

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

Adsorption and Reactions of Acetaldehyde on Pt(S) - [6(111) × (100)]

R. W. McCABE, C. L. DIMAGGIO and R. J. MADIX, *J. Phys. Chem.*, 1985, **89**, (5), 854-861

The adsorption and reactions of CH₃CHO with clean and O-pre-dosed Pt(S) - [6(111) × (100)] surfaces were studied by EELS and TPRS to examine the control of pollutants from ethanol-fuelled vehicles. Reaction pathways found were identical on both surfaces. Products formed included gases CO, CH₄, H₂, and adsorbed CH₃CO, H, CH₃, CO, C₂H₃, O and C, depending upon temperature.

The Influence of Preparation Methods of Platinized p-Type Indium Phosphide on Photoelectrochemical Properties

H. YONEYAMA, H. AZUMA and H. TAMURA, *J. Electroanal. Chem. Interfacial Electrochem.*, 1985, **186**, (1 and 2), 247-256

Comparative studies of the photoelectrochemical properties of platinized p-type InP were made for different methods of platinisation: electrodeposition under illumination (1), electrodeposition in the dark (2), and arc plasma spraying deposition (3). The highest activities and electrode stabilities for photoassisted H₂ evolution occurred at electrodes prepared by (1) and the most inferior properties were observed for method (2). Deposited Pt showed different morphologies depending on the method of platinisation.

Thermodynamic, Elastic and Structural Properties of Solid Solutions of Hydrogen in Pd-Si Metallic Glasses

R. S. FINOCCHIARO, Ph.D. Thesis, Northeastern Univ., 1983, *Diss. Abstr. Int. B*, 1985, **45**, (7), 2174-B

The H solubility and thermodynamics in Pd-Si were studied in the temperature range 10-90°C and H pressures of 0-100 torr. Pressure-composition-temperature diagrams were constructed and relative excess partial molar free energies, enthalpies and excess entropies are reported. There is a dramatic dependence of the H solubility on the Si concentration. A decrease in the H solubility is observed when the Si concentration increases from 14 to 22 at. %.

Phase Relationship and Thermodynamic Properties of the Pd-S System

J. R. TAYLOR, *Metall. Trans.*, 1985, **16B**, (1), 143-148
S pressures in the Pd-S system were measured for liquid mattes, PdS/liquid matte mixtures, Pd/matte, Pd₄S/matte and Pd/Pd₄S mixtures by various techniques. The phase diagram has been determined from 0-50 at. % S and microprobe analysis was used to confirm the identification of equilibrated phases.

Composition and Structure of Fission Product Precipitates in Irradiated Oxide Fuels. Correlation with Phase Studies in the Mo-Ru-Rh-Pd and BaO-UO₂-ZrO₂-MoO₂ Systems

H. KLEYKAMP, J. O. PASCHOAL, R. PEJSA and F. THÜMMER, *J. Nucl. Mater.*, 1985, **130**, 426-433

Composition and crystal structure of fission product precipitates in irradiated oxide fuels were studied by various techniques. Ru, Rh, Pd, Mo and Tc were found to form mono-phase or two-phase alloys in irradiated LWR, HRR and FBR oxide fuels. Metallic phases found were h.c.p. ϵ -Ru(Mo, Tc, Rh, Pd) solid solutions, b.c.c. β -Mo(Tc/Ru) and f.c.c. α -Pd(Ru, Rh).

Oxygen Potential and the Chemical State of the Fission Products Ruthenium, Rhodium and Palladium in Irradiated Oxide Fuels

M. S. CHANDRASEKHARAI, *J. Nucl. Mater.*, 1985, **130**, 366-374

Thermodynamic properties of intermetallic compounds of the type M₃U and M₃Pu where M = Ru, Rh or Pd are reviewed. The critical oxygen potential of the oxide fuel matrix necessary for their formation is suggested. Phase diagrams for PuM₃, UM₃ and the formation of the UM₃ phase are discussed. The UM₃ have rather unusual thermodynamic stability.

Potassium Coadsorption Induced Dissociation of CO on the Rh(III) Crystal Surface: An Isotope Mixing Study

J. E. CROWELL, W. T. TYSOE and G. A. SOMORJAI, *J. Phys. Chem.*, 1985, **89**, (9), 1598-1601

The coadsorption of K with CO on Rh(111) induces dramatic changes in the chemisorption properties of CO. Isotopic mixing shows that CO dissociation occurs with coadsorbed K, but does not occur on a K-free Rh(111) surface. The simultaneous desorption of K and CO for the dissociated state indicates that direct interactions are responsible for CO dissociation and that up to 3 CO molecules are dissociated per K atom.

Excited-State Properties of a Triply Ortho-Metalated Iridium(III) Complex

K. A. KING, P. J. SPELLANE and R. J. WATTS, *J. Am. Chem. Soc.*, 1985, **107**, (5), 1431-1432

The characterisation of the ground and luminescent excited states of a triply ortho-metallated complex fac-Ir(ppy)₃ are reported for the first time. The complex is one of the strongest transition metal photoreductants so far reported. A luminescent lifetime of 5.0 μ s was observed in ethanol/methanol glass at 77K, but could be extended to 2.0 μ s. The photoactivity in halocarbon solvents suggested that Ir(ppy)₃ may be strongly reducing in its excited state.

Oxygen Evolution and Corrosion on Ruthenium-Iridium Alloys

R. KÖTZ and S. STUCKI, *J. Electrochem. Soc.*, 1985, **132**, (1), 103-107

The initial stages of O₂ evolution and anodic corrosion on Ru-Ir alloys were investigated in 1N H₂SO₄ by voltammetry and XPS. The corrosion of Ru was significantly reduced by increasing Ir content; simultaneously the activity for O₂ evolution decreases. The reduced corrosion of Ru is paralleled by an increased tendency to oxide formation of the Ir. The stabilisation of Ru by Ir is assigned to the formation of a protective oxide layer with increased Ir.

CHEMICAL COMPOUNDS

Crystal Structure of Nonstoichiometric Tetranuclear Platinum Compound, cis-Diammineplatinum α -Pyrrolidone Violet, [Pt₄(NH₃)₈(C₄H₆NO)₄](PF₆)₂(NO₃)_{2.56}·5H₂O

K. MATSUMOTO, *Bull. Chem. Soc. Jpn.*, 1985, **58**, (2), 651-656

The nonstoichiometric Pt tetranuclear title compound, a Pt blue related compound was synthesised and its crystal structure solved by X-ray diffraction analysis. The crystal is triclinic with space group P $\bar{1}$. The cation is structurally identical with those of cis-diammineplatinum α -pyridone yellow, α -pyridone blue and α -pyrrolidone tan, and consists of 4 Pt atoms linked in a chain with bridging pyrrolidone ligands. The Pt-Pt bond distances are given, and the average Pt oxidation state is 2.14, therefore indicating that the compound is 44% of [Pt₄(NH₃)₈(C₄H₆NO)₄]⁴⁺ and 56% of [Pt₄(NH₃)₈(C₄H₆NO)₄]⁵⁺.

The Platinum Benzoic Acid Blues—A New Class of Blue Platinum Compounds

T. RAMSTAD and J. D. WOOLLINS, *Transition Met. Chem.*, 1985, **10**, (4), 153-155

The preparation of Pt blues from Pt(NH₃)₂(H₂O)₂²⁺ and benzoic or phthalic acids is described. The compounds were characterised and unlike pyrimidine blues the Pt blues appear not to be ionic.

Unique Structural Features of a Rh₆- μ_4 -t-BuAs Complex, Formed via As-C Bond Cleavage. Synthesis and Structure of a Rh₆ Pentagonal Pyramid: Rh₆(CO)₉(μ -t-Bu₂As)₂(μ_4 -t-BuAs)

R. A. JONES and B. R. WHITTLESEY, *J. Am. Chem. Soc.*, 1985, **107**, (4), 1078-1079

The synthesis, characterisation and X-ray crystal structure of the title complex was studied. It is thought to be the first example of a Rh₆ cluster where the framework is a pentagonal pyramid. Formation of the complex involves an As-C bond cleavage giving a t-BuAs unit bound to the cluster in a unique bridging manner with one As-Rh bond passing through the Rh₅ plane. Other unique features are described.

A Tetrairidium Cluster with a Bridging SO₂: The Synthesis, Fluxional Behaviour and Crystal Structure of Ir₄(CO)₉(μ_2 -CO)₂(μ_2 -SO₂)

D. BRAGA, R. ROS and R. ROULET, *J. Organomet. Chem.*, 1985, **286**, (1), C8-C12

The reaction of SO₂ with Ir₄(CO)₁₁(norborn-2-ene) yields the title cluster compound. X-ray diffraction shows that this compound contains a SO₂ ligand and two CO groups, all three bridging between the basal metal atoms. The lowest energy CO scrambling process has been determined by ¹³C NMR studies. The thermal stability and high solubility of this compound, compared to Ir₄(CO)₁₂ make it a good starting material for the synthesis of other clusters.

ELECTROCHEMISTRY

A Simultaneous Voltammetric and UV-Visible Reflectance Spectroscopic Investigation of the Adsorption of Carbon Monoxide on a Platinum Electrode in Aqueous Solution

N. COLLAS, B. BEDEN, J. M. LEGER and C. LAMY, *J. Electroanal. Chem. Interfacial Electrochem.*, 1985, **186**, (1 and 2), 287-297

The adsorption of CO on a smooth Pt electrode was studied by in situ u.v.-visible reflectance spectroscopy. Two types of adsorbed CO species were detected, depending on both the electrode potential and the degree of coverage. It is concluded that bridge bonded CO is adsorbed first at low coverage while linearly bonded CO predominates at high.

Electrocatalytic Oxidation of As(III). II. Kinetic Studies at Pt Electrodes

T. D. CABELKA, D. S. AUSTIN and D. C. JOHNSON, *J. Electrochem. Soc.*, 1985, **132**, (2), 359-364

The kinetics of As(III) electrocatalytic oxidation at a Pt rotating disc electrode were studied. PtOH formation was the first step in the production of surface oxides at Pt electrodes. The OH is reversibly adsorbed and can be stabilised by place exchange with surface Pt atoms to give OHPt, and ultimately oxidised further to give PtO. It is concluded that PtOH is the O transfer agent in the oxidation.

On the Electrosorption of Oxygen Species and Adlayer Growth on Noble Metal Surfaces

M. PEUCKERT, *J. Electroanal. Chem. Interfacial Electrochem.*, 1985, **185**, (2), 379-391

The surface chemistry of adsorption and surface phase formation on Pt, Rh, Ir and Au single crystal electrodes in 0.5M H₂SO₄ was studied between 0-4V versus a standard hydrogen electrode by XPS and cyclic voltammetry. Both methods gave complementary results which were interpreted as potential-dependent changes from physisorption of water to adsorption of hydroxyl groups, hydroxide film formation and eventual growth of thick adlayers of oxyhydroxide (Ir, Rh, Au) or hydroxide (Pt). (65 Refs.)

Electrocatalysts on Supports—III. Electrocatalytic and Adsorption Properties of Microdeposits and Thin Films of Platinum Group Metals

V. S. BAGOTZKY and A. M. SKUNDIN, *Electrochim. Acta*, 1985, 30, (4), 485–491

The adsorption and electrocatalytic properties of microdeposits of Rh on Au, Pd on Nb, Ru and Os on Ti and Pd thin films on glass C and Ni have been investigated. H adsorption on Rh and Ru microdeposits is characterised by a low binding energy, and on Pd films by a high binding energy. The cathodic H evolution rate on Ru microdeposits and Pd films on glass C and Ni is lower than those on the corresponding bulk metals.

Photoelectron Spectroscopic Studies of Electrode and Related Surfaces

P. M. A. SHERWOOD, *Chem. Soc. Rev.*, 1985, 14, (1), 1–44

A review of XPS studies of electrode surfaces and related surfaces is presented. XPS gives useful chemical information and is generally less destructive than other surface science methods. Noble metals present less problems over sample transfer than non-noble surfaces where oxidation may occur. Consideration is given to the structure of the electrode surface, anaerobic transfer, electrochemical cells, non-aqueous electrolyte systems, complex systems with mixed oxidation state oxides and variations with electrolyte concentration, electrochemically prepared surfaces, gas evolution electrodes, and Ru, Pd, Rh, Ir, Pt electrodes. (228 Refs.)

Electrochemical Reduction of Carbon Dioxide to Methane, Methanol, and CO on Ru Electrodes

K. W. FRESE and S. LEACH, *J. Electrochem. Soc.*, 1985, 132, (1), 259–260

Electroplated Ru/C and Ru/teflon electrodes were tested for CO₂ electrolysis in Na₂SO₄ or H₂SO₄ electrolytes. For Ru/C CH₄ yield increased with increasing temperature. The CH₄ could also be produced in the absence of C, using Ru/teflon electrodes. Small amounts of CH₃OH and CO were produced in local open circuit conditions.

PHOTOCONVERSION

Investigation of the Mechanism of Hydrogen Evolution during Photocatalytic Water Decomposition on Metal-Loaded Semiconductor Powders

R. BABA, S. NAKABAYASHI, A. FUJISHIMA and K. HONDA, *J. Phys. Chem.*, 1985, 89, (10), 1902–1905

The active sites for photocatalytic H₂ evolution have been identified for Pt, Pd, Ru, Ni and Sn metals loaded on TiO₂ suspensions by measuring the H isotope effect of the gases produced by water photodecomposition. The mechanism of H evolution is discussed, and the site is assigned mainly to the loaded metal, when the deposited metal is active.

Photocatalytic Systems with Light-Sensitive Coordination Compounds and Possibilities of their Spectroscopic Sensitization—An Overview

H. HENNIG and D. REHOREX, *Coord. Chem. Rev.*, 1985, 61, 1–53

The purpose of this review of photocatalytic reactions of light sensitive co-ordination compounds is to examine areas not extensively reviewed in English. Photoassisted reactions, the application of both photoinduced catalytic and photoassisted reactions mediated by light-sensitive complex compounds, especially photoinduced homogeneous catalysis of olefins and other photocatalytic organic syntheses, photocatalysis and unconventional photographic processes; the storage and conversion of solar energy, and photo polymerisations, are reviewed. Various platinum group metal complexes and their reactions are discussed. (281 Refs.)

Electrochemiluminescence of Osmium Complexes. Spectral, Electrochemical and Mechanistic Studies

H. D. ABRUNA, *J. Electrochem. Soc.*, 1985, 132, (4), 842–849

Detailed electrochemical, spectral and electrochemiluminescence (ECL) studies are presented for Os bipyridine and Os phenanthroline complexes. ECL was observed for a large number of complexes, but was less than expected. Surface ECL was observed when the complex is immobilised on the surface of the electrode. There was a good correlation between the observed ECL intensity and the solution luminescence quantum yield.

Photoelectrochemical Oxidation of Halide Ions at Naked, Catalytically Modified, and Polymer-Coated n-CdS Electrodes in Aqueous Media

K. RAJESHWAR, M. KANEKO, A. YAMADA and R. N. NOUFI, *J. Phys. Chem.*, 1985, 89, (5), 806–811

Photoanodes made of n-CdS have been stabilised in Cl₂- and Br₂-containing aqueous media by the use of a catalytically modified polymer coating of RuO₂. The RuO₂ was the catalyst in a polymer matrix comprising a PS backbone with pendant Ru(bpy)₃²⁺ moieties. Photoanodic corrosion of the n-CdS was suppressed by the coating. Photovoltages of up to 1.61 V were attained for the modified n-CdS/aqueous electrolyte interface comprising the Cl⁻/Cl₂ redox system at ~85 mW/cm². Implications for storage photoelectrochemical systems are discussed.

Photosensitized Cleavage of Acetylene to Methane

Y. DEGANI and I. WILLNER, *J. Chem. Soc., Chem. Commun.*, 1985, (10), 648–650

Photosensitised reductive cleavage of C₂H₂ to CH₄ is accomplished in an aqueous solution that includes [Ru(bpy)₃]²⁺ as sensitiser, triethanolamine as electron donor, and a [RuL₅(H₂O)]²⁺ complex that acts as electron acceptor and catalyst in the process.

Photoinduced Excited-State Reactions of Ruthenium(II) Complexes in Multiphase Systems

S. L. BUELL, Ph.D. Thesis, Univ. of Virginia, 1983, *Diss. Abstr. Int. B*, 1985, **45**, (7), 2171-B

A new heterogeneous photocatalyst utilising $[\text{Ru}(\text{bpy})_3]^{2+}$ irreversibly bound to a strongly acidic cation exchange resin is described. The limiting quantum yield for the photosensitised production of $^1\text{O}_2$ in methanol is 0.90, and the photooxidation yield for $^1\text{O}_2$ scavenging is 77%. Water added to the sensitiser decreases the photooxidation yield, but a water saturated sensitiser gives yields >20%. As a $^1\text{O}_2$ generator in methanol the $[\text{Ru}(\text{bpy})_3]^{2+}$ is comparable to homogeneous Rose Bengal and superior to heterogeneous Rose Bengal.

Highly Efficient Sensitization of Titanium Dioxide

J. DESILVESTRO, M. GRÄTZEL, L. KAVAN and J. MOSER, *J. Am. Chem. Soc.*, 1985, **107**, (10), 2988-2990

High efficiencies in the sensitisation of colloidal anatase particles and polycrystalline electrodes has been achieved on using tris(2,2'-bipyridyl-4,4'-dicarboxylate)Ru(II) dichloride as a sensitiser. A 44% incident light to current conversion efficiency was achieved.

Homogeneous Catalysis of the Photoreduction of Water. 6. Mediation by Polypyridine Complexes of Ruthenium(II) and Cobalt(II) in Alkaline Media

C. V. KRISHNAN, B. S. BRUNSCHWIG, C. CREUTZ and N. SUTIN, *J. Am. Chem. Soc.*, 1985, **107**, (7), 2005-2014

The emission from (polypyridine)Ru(II) complexes is quenched by (polypyridine)Co(II) complexes by parallel oxidative, reductive and energy-transfer pathways. The oxidative route is the basis for a new water photoreduction sequence—in mixed acetonitrile-water solvents relatively high cage-escape yields of $\text{Ru}(4,7\text{-}(\text{CH}_3)_2\text{phen})_3^{3+}$ and $\text{Co}(\text{bpy})_3$ are obtained. The Ru(III) complex is reduced by TEOA and the $\text{Co}(\text{bpy})_3$ reacts with water and/or TEOAH^+ to give H_2 . The maximum H_2 quantum yield obtained is 0.29 in 50% acetonitrile-water.

ELECTRODEPOSITION AND SURFACE COATINGS

On the Nature of Hydrogen in Electrolytic Palladium Precipitates. Optimisation of the Coulometric Methods of Measurement

D. WALZ, F. FRIEDRICH and CH. J. RAUB, *Metalloberflaechen*, 1985, **39**, (3), 99-103

H_2 in the crystal lattice of electrolytic Pd precipitates impairs mechanical properties. From the H_2 contents inferences on the state of the electrolyte and working conditions can be drawn. An improved method of determining H_2 contents in Pd layers in a relatively short time is described.

LABORATORY APPARATUS AND TECHNIQUE

A New Method of pH Control by Use of a Polypyrrole Coated Electrode

M. OKANO, A. FUJISHIMA and K. HONDA, *J. Electroanal. Chem. Interfacial Electrochem.*, 1985, **185**, (2), 393-396

By means of a polypyrrole coated Pt anode and a Pt counter electrode the pH of an aqueous solution can be changed quickly. A pH change between 4 and 10 was obtained.

Pyroelectric Enthalpimetric Detection

A. D'AMICO and J. N. ZEMEL, *J. Appl. Phys.*, 1985, **57**, (7), 2460-2463

High sensitivity and well resolved thermal response curves were obtained with a pyroelectric gas analyser which used Pd and Au electrodes on a LiTaO_3 wafer.

HETEROGENEOUS CATALYSIS

Catalytic Ignition and Heat Release of Fuel/Air Mixtures

P. CHO, Ph.D. Thesis, Northwestern Univ., 1984, *Diss. Abstr. Int. B*, 1985, **45**, (7), 2279-B

Ignition and heat release rates of fuel/oxygen/nitrogen over Pt wires were studied by microcalorimetry. Fuels studied were propane, butane, propylene, ethylene, CO and H_2 . For very low Reynolds number the flow velocity has negligible influence on ignition temperature. Variation in fuel concentration was an important factor as ignition temperatures of propane and butane decrease as the concentrations are increased from lean to rich mixtures, while the opposite trend is observed for propylene, ethylene, CO and H_2 . The effect of O concentration was also studied. Heat release rate showed H_2 /air mixture was diffusion limited.

Poisoning of Supported Platinum Catalysts: Deactivation by Carbon Monoxide for Methylcyclopropane Hydrogenolysis

D. E. DAMIANI, Ph.D. Thesis, Northwestern Univ., 1984, *Diss. Abstr. Int. B*, 1985, **45**, (7), 2244-B

The characterisation of a series of $\text{Pt}/\text{Al}_2\text{O}_3$ and Pt/TiO_2 catalysts by methylcyclopropane hydrogenolysis under different poisoning conditions was investigated, CO being the main poison used. The apparent activation energy for isobutane and n-butane formation slightly increased with increasing poisoning, when CO pulses were injected to the fluidised catalyst bed. Poisoning by partial desorption of preadsorbed CO gave similar results when poisoning was extensive. CO and H_2 coadsorption showed that when the poison and H_2 compete for adsorption sites, the relative strengths of their adsorptions is important in determining the deactivation rate. A Pt/TiO_2 catalyst free of SMSI lost activity faster than similar $\text{Pt}/\text{Al}_2\text{O}_3$ or Pt/SiO_2 catalysts for comparable levels of poisoning.

Improved H₂-D₂ Exchange Activity of Pt and Pd by UHV Treatment

S. NISHIYAMA, S.-I. MATSUURA, H. MORITA, S. TSURUYA and M. MASAI, *Appl. Catal.*, 1985, 15, (1), 185-195

The activity of polycrystalline Pt and Pd catalysts for the H₂-D₂ exchange reaction was enhanced by heating them at temperatures higher than 673K at 10⁻⁷ Pa for several hours. The enhanced activity is not ascribed to the desorption of contaminants by the UHV and heat treatment, but may be caused by surface rearrangement.

Behavior of Automotive Noble Metal Catalysts in Cycled Feedstreams

H. MURAKI, H. SHINJOH, M. SOBUKAWA, K. YOKOTA and Y. FUJITANI, *Ind. Eng. Chem., Prod. Res. Dev.*, 1985, 24, (1), 43-49

The response of Pt, Pd and Rh catalysts to perturbations in the feedstream stoichiometry were examined in laboratory experiments. NO, CO and hydrocarbon conversions were measured during cycled and steady feeds of equivalent stoichiometry. The activities of Pt and Pd catalysts were improved, particularly for NO, by a cycled feed. The light-off performance also improved during cycled feeding, due to the periodic operation. The order of periodic operation effect was Pt > Pd > Rh. The optimum frequencies for the maximum conversion increased with increasing amplitude and temperature.

Application of High Resolution Analytical Electron Microscopy to the Analysis of Automotive Catalysts

R. K. HERZ, E. J. SHINOVSKIS, A. DATYE and J. SCHWANK, *Ind. Eng. Chem., Prod. Res. Dev.*, 1985, 24, (1), 6-10

An automobile oxidation catalyst, which had been taken from an automobile driven for 34,800km of normal use was analysed by electron microscopy and compared to a fresh catalyst. It was found that there was no loss of Pt and Pd and no change in the Al₂O₃ support. Poison concentrations were too low to explain a loss in CO oxidation activity. Metal particles in the aged sample were 20-30nm in diameter, compared to 1-2nm in diameter for the fresh sample, this showing that sintering and loss of metal surface area were primarily responsible for the decreased CO conversion.

Periodic Operation Effects on Carbon Monoxide Oxidation over Noble Metal Catalysts

H. MURAKI, H. SOBUKAWA and Y. FUJITANI, *Nippon Kagaku Kaishi*, 1985, (2), 176-181

The periodic effects of the CO-O₂ reaction over Pt, Pd, Rh, Ru and Ir catalysts, supported on α -Al₂O₃ were examined. The period of the feed composition was varied from 0.1-20 s. The average reaction rate was significantly increased by injecting CO and O₂ periodically and alternately to the reactor, compared to the steady state position. The optimum period for the maximum CO conversion increased in order Rh < Pd = Ru < Pt < Ir and with a decrease in temperature and stoichiometric 2[O₂]:[CO] ratio.

Hydrogenation of Buta-1,3-diene on Supported Metal Catalysts in Aqueous Solution. Part 1.—Differences in the Catalytic Action of Al₂O₃-Supported Pt, Pd, Rh and Ru Catalysts

K. SHIMAZU and H. KITA, *J. Chem. Soc., Faraday Trans. 1*, 1985, 81, (1), 175-183

The catalytic action during the deuteration of buta-1,3-diene on Pt, Pd, Rh and Ru catalysts, supported on Al₂O₃ in 0.5 mol/dm³ D₂SO₄ has been examined. Results are discussed in terms of two steps, namely the formation of the half-hydrogenated species and the ionisation of adsorbed H. The rate for the former step is Pd > Pt >> Rh > Ru and for the latter step the rate is in the order Pt >> Pd > Rh > Ru.

Effect of Titania on the Chemisorption and Reaction Properties of Pt

R. A. DEMMIN, C. S. KO and R. J. GORTE, *J. Phys. Chem.*, 1985, 89, (7), 1151-1154

The unusual adsorption and reaction properties observed on Pt/TiO₂ catalysts for CO and H₂ chemisorption, and reactions have been reproduced on a Pt foil with a TiO₂ overlayer. The TiO₂ prevents adsorption of CO and H₂ but does not prevent the Pt from catalysing the methanation. The methanation may be structure sensitive on Pt and this sensitivity may explain the different reactivities obtained on catalysts with different supports.

Transition Metals in Organic Synthesis: Hydroformylation, Reduction and Oxidation, Annual Survey Covering the Year 1983

L. MARKÓ, *J. Organomet. Chem.*, 1985, 283, (1-3), 221-337

A survey for 1983 covering hydroformylation, using Pt and Rh catalysts, heterogeneous catalyst systems of supported complexes; the water gas shift reaction, reductions with CO + H₂O; hydrogenations and reductions, with Pt, Pd, Rh, Ir, Ru and Os catalysts being used; diene and alkyne hydrogenation with Pt, Pd, Ir and Rh catalysts; hydrogen transfer reactions, reductions with molecular H₂ and oxidations, are reviewed. (521 Refs.)

Initial Changes of the Catalytic Properties of Platinum Containing Catalysts. II. Selectivity Changes of Mono- and Bimetallic Pt/Al₂O₃ Catalysts

Z. PAÁL, M. DOBROVOLSZKY, J. VÖLTER and G. LIETZ, *Appl. Catal.*, 1985, 14, (1-3), 33-46

Profound changes have been observed in the product composition of n-hexane transformations over Pt, Pt-Sn and Pt-Pb supported on Al₂O₃ during the initial period of the catalyst lifetime. The number of fragments per hexane molecule decomposed decreased with decreasing cracking activity over each catalyst. Isomerisation selectivity increased over bimetallics after the first few pulses, which was partly due to acid isomerisation over Pt-Pb/Al₂O₃. Addition of Sn increases aromatisation and decreases cracking.

Effects of Oil Phosphorus on Deactivation of Monolithic Three-Way Catalysts

W. B. WILLIAMSON, J. PERRY, H. S. GANDHI and J. L. BOMBACK, *Appl. Catal.*, 1985, **15**, (2), 277-292

The deactivation of Pt-Rh monolithic automotive three-way catalysts by P and Zn from engine oil-derived contaminants has been investigated. The combustion of isooctane containing a ten-fold excess of Zn dialkyldithiophosphate (ZDP) oil additive decreased 3-way conversions substantially when compared to normal oil consumption levels. The combustion of isooctane containing Zn-free cresyl diphenyl (CDP) phosphate gave greater P-retention on the catalyst than for ZDP-containing fuel, but CDP was much less detrimental to three-way activity than ZDP. P was less of a poison than Pb for three-way catalysis. Mechanisms are discussed.

Hydrogenation of Alkenes and Alkynes Catalyzed by Polymer-Bound Palladium(II) Complexes

S. D. NAYAK, V. MAHADEVAN and M. SRINIVASAN, *J. Catal.*, 1985, **92**, (2), 327-339

A polymer-supported Pd(II) species was prepared by oxidative addition between Pd(PPh₃)₄ and chloromethylated crosslinked PS. This catalyst was used for the hydrogenation of alkenes and alkynes under mild conditions. Quantitative data on hydrogenation rates, recycling efficiency of the catalyst and solvent effects on the reaction are presented.

An Infrared Study of the Hydrogenation of Carbon Dioxide on Supported Rhodium Catalysts

M. A. HENDERSON and S. D. WORLEY, *J. Phys. Chem.*, 1985, **89**, (8), 1417-1423

An i.r. study of the methanation of CO₂ on supported Rh catalysts was performed. Turnover frequencies are in the order TiO₂ > Al₂O₃ > SiO₂. CH₄ was the only hydrocarbon product observed. CO₂ hydrogenation turnover frequencies are larger than those for CO under similar reaction conditions. A key surface intermediate during methanation is a carbonyl hydride species which can be produced in the absence of H₂ by migration of H from the support to Rh. The CO₂ dissociation was enhanced by the presence of H₂ and impurity B.

Decomposition of Formic Acid on Supported Rh Catalysts

F. SOLYMOSI and A. ERDŐHELYI, *J. Catal.*, 1985, **91**, (2), 327-337

The decomposition of HCOOH was studied on supported Rh catalysts in a flow reactor at 380-520K. The dominant process in the decomposition was dehydrogenation which followed first-order kinetics. The activity of the catalysts, based on turnover frequencies decreased in the order TiO₂ > Al₂O₃ > MgO ≈ SiO₂ of their supports. CO in the gas stream inhibited the reaction. Weakly held HCOOH, adsorbed CO and formate species were on the surface during the reaction. (46 Refs.)

Reduction of NO by H₂ over Silicon-Supported Rhodium: Infrared and Kinetic Studies

W. C. HECKER and A. T. BELL, *J. Catal.*, 1985, **92**, (2), 247-259

The kinetics of NO reduction by H₂ were investigated over a Rh/SiO₂ catalyst. Catalyst pretreatment determined specific activity and product selectivity. Pre-oxidation in NO increases the NO reduction activity to 50% over that observed when the catalyst is prereduced. Pre-oxidised catalyst favours N₂ formation. At NO conversion levels below 60% the surface is saturated by adsorbed NO.

Methane Synthesis in the H₂O + CO Reaction over Titania-Supported Rh and Rh-Pt Catalysts

F. SOLYMOSI, A. ERDŐHELYI and I. TOMBÁ CZ, *Appl. Catal.*, 1985, **14**, (1-3), 65-67

Rh/TiO₂ was found to be a very active catalyst for CH₄ formation in the H₂O + CO reaction and its catalytic activity was enhanced by a factor of 5 by the presence of Pt.

Selective Reduction of Various Functional Groups and Carbonylation of Olefins Using CO and H₂O in the Presence of Rhodium Cluster Catalysts

K. KANEDA, M. KOBAYASHI, T. IMANAKA and S. TERANISHI, *Nippon Kagaku Kaishi*, 1985, (3), 494-502

The water gas shift reaction and its application to the reduction of various functional groups and to the carbonylation of olefins were studied using Rh carbonyl complex amine (or pyridine) systems. At 700 mm Hg for the CO pressure and 100°C Rh₆(CO)₁₆-ethylenediamine has high catalytic activity for the water gas shift reaction. Heterogenisation of Rh₆(CO)₁₆ on diaminated PS increases its catalytic activity.

Selective Hydrogenation of α,β -Unsaturated Carbonyl Compounds and Nitriles Catalyzed by Polymer-Supported Rhodium Carbonyl Complexes

T. KITAMURA and T. JOH, *Nippon Kagaku Kaishi*, 1985, (3), 473-478

The hydrogenation of α,β -unsaturated carbonyl compounds and nitriles with CO and water was investigated using Rh carbonyl clusters on resin beads. Amberlite IRA-93 and Amberlyst A-21 beads were the best. Hydrogenation proceeded in a dioxane:hexane ratio of 3:7. Rh species partially migrated during the reaction from the resin beads to the solution in THF. C=C and α,β -unsaturated carbonyl compounds and nitriles were selectively hydrogenated. Simple aldehydes were hydrogenated to alcohols. These resin-supported catalysts were stable under N₂ or CO atmospheres and could be reused without loss of catalytic activity. The hydrogenation rates with resin-supported catalysts were greater than those with the homogeneous.

Structure and Reactivity of Aromatic Polymers/Ruthenium Catalysts

F. CIARDELLI and P. PERTICI, *Z. Naturforsch. B*, 1985, **40**, (2), 133-140

Ru/PS systems have been examined by EXAFS, TEM and i.r. and Raman spectroscopies. A structure based on small metal clusters bound to the polymer by a single Ru-arene binding is proposed. The validity of this approach was confirmed by making a similar product from poly-1-vinylnaphthalene in place of PS. Both systems were active for hydrogenation of a large variety of unsaturated groups such as olefinic double bonds, mononuclear aromatic hydrocarbons, ketones, nitriles, nitroaromatics and oximes. Catalytic activity, chemio- and stereoselectivities are discussed in terms of the proposed structure.

Carbon-Supported Fe-Ru Catalysts Prepared from Stoichiometric Mixed-Metal Carbonyl Clusters

M. KAMINSKY, K. J. YOON, G. L. GEOFFROY and M. A. VANNICE, *J. Catal.*, 1985, **91**, (2), 338-351

Highly dispersed Fe-Ru bimetallic crystallites were obtained on an amorphous C black using mixed-metal carbonyl precursors. The catalysts were characterised by chemisorption of CO and H₂ at 195 and 300K, and their kinetic properties in the CO hydrogenation reaction were determined. The presence of Ru helped reduction of the Fe and activated the clusters at 473K. Surface enrichment in Fe occurred in the small crystallites after reduction. Turnover frequencies for CH₄ and total hydrocarbon formation increased in parallel with the increase in surface Ru concentration, but turnover frequency for CO₂ smoothly decreased. Scanning transmission electron microscope micrographs showed a raft-like structure for the metal crystallites in the small pore structure of the C, which may be responsible for differences in catalytic behaviour between C and other supports. (45 Refs.)

HOMOGENEOUS CATALYSIS

Palladium-Catalyzed Carbonylation of Organic Halides with Terminal Acetylenes in the Presence of Amines—Novel Acetylenic Ketone Synthesis

M. TANAKA, T. KOBAYASHI and T. SAKAKURA, *Nippon Kagaku Kaishi*, 1985, (3), 537-546

Organic halides were carbonylated with terminal acetylenes by Pd complexes in the presence of bases at 20 atm of CO and 120°C to give acetylenic ketones. Phosphine basicity, methylene chain length or framework between the two phosphine groups profoundly affected the reactivity. Arsines accelerated the insertion of CO compared to phosphines. Using strong bases such as triethylamine and tripropylamine was essential for high yield synthesis of 1,3-diphenyl-2-propyn-1-one. This new reaction could be applicable to a variety of aromatic heteroaromatic and vinylic halides combined with terminal acetylenes. (56 Refs.)

Palladium Chloride and Polyethylene Glycol Promoted Oxidation of Terminal and Internal Olefins

H. ALPER, K. JANUSZKIEWICZ and D. J. H. SMITH, *Tetrahedron Lett.*, 1985, **26**, (19), 2263-2264

Both terminal and internal olefins can be efficiently converted to ketones in polyethylene glycol and water using Pd chloride as catalyst.

Palladium Catalysed Reaction of Butadiene Monoxide with Carbon Dioxide

T. FUJINAMI, T. SUZUKI, M. KAMIYA, S.-J. FUKUZAWA and S. SAKAI, *Chem. Lett. (Jpn.)*, 1985, (2), 199-200

CO₂ readily reacts under mild conditions with 1,3-butadiene monoxide in the presence of a catalytic amount of tetrakis(triphenylphosphine)-Pd under ordinary pressure at 0°C to give vinyl ethylene carbonate in quantitative yield.

Incorporation of a Recyclable Surface-Active Electron Donor in Synthetic Vesicles. Application to Photosensitized Hydrogen Formation by Vesicle-Stabilized Rh-Coated Colloidal CdS Particles

R. RAFAELOFF, Y.-M. TRICOT, F. NOME, P. TUNDO and J. H. FENDLER, *J. Phys. Chem.*, 1985, **89**, (7), 1236-1238

Colloidal Rh-coated CdS particles were in situ generated in thiol-functionalised surfactant/dioctadecyldimethylammonium chloride (DODAC) mixed vesicles. Under u.v. irradiation the surfactant acted as a recyclable electron donor and promoted H generation. This vesicle-integrated electron donor could be chemically regenerated to resume H production at the same rate as during its first oxidation. This is a new concept in surfactant stabilised colloidal semiconductor system and makes a cyclic process of H generation possible.

Alkylation of Benzene with α -Diazoketones via Cycloheptatrienyl Intermediates

M. A. MCKERVEY, D. N. RUSSELL and M. F. TWOHIG, *J. Chem. Soc., Chem. Commun.*, 1985, (8), 491-492

The combination of Rh(II)trifluoroacetate and trifluoroacetic acid catalysts was found to provide an efficient means of benzene alkylation and produced a range of alkyl and aryl benzyl ketones in excellent yields in one operation. The catalysts were used sequentially.

Ruthenium-Catalysed Oxidation of Secondary Amines to Imines Using *t*-Butyl Hydroperoxide

S.-I. MURAHASHI, T. NAOTA and H. TAKI, *J. Chem. Soc., Chem. Commun.*, 1985, (9), 613-614

The oxidation of secondary amines by Ru(II) complexes, such as RuCl₂(PPh₃)₃ and *t*-butyl hydroperoxide in benzene as oxidant under mild conditions, gave corresponding imines in high yields.

The Selective Homogeneous Hydrogenation of Alkynes in the Presence of Alkenes Catalyzed by [RuH(PMe₂Ph)₅]PF₆

M. O. ALBERS, E. SINGLETON and M. M. VINEY, *J. Mol. Catal.*, 1985, **30**, (1-2), 213-217

The homogeneous hydrogenation of alkynes with cationic Ru(II) complexes [RuHL₅]PF₆ (L = PMe₂Ph, P(OMe)₂Ph, PMe₂(C₆H₄OMe-o), AsMe₃) as catalysts in which the title complex selectively reduces internal and terminal alkynes without hydrogenating the corresponding olefin is reported. This complex is a precursor to the most efficient catalyst known to date for the selective hydrogenation of alkynes. The catalyst shows negligible tendency to isomerise or hydrogenate olefinic substrates.

Ruthenium-Catalyzed Oxidation of Alcohols with Sodium Bromate

Y. YAMAMOTO, H. SUZUKI and Y. MORO-OKA, *Tetrahedron Lett.*, 1985, **26**, (17), 2107-2108

A convenient and effective method for the oxidation of secondary alcohols to ketones using NaBrO₃ in the presence of catalytic amounts of Ru trichloride hydrate is described.

CHEMICAL TECHNOLOGY

Catalytic Etching of Platinum during Ethylene Oxidation

N. L. WU and J. PHILLIPS, *J. Phys. Chem.*, 1985, **89**, (4), 591-600

Catalytic etching of Pt foils during ethylene oxidation was studied by SEM and TEM. The etching was a strong function of surface temperature and C₂H₄ : O₂ ratio in the gas phase. A novel model was developed to explain all the regions of the phase diagram, and showed five regions on the plane defined by surface temperature and O₂ : C₂H₄ ratio and three types of catalytic etching. The etching was attributed to formation of methylene radicals above ~770K in the boundary layer over the catalyst.

NEW PATENTS

METALS AND ALLOYS

Magneto-resistive Materials

INTERNATIONAL BUSINESS MACHINES CORP.

U.S. Patent 4,476,454

New magneto-resistive materials are alloys of Ir with Fe, Ni and/or Co.

Permanent Magnet Materials

RESEARCH INSTITUTE OF ELECTRIC & MAGNETIC ALLOYS

U.S. Patent 4,481,045

A permanent magnet having a high coercive force and large maximum energy product is an alloy of Fe with 25-40 at.% Pd or 19.5 at.% Pd and 0.1-27.5 at.% Ag.

TEMPERATURE MEASUREMENT

Semiconductor Chip with Platinum Thin Film Resistor for Temperature Sensing

Res. Discl., 1985, (251), 141

A Pt resistor is formed on a semiconductor chip and is connected as a temperature sensitive resistor in a temperature measuring circuit. The resistor is a thin film and is ~100µm long, 0.5µm wide and a few Å thick. It can be formed by ion beam sputtering, patterned by photoresist techniques and etched by ion beam milling. The TCR is very reproducible. The Pt resistor can operate at high temperatures and resists oxidation.

Interpolation Procedures for Ceramic-Encapsulated Rhodium-Iron Alloy Resistance Thermometers in the Temperature Range 77 to 273K

L. M. BESLEY, *J. Phys. E*, 1985, **18**, (3), 201-205

The thermometric characteristics of six ceramic-encapsulated Rh-Fe alloy resistance thermometers were studied between 32 and 273.15K. Data are given for the resistance-temperature relationship and the self-heating. Interpolation means were investigated for the range 77-273.15K. An eleven-term polynomial fitted to many points gives a precision of ±0.5mK over this range.

MEDICAL USES

Circadian Timing of Cancer Chemotherapy

W. J. M. HRUSHESKY, *Science*, 1985, **228**, (4695), 73-75

Circadian timing of adriamycin and cis-platin was found to influence toxicity substantially. Administering adriamycin in the morning and cis-platin in the evening caused fewer complications, dose reductions and treatment delays than administering adriamycin in the evening and cis-platin in the morning, in a study of 31 patients with advanced ovarian cancer.

Superconducting Type II Material

STATE UNIVERSITY OF NEW YORK RESEARCH FOUNDATION

U.S. Patent 4,485,152

A new superconducting type II Pd-Cu alloy hydride material includes a contiguous surface at which at least a portion of the alloy region contains H and at least a portion of the Pd region contains H.

Cutting Material

DEGUSSA A.G.

German Offen. 3,319,487

An improved cutting material is a laminate of two to five layers of metal and two to five layers of ceramic. The ceramic is Al₂O₃ or Si nitride and the metal is chosen from Pt, W, Mo, Zr, Hf, Nb, Ta, Au and their alloys.