

ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Interaction of Oxygen with Pt(110)

R. DUCROS and R. P. MERRILL, *Surface Sci.*, 1976, **55**, (1), 227-245

Spectroscopic studies of the interaction of O₂ with Pt(110) showed that above 800°C the O₂ nucleates an elongated (2 × 2) LEED pattern which corresponds to a transition oxide leading eventually to an epitaxial growth of PtO with the (100) face oriented along the [31] direction of the Pt(110) substrate. The PtO overlayer does not react with H₂ or CO but decomposes above 1000°C.

Adsorption of Hydrogen on a Pt(111) Surface

K. CHRISTMANN, G. ERTL and T. PIGNET, *Surface Sci.*, 1976, **54**, (2), 365-392

Spectroscopic and contact potential studies of H₂ adsorption on a Pt(111) surface showed that H₂ adsorbed dissociatively on Pt(111) with a relatively sticking coefficient and reached at least 50% of monolayer coverage at 150K. The adsorption energy is less than 10 kcal/mole at low coverages and falls continuously for relative coverages over 50% of saturation.

Oxidation of Hydrogen on Polycrystalline Platinum Studied by Molecular Beam Reactive Scattering

N. PACIA and J. A. DUMESIC, *J. Catalysis*, 1976, **41**, (1), 155-167

A technique involving a reactive molecular beam striking a polycrystalline Pt ribbon immersed in a controlled gaseous atmosphere was used to study adsorption, molecular desorption and atomisation of H₂ on Pt at 1350-1700K and pressures <10⁻⁷ torr. The oxidation studies of H₂ at 300-1700K and pressure of <10⁻⁶ torr showed that reaction takes place between O₂ and H₂ chemisorbed species. The activation energy was 20 kcal/mole.

Diffusion Kinetics of Au through Pt Films about 2000 and 6000Å Thick, Studied with Auger Spectroscopy

C. C. CHANG and G. QUITANA, *Thin Solid Films*, 1976, **31**, (3), 265-273

Spectroscopic studies of the diffusion kinetics of Au through Pt films were made on Pt-Au couples with ~2000 and 6000Å Pt films heat treated at 250-350°C in 1 atm N₂ ambient. Au initially diffused across thin (<6000Å) Pt film by grain boundary migration with an over-all activation energy of 0.96 eV for 2250Å Pt films. The out-diffusion rate was inversely proportional to film thickness from about 2000-6000Å.

Platinum-Aluminium, Platinum-Gallium and Platinum-Indium Binary Systems

P. GUEX and P. FESCHOTTE, *J. Less-Common Metals*, 1976, **46**, (1), 101-116

Spectroscopic studies of the binary systems Pt-Al, Pt-Ga and Pt-In showed the existence of PtAl₂ and Pt₃Al compounds and in the Pt-Ga system PtGa₆, Pt₃Ga₇, PtGa₂, Pt₂Ga₈ and PtGa compounds. In the Pt-In system eight intermetallic compounds were found: Pt₃In₇, PtIn₂, Pt₂In₃, PtIn, Pt₆In₅, Pt₂In, Pt₃In₂ and Pt₃In. The differences in the stabilities of the intermediate phases and in the solubilities of the solids are discussed.

Surface Tension and Density of Liquid Pt-Pd, Pt-Si and Rh-Si Alloys

E. L. LUBININ, V. M. VLASOV, N. A. VATOLIN, A. I. CHEGODAEV, A. I. TIMOFEEV and N. YU. NEGODAeva, *Izv. Akad. Nauk S.S.S.R., Metall.*, 1976, (2), 94-97

Studies of the structure of liquid Pt-Pd, Pt-Si and Rh-Si alloys were made by measuring their surface tension and density dependence on concentration and temperature. The results show a weak interaction of the components in the Pt-Pd system and formation of chemical compounds at 33 at.% Pt and 40 at.% Rh in the Pt-Si and Rh-Si systems respectively.

The Structure of Skeleton Platinum, Iridium and Platinum-Iridium Catalysts

N. V. KROPOTOVA, A. D. SEMENOVA, V. I. FADEEVA and G. D. VOVCHEENKO, *Zh. Fiz. Khim.*, 1976, **50**, (2), 384-386

X-ray analysis and electron microscopy were used to study the structure of skeleton Pt, Ir and 10-90% Pt-Ir catalysts. The lattice constant values for skeleton Pt and Ir are shown to differ only slightly from the corresponding values for pure Pt and Ir. The linear dimensions of Pt-Ir crystallites were 30-50Å. The structure of the catalysts depends on the chemical composition during the transition from skeleton Pt to Ir.

Diffusion Mechanisms in the Pd-Au Thin Film System and the Correlation of Resistivity Changes with Auger Electron Spectroscopy and Rutherford Backscattering Profiles

P. M. HALL, J. M. MORABITO and J. M. POATE, *Thin Solid Films*, 1976, **33**, (1), 107-134

Interdiffusion in the Pd-Au thin film system at 175-300°C was studied using electrical and compositional profiling methods. The diffusion coefficients of Pd in the Au grain boundaries were

$\sim 10^{-11}$ cm²/s at 300°C and $\sim 10^{-13}$ at 175°C. The activation energy for the boundary diffusion is lower in the Pd film than in the Au film.

Specific Heat, Electrical Resistance, and other Properties of Superconducting Pd-H Alloys

C. A. MACKLIET, D. J. GILLESPIE and A. I. SCHINDLER, *J. Phys. Chem. Solids*, 1976, **37**, (4), 379-388

Specific heat and electrical resistance for a series of Pd-H alloys with H/Pd atomic ratios of 0.82-0.88 were measured at 1.2-4.2K. Superconductive transitions in the resistance were observed and the specific heat data revealed broad peaks with characteristics depending strongly on H concentration. A marked suppression of superconductive effects, probably due to Fe impurities, was observed in Pd-H alloys based on one particular Pd ingot.

Effects of Contamination on the Interaction of Hydrogen Gas with Palladium: A Review

R. G. MUSKET, *J. Less-Common Metals*, 1976, **45**, (2), 173-183

The effect of contamination in the Pd-H system on the catalytic activity of Pd is discussed. The segregation of bulk impurities at the surface, formation of corrosion products prior to the interaction with H₂ and chemisorption of impurities in the H₂ gas are shown to be the main causes of contamination. Pd/S and Pd/C surface layers affect the Pd/H₂ interaction even when the impurity concentration is <10 p.p.m. General precautions, Pd treatments and H₂-gas purification procedures for the minimisation of the problems are suggested.

Electron Spectroscopic Studies of the Oxidation of Ni-Pd Alloys

K. WANDELT and G. ERTL, *Z. Naturf. A*, 1976, **31**, (2), 205-210

Electron spectroscopy studies were made of the oxidation of polycrystalline samples of Ni-Pd alloys at 600°C and 2×10^{-5} torr O₂. Identical overlayers formed on all samples, except on pure Pd, were identified as NiO. The rate of oxidation was unexpectedly found to increase with increasing Pd content.

Absorption of Hydrogen by Vanadium-Palladium Alloys

D. ARTMAN, J. F. LYNCH and T. B. FLANAGAN, *J. Less-Common Metals*, 1976, **45**, (2), 215-228

The absorption of H₂ by 1-8 at.% V-Pd alloys was studied using pressure-composition isotherms determined at 273-373K. The results show that at a given H₂ content, the equilibrium H₂ pressure progressively increases with V content. The isobaric solubility of H₂ at 1 atm and 298K decreases from H/Pd=0.7 for pure Pd to 0.024 for 6%V-Pd alloy.

Dilatometric Measurements of a Palladium-Alloy, Hydrogen Diffusion Membrane under Operating Conditions

D. FORT and I. R. HARRIS, *J. Less-Common Metals*, 1976, **45**, (2), 247-260

The H₂ solubility in two membranes made of Pd-7.5% Y alloy 0.013cm thick was studied by measuring the membrane deflection and relating this to the simultaneously measured permeability. No hysteresis in the membrane deflections was observed between heating and cooling after hydrogenation but considerable hysteresis due to surface poisoning was found in the flow rates upon heating above 495K. A mechanism for this poisoning and means of reducing it are discussed.

Gadolinium-Rhodium System and Rhodium Alloys with Other Lanthanides. The Alloys of Ruthenium with Gadolinium and Dysprosium and their Magnetic Properties

O. LOEBICH and E. RAUB, *J. Less-Common Metals*, 1976, **46**, (1), 1-6, 7-15

Differential thermal analysis, metallographic and X-ray diffraction techniques were used to study the phase diagrams of Gd-Rh, Gd-Ru and Dy-Ru alloys. The nine intermetallic phases, Gd₃Rh, Gd₇Rh₃, Gd₅Rh₃, Gd₃Rh₂, Gd₄Rh₃, GdRh₃, GdRh, GdRh₂ and GdRh₅, were found in the Gd-Rh system and three new phases, Ln₃Ru, Ln₂Ru and Ln₇Ru₂₇, were found in addition to the already known Laves phase LnRu₂ (Ln = lanthanide) in the Gd-Ru and Dy-Ru systems.

Semiconducting Ternary Oxides of Iridium, Titanium and Calcium: Magnetic and Electrical Properties

B. JEŹOWSKA-TRZEBIATOWSKA, T. NOWAKOWSKI and J. MROZIŃSKI, *Mater. Res. Bull.*, 1976, **11**, (1), 37-41

Studies of magnetic and electrical properties of sintered oxides of a general formula CaIrxTi_{1-x}O₃ (x=0.25, 0.33, 0.50, 0.66 and 0.75) showed that all these compounds exhibit semiconducting properties at 77-700K. A non-linear relation of temperature versus reciprocal magnetic susceptibility was found.

Quenching of the Luminescence of the Tris(2,2'-bipyridine) Complexes of Ruthenium(II) and Osmium(II). Kinetic Considerations and Photogalvanic Effects

C.-T. LIN and N. SUTIN, *J. Phys. Chem.*, 1976, **80**, (2), 97-105

A spectrofluorimetric method was used to study the quenching of the charge-transfer excited states of Ru(bpy)₃²⁺ and Os(bpy)₃²⁺ by O₂, Fe³⁺, Co(phen)₃²⁺, Ru(NH₃)₆³⁺, Os(bpy)₃²⁺ and Fe(CN)₆³⁻. The reduction potential of the Os(bpy)₃²⁺/Os(bpy)₃²⁺ couple was estimated to be -0.96v. The Ru(bpy)₃²⁺-Fe³⁺ system exhibits a large photogalvanic effect.

CHEMICAL COMPOUNDS

π -Allylmetal Chemistry. II. A Novel Method to Prepare π -Allylplatinum(II) Complexes from Allylamines

H. KUROSAWA, *Inorg. Chem.*, 1976, **15**, (1), 120-124
The reactions of several allylic amines with cationic Pt(II) hydrides give certain complexes as described, the amines in which the allylic group in the parent amines is replaced by hydrogen, in varying yields depending on the structure of the allylic moieties in the amines used. Different reactivity patterns of the formation of π -allylplatinum(II) complexes from allylamines and alcohols or ethers with cationic Pt(II) hydrides are discussed in terms of the differences in basicities of the N and O donors towards both Pt and the proton.

Synthesis and Characterisation of Seven-coordinate Hydrido-complexes of Ruthenium with Carborane: X-ray Diffraction Study of 2, 1, 7-[(PPh₃)₂RuH₂C₂B₉H₁₁]

E. H. S. WONG and M. F. HAWTHORNE, *J. Chem. Soc., Chem. Commun.*, 1976, (7), 257-258

Two novel Ru complexes have been prepared via oxidative addition of 7, 8- and 7, 9-C₂B₉H₁₂ to [(PPh₃)₃RuHCl] and one of them, 2, 1, 7-[(PPh₃)₂RuH₂C₂B₉H₁₁], reversibly eliminates its hydride ligands as H₂ when heated in vacuo. Solutions of some of the complexes produced are active in the catalytic hydrogenation of olefins.

ELECTROCHEMISTRY

Boosting the Corrosion Resistance of Electrolytic Chrome Coatings by Palladium Modification

N. D. TOMASHOV, G. P. CHERNOVA and T. A. FEDOSEEVA, *Zashchita Metal.*, 1976, **12**, (1), 3-6

Studies of the corrosion resistance of electrolytic Cr showed that additions of 1-3% Pd increase considerably the resistance of Cr deposits to attack by 20% H₂SO₄ and 5-10% HCl solutions.

A Study of Gas Evolution in Teflon Bonded Porous Electrodes. III. Performance of Teflon Bonded Pt Black Electrodes for H₂ Evolution

A. C. C. TSEUNG and P. R. VASSIE, *Electrochim. Acta*, 1976, **21**, (4), 315-318

Studies of steady-state and potentiostatic transient H₂ evolution made on Teflon bonded Pt black, platinised Pt and Pt foil electrodes in 5N H₂SO₄ at 25°C showed that Teflon bonded electrodes gave the highest performance. The porous hydrophobic Teflon does not allow any expelling of the electrolyte from the pores of the electrode, thus ensuring greater utilisation of the available Pt surface area.

Hydrogen Overpotential and Underpotential at Palladium-black and Platinum-black Surfaces

F. A. LEWIS, A. OBERMANN and G. HODES, *Surface Tech.*, 1976, **4**, (1), 79-87

A square-wave constant-current pulse technique was used to study the η_1 component of H overpotential at Pd-black-coated electrodes of Pd, Pd-Ag, Pd-Pt, Nb and Ta in H-saturated acidic solutions. The results show that η_1 component of overpotential represents a combination of locally higher values of the chemical potential of adsorbed H and lower values of H ion concentration, at or near to surface sites where H is preferentially discharged.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodeposition of Ruthenium Deposits for the Surface Hardening of Electrical Contacts

A. F. BOGENSCHÜTZ, J. L. JOSTAN and W. MUSSINGER, *Galvanotechnik*, 1976, **67**, (2), 98-105

Electrodeposits of Ru deposited from two electrolytes containing (NH₄)₂[Ru(NO)Cl₅] and Na₂[Ru(NO)₄(NO)OH] were studied and the deposition conditions are discussed. Their coating properties are considered and compared with the properties of Rh.

LABORATORY APPARATUS AND TECHNIQUE

Construction of an Inexpensive Platinum Electrode

R. SIMPSON and J. G. BERBERIAN, *Rev. Sci. Instrum.*, 1976, **47**, (2), 198-200

An inexpensive method of producing a chemically inert electrode suitable for conductivity and permittivity measurements, which consists of applying a Pt organometallic compound to a suitable glass substrate and reducing the compound to Pt, is described. Seven to ten layers of Pt are built up to achieve the required properties and the electrode is amenable to Pt blacking. Correct preparation of the glass substrate and careful heat treatment of the individual layers of Pt are found to be essential.

Catalytic Determination of Palladium(II) and Inhibitors by the Application of Palladium(0) Catalysis in the Reduction of Dyes in the Presence of Hypophosphite

V. V. S. ESWARA DUTT and H. A. MOTTOLA, *Anal. Chem.*, 1976, **48**, (1), 80-84

Submicrogram amounts of Pd(II) are determined during Pd(0) catalysis of hypophosphite reduction

of dyes by a variable-time procedure based on the in situ generation of Pd(0). The effect of a series of inhibitors, particularly S-containing species, provides the basis for a sensitive determination of inhibitors at the sub-p.p.m. level.

HETEROGENEOUS CATALYSIS

The Influence of Heat Treatment on the Catalytic Activity of Adsorption Pt/Al₂O₃ Catalysts during the Hydrogenation of Unsaturated Compounds. IV. Hydrogenation of Nitrobenzene

B. ZHANABAEV, D. V. SOKOL'SKII and A. N. SARTAeva, *Zh. Fiz. Khim.*, 1976, 50, (2), 527-529

The influence of calcination treatment in H₂ atmosphere of 0.1-1.0% Pt/Al₂O₃ catalysts on their activity in hydrogenation of nitrobenzene was studied. It is shown that the activity increases with the calcination temperature. This is due to the dissociation of crystals on the carrier surface resulting in a higher degree of dispersion of metal.

Mechanism of Catalysis of Hydrocarbon Reactions by Platinum Surfaces

G. A. SOMORJAI and D. W. BLAKELY, *Nature*, 1975, 250, (5536), 580-583

Studies of the activity of crystal surfaces of platinum, being used as catalysts for a variety of hydrocarbon reactions, and their atomic structure and surface composition show three types of surfaces distinguishable by their reactivities. Pt(111) has low density of surface imperfections compared to the number of surface atoms, Pt(557) has a stable surface structure, and Pt(679) has both high step and high kink densities. Atomic steps and kinks are active sites where H-H and C-H bonds break, additionally kinks break C-C bonds. The structure of the carbonaceous overlayer which covers the catalyst during use also influences the activity.

Kinetics of the Isomerisation of *n*-Hexane on a Bifunctional Catalyst: Pt/SiO₂-Al₂O₃ as a Function of the Metal Loading

F. CHEVALIER, M. GUISET and R. MAUREL, *Compt. Rend., Sér. C*, 1976, 282, (1), 3-5

Studies of the activity of 0.004-0.8% Pt/SiO₂-Al₂O₃ catalysts made during the isomerisation of *n*-hexane showed that activity increased with the increase of the metallic areas and then reached a limit. Simultaneously the order to H was shifted from zero to one. This is in agreement with the usual bifunctional mechanism.

Gas-phase and Liquid-phase Hydrogenation of Acetone on Adsorption Platinum Catalyst

L. V. RUSALINA, L. B. MARTYSHKINA, ZH. V. STREL'NIKOVA, *Zh. Fiz. Khim.*, 1976, 50, (1), 87-90
Studies of gas- and liquid-phase hydrogenation of acetone over Pt/Al₂O₃ catalysts at 40°C show

that the activity in the gas-phase hydrogenation is one order of magnitude higher than in the liquid-phase hydrogenation. This is explained by a local decrease in entropy, and adsorption of molecules of the solvent and acetone, affecting the value of the Pt-H bond energy.

Studies on Catalytic Hydrogenation. I. The Influence on Reaction Rates of the Metal-Carrier Ratio of Solvents and Acidity

R. BALTZLY, *J. Org. Chem.*, 1976, 41, (6), 920-928

Catalytic hydrogenation of cyclohexene, acetophenone, benzene, nitrobenzene and other substrates was carried out over Pt/C, Pd/C and Rh/C in aqueous methanolic and aqueous acetic acid solutions. It is shown that Pt/C is highly sensitive to acidity, whereas Pd/C is sensitive to it only in the reduction of C-O functions. Rh/C is inhibited by acidity in reductions of benzene and acetophenone but not in reduction of cyclohexene.

Transfer Hydrogenation and Transfer Hydrogenolysis. VIII. Hydrogen Transfer from Amines to Olefins Catalysed by Heterogeneous and Homogeneous Catalysts

T. NISHIGUCHI, H. IMAI, Y. HIROSE and K. FUKUZUMI, *J. Catalysis*, 1976, 41, (2), 249-257

Studies of the H₂ transfer from indoline to cycloheptene showed high catalytic activity of Pd/C, Pd/asbestos and Pd-black as well as RuCl₂(PPh₃)₃, RhCl₃·2H₂O, IrCl₃, (NH₄)₂PdCl₄ and RhH(PPh₃)₄. The rate of H₂ transfer was at first proportional to the amine concentration and then became independent of it, showing the poisoning effect of the olefin.

Oxidation of an Automobile Exhaust Gas Mixture by Fibre Catalysts

D. M. NICHOLAS, Y. T. SNAH and I. A. ZLOCHOWER, *Ind. Engng. Chem. Product Res. Dev.*, 1976, 15, (1), 29-35

The conversions of CO, C₂H₄ and C₃H₈ by a reactor packed with Pt impregnated porous fibre catalyst were studied at preheat temperatures of 180-560°C. The results showed that a lesser amount of fibre catalyst carrier performs better than the conventional catalysts (Al₂O₃ and SiO₂ gel beads) under all reaction conditions, when the average pore size of the fibre catalyst is large and the fibre catalyst is tightly packed.

Liquid Hydrogenation of Eugenol over Platinum under Hydrogen Pressure

A. M. SOKOL'SKAYA, D. V. SOKOL'SKII, S. A. RYABININA and A. UALIKHANOVA, *Kinet. Kataliz*, 1976, 17, (1), 236-237

The hydrogenation of eugenol over Pt-black was carried out in H₂O and 96% C₂H₅OH at 10-50°C and H₂ pressure of 10-100 atm. It is shown that the reaction order with respect to H₂ changes from first to zero order depending on the H₂ pressure. The activation energy is 4-6 kcal/mole.

Hydrocracking of *n*-Octane on Platinum-Zeolite Catalysts

A. M. TSYBULEVSKII, V. I. BOCHAROV, I. M. KAL'SHTEIN, L. G. ITTERMAN, V. YU. KONOVALENKO and T. R. BANKOVSKAYA, *Neftekhimiya*, 1976, 16, (1), 38-44

The hydrocracking of *n*-octane was carried out on 0.6 and 0.8% Pt/zeolite Y catalysts, prepared by ion exchange and impregnation methods. It is found that the catalyst containing 0.8% Pt, of which 0.6% is deposited by ion exchange from Pt tetraammoniate solution, and 0.2% by impregnation from H_2PtCl_6 solution, is most active.

Activation of Platinum-Alumina Catalysts for the Hydrogenation of Aromatic Hydrocarbons

A. H. ABOUT-GHEIL and J. COSYNS, *J. Appl. Chem. Biotechnol.*, 1976, 26, (1), 15-22

Studies of 0.35% Pd/ Al_2O_3 catalysts containing 0.0, 0.40 or 0.87% Cl during the hydrogenation of aromatic hydrocarbons showed that chlorination of the catalyst greatly increased its hydrogenation activity. The activation energies obtained for hydrogenation of aromatics over catalysts reduced at 200-500°C were 10.14-6.50 kcal/mole. These energies decreased with increasing Cl content, and with its reduction temperature.

Influence of Tetraethyllead and Lead Scavengers on Oxidation of Carbon Monoxide and Hydrocarbons over Pt and Pd

K. OTTO and G. N. MONTREUIL, *Environ. Sci. Technol.*, 1976, 10, (2), 154-158

The activity of monolithic Pt and Pd catalysts exposed to the combustion products of isooctane fuel containing tetraethyllead (TEL) ethylene dibromide (EDB) and ethylene dichloride (EDC) poisons was studied. A decrease of activity in the oxidation of CO and HC was found only for EDB, but complete recovery of the activity occurred when Br was eliminated. Catalysts containing Pd were deactivated by EDB to a higher degree than catalysts containing Pt. TEL caused permanent deactivation and irreversible loss of the Pt-Pd surface area.

Change in the Surface Layer Composition of Palladium-Rhodium Alloys under the Catalytic Reaction

T. S. USTINOVA, E. S. SHPIRO, V. S. SMIRNOV, V. M. GRYAZNOV, G. V. ANTOSHIN and KH. M. MINACHEV, *Izv. Akad. Nauk, S.S.S.R., Ser. Khim.*, 1976, (2), 441-444

The composition of the surface layer of 5 and 10% Rh-Pd catalysts after dehydrogenation of cyclohexane at $\leq 450^\circ C$ was studied by X-ray photoelectric spectroscopy. The results show an increase of Rh content in the surface layer of the catalyst, which accounts for the increased dehydrogenation rate of cyclohexane to benzene.

$(CO_2B)_{10}RhH_6$ and $(Ni_2B)_{10}RhH_{15}$ as Versatile Catalysts for Hydrogenation, Hydrogenolysis and Methanation Reactions

R. W. MITCHELL, L. J. PANDOLFI and P. C. MAYBURY, *J. Chem. Soc., Chem. Commun.*, 1976, (5), 172-173

Hydrogenation and hydrogenolysis of *cis*-but-2-ene carried out over $(CO_2B)_{10}RhH_6$ and $(Ni_2B)_{10}RhH_{15}$ catalysts supported on glass wool, show that at 62°C the Ni containing catalyst gave almost 50% hydrogenation to *n*-butane increasing to ~100% at 90°C. Hydrogenolysis gave ~100% methane at 300°C. The catalysts were also effective for CO to CH_4 conversion and showed no loss in activity with time (48h) at temperatures up to 500°C.

The NO-CO Reaction in the Presence of Excess O_2 as Catalysed by Iridium

S. J. TAUSTER and L. L. MURRELL, *J. Catalysis*, 1976, 41, (1), 192-195

Studies of 0.1 and 0.001% Ir/ Al_2O_3 catalysts for control of automotive NO_x showed that 90% conversion of NO takes place in the presence of 75% excess of $NO+O_2$ oxidants. The catalyst containing 0.001% Ir required higher temperature to achieve complete removal of CO but the partitioning of CO between NO and O_2 was independent of space velocity and Ir content.

HOMOGENEOUS CATALYSIS

Linear Carboxylic Acid Esters from α Olefins. I. Catalysis by Homogeneous Platinum Complexes

J. F. KNIFTON, *J. Org. Chem.*, 1976, 41, (5), 793-797

The activity and selectivity of ligand-stabilised Pt(II)-Group 4B metal halide complexes in catalysing the homogeneous carbonylation of olefins to carboxylic acid and esters were studied. Catalysts with up to 98 mol.% selectivity were $[(C_6H_5)_3As]_2PtCl_2-SnCl_2$, $[(C_6H_5)_2ClAs]_2PtCl_2-SnCl_2$ and $[(C_6H_5O)_3P]_2PtCl_2-SnCl_2$. The catalyst and olefin composition and the nature of the nucleophilic co-reactant were found to affect both the activity and selectivity of the Pt.

Catalytic Properties of Precious Metal Complexes: Carboxylation of Methanol to Acetic Acid by Rhodium Compounds

D. BRODZKI, C. LECLÈRE, B. DENISE and G. PANNETIER, *Bull. Soc. Chim. Fr.*, 1976, (1-2), 61-65

Studies of the carboxylation of methanol to acetic acid over a Rh complex catalyst, $[RhClcod]_2$ (cod= η -cyclooctadiene-1,5) or $[RhCl(CO)_2]_2$, in methyl iodide at 250-350°C and at 300-700 bars showed that reaction rate was directly proportional to the concentrations of the Rh compound and methyl iodide. The reaction rate is lowest in the case of derivatives of bidentate ligands.

Further Studies on the Homogeneous Hydroformylation of Alkenes by Use of Ruthenium Complex Catalysts

R. A. SANCHEZ-DELGADO, J. S. BRADLEY and G. WILKINSON, *J. Chem. Soc., Dalton Trans.*, 1976, (5), 399-404

Studies of the use of tertiary-phosphine-Ru complexes in the catalytic hydroformylation of alkenes have been carried out and are described. Under the conditions required for the reaction to take place $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2$ is recovered from all the effective mononuclear complexes and may be used repeatedly without apparent loss of catalytic activity. The results suggest the reaction involves $\text{Ru}(\text{H})_2(\text{CO})_2(\text{PPh}_3)_2$ as the principal active catalytic species. $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2$ is also active for the hydrogenation of alkenes and aldehydes, and mechanisms are proposed.

Transfer Hydrogenation and Transfer Hydrogenolysis. IX. Hydrogen Transfer from Organic Compounds to Aldehydes and Ketones Catalysed by Dihydridotetrakis(triphenylphosphine)ruthenium(II)

H. IMAI, T. NISHIGUCHI and K. FUKUZUMI, *J. Org. Chem.*, 1976, 41, (4), 665-671

Studies have shown that even under mild conditions $\text{RuH}_2(\text{PPh}_3)_4$ has excellent catalytic activity for the transfer of hydrogen from ethers, hydroaromatic compounds, tertiary amines and alcohols to aldehydes and ketones. The mechanism of the hydrogen transfer from alcohols to the aldehydes was also studied and data suggest that the rate of

reaction is determined by the coordination of the alcohols to the complex.

ELECTRICAL AND ELECTRONIC ENGINEERING

Schottky Barrier Heights of Nickel-Platinum Silicide Contacts on *n*-type Si

L. E. TERRY and J. SALTICH, *Appl. Phys. Lett.*, 1976, 28, (4), 229-231

Studies of the barrier heights of NiPt silicide-*n*-type Si, and the saturation current density of the diodes, for various concentrations of Ni and Pt showed them to change smoothly from that of NiSi-Si to PtSi-Si with increasing amounts of Pt in the NiPt films. The barrier is 0.69eV for 19 wt.% Pt and the height is 0.78eV for 67 wt.%Pt.

MEDICAL USES

Studies of Rhodium(II) Carboxylates as Anti-tumour Agents

L. C. RAINEN, *Diss. Abstr. B*, 1976, 36, (7), 3299-B

Studies of interactions of Rh(II) carboxylates with synthetic and natural macromolecules showed that they differ in anti-tumour, toxic and inhibitory properties when applied to either *in vivo* or *in vitro* systems. The more potent drugs formed more stable complexes, but the more lipophilic drugs were more effective as anti-tumour agents because of increased permeability into the cell and enzyme active centres.

NEW PATENTS

METALS AND ALLOYS

Platinum Group Metal Alloys

JOHNSON, MATTHEY & CO. LTD.

German Offen. 2,530,245

Alloys suitable for withstanding high temperatures in glassmaking and aircraft consist of at least 40% Ni or Co, up to 30% Cr and up to 15% of one or more of the six Pt group metals. Small amounts of Ti, Al, Mo and W may also be present.

ELECTRODEPOSITION AND SURFACE COATINGS

Electrodeposition of Ductile Palladium

INTERNATIONAL BUSINESS MACHINES CORP.

U.S. Patent 3,920,526

An aqueous electrodeposition bath for electrodepositing non-porous, ductile Pd consists of 16-32 g/l $\text{Pd}(\text{NH}_3)_2 \text{Cl}_2$ and 65-250 g/l of NH_4Cl and aqueous NH_3 to provide a pH ≥ 8.8 .

Electroplating a Gold-Platinum Alloy

U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

U.S. Patent 3,923,612

An aqueous electrolyte solution for the electro-deposition of Pt-Au alloys consists of an alkali metal hexahydroxyplatinate and an alkali metal aurate where the pH of the solution is above 11.0. A typical solution containing 21 g/l Pt as $\text{K}_2\text{Pt}(\text{OH})_6$ and 2.8 g/l Au as KAuO_2 was used to plate clean brass parts. The bath was operated at 65°C using a 0.2A current. The composition of the final deposit was 30%Pt-70%Au and the deposit was of high quality.

Bright Palladium Electrodeposits

AMERICAN CHEMICAL & REFINING CO. INC.

U.S. Patent 3,925,170

A bright plating bath contains 0.02-0.25g mole/l Pd, 0.9-3.6g mole/l NH_4OH , 0.1-0.7g mole/l alkali metal or NH_4 salt electrolyte, a Co and/or Ni brightener and a small amount of cetyl trimethyl NH_4Br .