCl}_2(\text{Pybox})$ complex, which showed powerful catalytic activity for the hydrosilylation of ketones with diphenylsilane in the presence of Ag tetrafluoroborate. Acetophenone was reduced to 1-phenylethanol in 91% yield and in 94% ee. Substituents on the oxazoline rings and on the pyridine ring were also examined.

Oxidative Regeneration of Phosphine-Modified Rhodium Hydroformylation Catalysts

E. V. SLIVINSKII, V. I. KURKIN, M. M. ALI, G. A. KORNEEVA, R. A. ARONOVICH, O. YU. PESIN, M. A. MORGULIS and YU. I. SOLOVETSKII, *Neftekhimiya*, 1995, 35, (2), 159–163

Studies were made of oxidative regeneration of deactivated PPh_3/Rh catalyst during hydroformylation of olefins in atmospheric O_2 . The results showed that the application of ozonisation, ultrasound and exposure to light of accelerated electrons noticeably intensified the regeneration of deactivated catalysts.

Chiral Ruthenium(II)-Bis(2-oxazolin-2-yl)pyridine Complexes. Asymmetric Catalytic Cyclopropanation of Olefins and Diazoacetates

H. NISHIYAMA, Y. ITOH, Y. SUGAWARA, H. MATSUMOTO, K. AOKI and K. ITOH, *Bull. Chem. Soc. Jpn.*, 1995, 68, (5), 1247–1262

The title chiral Ru(II) complex, which was prepared in situ from optically active bis(2-oxazolin-2-yl)pyridine (Pybox-*ip*) (1) and $[\text{RuCl}_2(\text{p-cymene})_2]$ (2), exhibited efficient activity for the asymmetric cyclopropanation (ACP) of styrene and a number of diazoacetates, to give the corresponding *trans*- and *cis*-2-phenylcyclopropane-1-carboxylates in good yields of 66–87%. A mixture of (1) and (2) in ethylene produced the *trans*- $\text{RuCl}_2(\text{Pybox-}ip)$ (ethylene) complex which also proved to be a powerful catalyst for ACP.

ELECTRICAL AND ELECTRONIC ENGINEERING

Magneto-Optical Enhancement in Pt/(Ni_{1-x}Co_x) Multilayers

R. KRISHNAN, M. NÝVLT, V. PROSSER, M. SEDDAT, Z. SMETANA, M. TESSIER and S. VISNOVSKÝ, *J. Magn. & Magn. Mater.*, 1995, 148, (1–2), 283–284

Magneto-optical (MO) polar Kerr rotation (PKR) and ellipticity spectra of Pt/(Ni_{1-x}Co_x) multilayers with $x = 0, 0.3$ and 1, prepared by evaporation under UHV, were studied. Layers formed at the Pt-magnetic layer interfaces resulted in a surface-induced perpendicular magnetic anisotropy and enhanced PKR in the near-UV spectral region. The possibility of optimising the MO characteristics, by changing x and the growth parameters, makes this Pt multilayer important for obtaining MO storage media able to work in blue light.

Improvement of Electrical Characteristics of Pt-Diffused Devices

B. DENG, C. SHU and H. KUWANO, *Jpn. J. Appl. Phys.*, 1995, 34, (6A), 2969–2973

The electrical characteristics of Pt-diffused p^+n diodes were improved by reducing Pt-induced adverse effects. Pt diffusion induces mobile Pt ions to diffuse into the SiO_2 films and also changes the surface conditions near the Si- SiO_2 interface, thus increasing the leakage current. The Pt-diffused dipolar devices with a (100) substrate and a phosphosilicate glass film on SiO_2 film are effective in both the preservation of electrical stability and reduction of leakage current.

Spin-Valve Memory Elements Using [CoPt/Cu/Ni-Fe-Co/Cu] Multilayers

Y. IRIE, H. SAKAKIMA, M. SATOMI and Y. KAWAWAKE, *Jpn. J. Appl. Phys.*, 1995, 34, Part 2, (4A), L415–L417

Development of a new type of magnetoresistive memory using magnetic spin-valve multilayers, where magnetisation switching of the semi-hard magnetic CoPt layer is used for data storage and that of the soft magnetic NiFeCo layer is used for data readout, is reported. The fabricated memory element was made of a word line of Au film and a magnetoresistive sense line of [CoPt/Cu/Ni-Fe-Co/Cu] multilayers.