ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Calorimetric Heats of Adsorption of Hydrogen on Platinum Films
S. ČERNÝ, M. SMUTEK and F. BUZEK, J. Catalysis, 1975, 38 (1-3), 245-256

Four Pt films were prepared at a pressure of 10⁻⁹ Torr and heats of adsorption of H were measured calorimetrically up to an equilibrium pressure of 10⁻⁴ Torr. The initial heats were estimated as 22.0, 22.6, 21.2 and 19.2 kcal/mole; whereas the integral heats were found to have approximately the same value of about 17 kcal/mole on the four films in the investigated range of coverage.

An UV Photoemission Study of NO and CO Adsorption on Pt(100) and Ru (1010) Surfaces
H. P. BONZEL and T. E. FISHER, Surface Sci., 1975, 51, (11), 213-227

UV photoemission spectroscopic (UPS) studies of the adsorption of NO, CO and O₂ on Pt(100) and Ru(1010) surfaces at 100°C showed it to be non-dissociative. The UPS spectra exhibited two major emission peaks at initial state energies of -8.8eV and -11.4eV for Pt(100) and -7.4eV and -10.6eV for Ru(1010). The NO adsorption behaviour of Pt and Ru with regard to the NO reduction reaction on these catalysts are discussed.

On the Photolysis of [Pt(NH₃)₄]Cl₄ Aqueous Solutions

The mechanism of phototransformation of [Pt(NH₃)₄]Cl₄ solutions in relation to the radiation energy and pH of the medium was studied. It is shown that the ultraviolet radiation facilitates the formation of complex amides which are responsible for the observed oxidation—reduction transformations.

Investigation of Sub-solidus Equilibria in the Platinum-Aluminium System Using Diffusion Couples

Studies of the Pt-Al system were carried out by X-ray diffraction, microprobe and metallographic examinations of Pt aluminate layers formed on Pt by the diffusion of Al from a pack-aluminizing process. The compositions and stability of most phases are in good agreement with the currently accepted phase diagram, but a new single phase of nominal composition Pt₅Al was found and therefore a modification to the existing phase diagram is proposed.

Resistivity Minima in Quench-condensed Films of Palladium

Studies of the electric resistivity of quench-condensed Pd films 100-700Å thick and at 2-30K showed a shallow low temperature minimum in thin quench-condensed Pd films. The depth and temperature of this minimum depended on the residual resistivity of the film.

Study of Decomposition and Ordering Processes in Copper-Palladium-Silver Alloys

X-ray and electron microscopy studies of the decomposition and ordering processes in Cu,Pd+8at.%Ag showed that the ordering at concentrations 18-30at.%Pd is accompanied by the formation of periodic antiphase domains. The ordering suppresses the discontinuous decomposition of the alloy, promoting precipitation of highly dispersed Ag which causes an increase in strength. Ag additions to Cu,Pd lower the critical temperature of ordering.

Solubility of Hydrogen in Small Particles of Palladium
M. BOUDART and H. S. HWANG, J. Catalysis, 1975, 39, (11), 44-52

The solubility of H in Pd which is defined as the number of dissolved H atoms divided by the total number of metal atoms was measured at 273-343K from 13.3-53.3kPa. The solubility decreased linearly with increase of the percentage dispersion of metal.

Experimental Study of the Critical-point Behaviour of the Hydrogen in Palladium System. III. Spinodal Curves and Isotherm Relations

Spinodal curve of the PdH system was determined by measuring the anelastic relaxation and the solubility for H in Pd. Comparison of the solubility data with the isotherm equation due to Lacher, which is based on a mean-field approximation, shows that the equation works reasonably well for 0<p<0.3.
Electrical Resistivity of Pd-H\textsubscript{x}: I. Residual Resistivity
Studies of the electrical resistivity of PdH\textsubscript{y} alloys show that the residual resistivity goes through a maximum at 0.73 and then drops sharply as x approaches 1. The results show that the residual resistivity for 0.8 < x < 1 is mainly due to vacancies in the H lattice and that H atoms occupy only the octahedral sites of the Pd lattice.

Tunnelling Experiments on Superconducting Palladium-Deuterium Alloys
Superconducting tunnelling studies made on D/Pd showed that this Pd-D alloy is a weak coupling superconductor (2\textDelta/\kappa T_c = 3.6). The results show that the high energy localized modes of D in Pd-D share in the electron-photon-interaction which lead to superconductivity.

Superconductivity in the Palladium-Hydrogen System
Band theory and phonon measurements are used to calculate the electron-phonon coupling constant, \lambda, for Pd and PdD. The results indicate that superconductivity is absent in Pd metal because of the large value of the Coulomb pseudopotential, \mu*, and that superconductivity occurs in PdD primarily because of coupling with the optic phonons.

The specific heat capacities of the intermetallic phases Pd\textsubscript{x}In, Pd\textsubscript{1-x}In, Pd\textsubscript{1-x}In, Pd\textsubscript{x}Sn, Pd\textsubscript{x}Sn and PdSn were measured at 150-298K using differential scanning calorimetry. Significant negative deviations from Neumann-Kopp behaviour were found in the heat capacities of all phases. A possible explanation in terms of changes in electronic and vibrational heats on alloying is suggested.

Coexistent Phases of the FeSi-type Crystal Structure in Ni-Pd-Ga and Ni-Pt-Ga Alloys
The valence electron concentration and the concentration of the outer core electron in the Ni\textsubscript{x}Pd\textsubscript{30-m}Ga\textsubscript{30}, Ni\textsubscript{x}Pt\textsubscript{30-m}Ga\textsubscript{30} phases (m = 0-30) did not change over their linearly extended homogeneity ranges, but the concentration of the inner core electrons changed. At lower Pd and Pt contents and at 700°C the alloys consisted of phases Ni\textsubscript{x}PdGa\textsubscript{30} and Ni\textsubscript{x}PtGa\textsubscript{30}, respectively. It is assumed that in the coexistent phases the commensurability of the core electron correlation to the crystal structure exhibits a small but characteristic difference.

The Effect of Hydrogen on the Superconducting Transition Temperature of some Body-centred Cubic Niobium-Palladium, Niobium-Palladium-Molybdenum and Niobium-Palladium-Tungsten Alloys
The superconducting transition temperature of Nb\textsubscript{1-x}Pd\textsubscript{x} (0.15 < x < 0.35), (Nb\textsubscript{1-x}Pd\textsubscript{x}Mo\textsubscript{y} (0.15 < x < 0.24), 0.0 < y < 0.1) and (Nb\textsubscript{1-x}Pd\textsubscript{x}W\textsubscript{y} (x = 0.20; y < 0.1) alloys was increased by the introduction of H into these alloys by the electrolysis of H\textsubscript{2}SO\textsubscript{4}. For the Nb-Pd and Nb-Pd-Mo alloys, this effect is accompanied by the loss of body-centred cubic symmetry in the host metal lattice.

Effect of Palladium Alloying Additions on the Environmental Cracking Resistance of Titanium-7Al-2Nb-1Ta Alloy
Studies of the environmental cracking of a high-strength Ti-7Al-2Nb-1Ta (Ti-721) alloy with 0.25-1.56% Pd additions in 3.5% NaCl solution were made by means of notched specimens to which a rising-load was applied. An increase in the fracture toughness K is observed in alloys with 0.38-1.56% Pd as compared to plain Ti-721. An addition of 0.26% Pd is found sufficient to bring about passivity in the unstressed alloy although the ordinary alloy shows active corrosion. The rapid crack propagation velocity however remains unaltered by Pd additions.

Gaseous Phosphorus Compounds. XI. Thermodynamic Investigation of the Gaseous Molecule RhP\textsubscript{3}
The atomisation energies, \Delta H\textsubscript{atom} of the gaseous molecule RhP\textsubscript{3} measured by the Knudsen effusion-mass spectrometry was determined as 199±5.0 kcal/M. The atomisation energy of RhP\textsubscript{3} was derived from the third law enthalpy change. Thermodynamic data favour the asymmetric Rh-P-P structure for RhP\textsubscript{3}.

Structure and Superconductivity of Meta-stable Phases in Liquid-quenched Zr-Rh Alloys
0-36at.% Rh-Zr alloys were rapidly quenched from the liquid state. A b.c.c. solid solution of
Zr is retained up to 17 at. % Rh beyond the maximum equilibrium solubility limit of 8 at. % Rh. Broad maxima in the X-ray and electron diffraction patterns, indicative of a non-crystalline structure, are obtained for alloys containing 18–27 at. % Rh. The non-crystalline phase shows a sharp superconducting transition at 4.1 K.

Superconductivity in Zr-Ir System
Studies of superconductivity in the 10–75 at. % Ir-Zr alloys were carried out using an induction method. Superconducting properties were detected in Zr-Ir (Tc = 2.1 K) and Zr2Ir (Tc = 7.3 K) and also in ZrIr in as cast and as quenched from 1400°C conditions. These alloys Zr-Ir and ZrIr are not superconducting above 1.85 K. Superconducting properties of ZrIr3 (Tc = 4.03 K) and of alloy with 10 at. % Ir (Tc = 5.5 K) were also confirmed.

Study of Thermal Dissociation of Ruthenium Dioxide and Rhodium Sesquisioxide
High temperature mass spectrometric studies of the dissociation of RuO2 and Rh2O3 were carried out at 985–1190 K and at 777–910 K, respectively. In both cases the dissociation products were the corresponding metals in a solid state and O2 gas. The heats of reaction ΔH°101 were found to be 73.2 kcal/mol and 53.89 kcal/mol for the dissociation of RuO2 and Rh2O3, respectively. The corresponding dissociation pressures are also given.

CHEMICAL COMPOUNDS
Importance of Chemical Effects in Determining the Free-electron-like Band Structure of K2Pt(CN)2Br3,3H2O
It is shown that a three-band model for the linear Pt chains in K2Pt(CN)2Br3,3H2O is inappropriate for a description of the electronic structure. The chemical effects of the ligands force an s-d hybridisation which is k independent and leads to free-electron-like bands within a basically tightly binding scheme. This results in an explanation of the band structure deduced experimentally. A highly simplified model is also presented to explain the 5/6th occupancy of the band.

Mononucleoside Platinum Complexes
New mononucleoside complexes K[Pt(Nuc)Cl2] (Nuc = nucleoside, Guo = guanosine, Ino = inosine and Xao = xanthosine) and the bridge complex K2[PtCl6](Ado) were prepared by reacting K2[PtCl6] and the nucleoside at 60–70°C in HCONMe2 or MeCONMe2. The equilibrium ratio of K2[PtCl6] and nucleoside is essential in the preparation of the adenosine complex but not for the synthesis of the Guo, Ino and Xao complexes. K[Pt(2,6-lutidine)Cl2] and K[Pt(NH3)Cl2] were also prepared and described.

Crystal and Molecular Structures of cis- and trans-Dichloro(bispyridine)platinum(II)
Crystal structure studies of cis- and trans-dichlorobispyridineplatinum(II) [(I) and (II)] showed that crystals of (I) are monoclinic, space groups P2/c, with a = 9.408, b = 17.110, c = 15.270 Å, β = 98.53°, Z = 8; crystals of (II) are triclinic, space group P1, with a = 7.695, b = 7.091, c = 5.542 Å, α = 87.6, β = 83.7, γ = 79.3°, Z = 1. Shortest Pt-Pt distances are 4.967 Å and 5.542 Å.

Isomerisation of bis-Thioxane Complexes of Platinum(II)
The isomerisation of bis-thioxane Pt(II)chloride with trans configuration in the crystalline state produces a corresponding cis-isomer. The isomerisation of trans-[Pt(R,S)2(H2O)2]2+ into cis-[Pt(R,S)(H2O)]3+ (where R,S = thioxane and diethylsulphide) also takes place in the same solution. The first and second dissociation constants are found to be of the order of 10−3–10−4 and 10−4, respectively.

The Preparation of Acy1- and Sulphonato-Platinum(II) Complexes from Bis(triphosphine)Platinum Ethylene
The acyl-Pt complexes trans-[PtCl(COR)L2], where L = PPh3, were obtained in high yield from the reaction between [Pt(L2)(C2H4)] and the acyl chlorides RCOCI, where R is Ph, CH3OMe-p, C6H4Cl-p, CH2=CH2, CH3=CHMe, CMe=CH2, or CH=CHPh. The sulphonato complexes trans-[PtCl(SO2R)L2], where R is Ph or Me were obtained analogously from the sulphonyl chlorides, RSO2Cl. The complex trans-[PtCl(COCH=CHPh-trans)L2] undergoes decarbonylation on heating to give trans-[PtCl(CH=CHPh-trans)L2].

Selective Hydrogenation of Dimethylene-carbinol on a Complex Palladium Catalyst
A modified method of preparation of a complex PdCl2(PPh3)2 catalyst for selective hydrogenation of dimethylene-carbinol was developed. The
method uses a 4:1 mixture of benzol and ethanol as a solvent and hydrazine as an activator. The catalyst shows high activity and selectivity.

Platinum and Palladium Complexes of Thiénylpyridine. I. Compounds Containing Metal-Carbon Bonds


The synthesis of Pd(II) and Pt(II) complexes of 2-(2'-thienyl)pyridine (TP) was carried out in order to determine the mode of coordination and the effect of an adjacent thienyl group on the coordination of an n-donor ligand. In the complex Pt(C,H,NS)(C,H,NS) the Pt atom is coordinated by two pyridyl nitrogens trans to one another, a thienyl C, and an I which lies slightly below the plane formed by the Pt and the other 3 coordinating atoms. The metal to C σ-bond forms due to the thiophene ring activity and the chelate stability.

Equilibrium Energetics of cis-trans Isomerisation for a Series of Palladium(II)-Phosphine Complexes. Study of Phosphine Electronic Effects


The n.m.r. studies of the cis-trans isomerisation of the series of para-substituted phosphine complexes, [(p-2-ZC,H,NS)(C,H,NS)PdX2 (n = 1, Z = OCH, CH, H, Cl) n = 2, Z = CH, H, Cl; X = CH, H, Cl; X = 1, N)] show that the cis isomer is thermodynamically more stable than the trans for both complex to be cis-dibromo-trans-bis-(trimethylphosphine) PtCl4. The long bond of 1.625Å reported for [IrO,(dppe),] is an artefact caused by the disorder in the crystal.

Crystal Structure and Molecular Geometry of Ir(B5H10)Br2(CO)(PMe,Ph), a Product from the Oxidative Addition of Bromopentaborane to IrCl(CO)(PMe,Ph)2 and some Comments on the Structural trans Influence of σ-Bonded Boron


A single crystal X-ray diffraction study of the complex Ir(B5H10)Br2(CO)(PMe,Ph), shows that the complex belongs to the centrosymmetric monoclinic space group P1, with a = 13.824 Å, b = 10.661 Å, c = 13.611 Å and β = 104.9°. The molecular geometry determinations show the complex to be cis-dibromo-trans-bis-(trimethylphosphine)(2-pentaboranyl)-carbonyliridium(III). The cis and trans angles, and the Ir-P and Ir-Br distances are given.

Bi-heterometallic Hydrido Transfer between Iridium and Platinum


Hydrido transfer from IrH2L3 to PtCl4L4 or PdCl2L4, where L = PR3, occurs readily at room temperature, and in the case of the Pt dimer proceeds via a hydrido bridged Pt-Ir complex.

Preparation, Structure, and Properties of Europium Ruthenium Hydride


EuRuH4 was prepared by reaction of EuH2 and Ru at 800°C and in 1 atm of H2. X-ray powder studies showed that the structure is consistent with the Fm3m space group. Magnetic susceptibility measurements at 77–296K showed that EuRuH4 obeys a Weiss-Curie law with β = 1.43K indicative of ferromagnetic interactions. Electrical resistivity measurements indicate that EuRuH4 behaves as a semiconductor.
Improved Synthesis of Cyclo-olefin Complexes of Ruthenium via Metallic Zinc Reduction


A new method of preparation of cyclo-olefin complexes of Ru used in homogeneous catalysis is described. &-Cyclo-olefin Ru(O) and -Ru(II) complexes can be prepared in high yields by reaction of cyclo-olefins and RuCl3·3H2O in the presence of Zn dust and C6H5OH. A possible mechanism for the formation of Ru(O) compounds is given.

Thermal and Light-induced Decomposition of Azido(bis-2,2'-bipyridine) Complexes of Ruthenium(III)

Ru(II) complexes Ru(bipy)2N32 (bipy is 2,2'-bipyridine) and Ru(bipy)2(L)(N3)+ (L = acetonitrile or pyridine) are oxidised to Ru(III) electrochemically using Br2 or Ce(IV). Ru(II) complexes undergo thermal and light-induced decomposition reactions in acetonitrile in which the azide to metal electron transfer occurs. The results of kinetic studies are consistent with either rate-determining intramolecular electron transfer or metal-nitrene formation.

Hydrocarbon Complexes of Ruthenium. Part VI. Cyclic Dienyl Complexes

Studies of the reaction of cyclopentadiene, cyclohexa-1,3-diene and cyclohepta-1,3-diene with [Ru(MMe3)(CO)3] (M = Si or Ge) or [Ru2SiMe4(CO)5] showed the yield of dienyl complexes [Ru(MMe3)(CO)3] in yields about 1.5-3.4% yield. Cyclohexane-1,3-diene gives [Ru(CO)3(1-2:3-4-\gamma,C6H4)] as the major product with both Ru complexes, whereas cyclopentadiene and cycloheptane-1,3-diene give the corresponding [Ru(CO)3(1-2:3-4-\gamma,C6H4)] complex with yield [Ru2SiMe4(CO)5].

Synthesis and Properties of Osmium(II) and Osmium(III) Ammine Complexes of Aromatic Nitrogen Heterocycles

The reaction of nitrogen heterocycle with the bis(dinitrogen)tetraammine-osmium(II) ion led to the formation of Os(II) complexes of the type [N2]+(L) = pyrazine, N-methylpyrazinium, isonicotinamide and isonicotinic acid. Os(III) compounds with the general formula, [NH3]2OsX(L)LX, where L = pyrazine, X = Cl-, Br-; and L = isonicotinic acid, X = Cl- were isolated and reduced to Os(II) ions.

ELECTROCHEMISTRY

Comparative Study of Adsorption and Oxidation of Formic Acid and Methanol on Platinised Electrodes in Acidic Solution

The results of radio- and electrochemical studies of the adsorption of HCOOH and CH3OH and the oxidation of their chemisorption products on a platinised electrode in 0.5M H2SO4 are presented and the mechanism of the electrode processes is discussed.

The Anodic Oxidation of Hydrogen on Platinised Tungsten Oxides. III. Mechanism of H2 Oxidation on Platinised Lower Tungsten Oxide Electrodes

The mechanism of H2 oxidation on platinised lower tungsten oxide (WO3, where 2<z<3) electrodes is explained in terms of hydrogen tungsten bronze formation on the surface of WO3 film. The performance of these electrodes is initially lower than the corresponding WO3 electrodes, but it improves with time as the surface is converted to WO3 rich layers. The electrodes have higher long-term stability.

A Study of Electrochemical Preparation of Chlorates

The current yield and total power consumption per unit mass of product was measured in a laboratory electrolyser for the preparation of chlorates, using activated Ti anodes. With these anodes whose active layers are formed by a mixture of RuO2 and TiO2 the current yield reaches 94% at the current density of 0.4-1.0A/cm2 at 60-80°C and pH between 6.2-6.3. The effects of additions of Fe, Ca and Na to the electrolyte are discussed.

Mechanism of the Reduction of Dimeric Ruthenium(IV) in Hydrochloric Acid Solutions

The mechanism by which dimeric Ru(IV), [Ru(IV)2OCl6] is reduced to Ru(III) in HCl solutions has been elucidated using a variety of electrochemical techniques. The results are consistent with an electron-transfer-chemical step-electron transfer process involving the irreversible reduction of the dimer to a mixed oxidation state intermediate, which subsequently decomposes to form monomeric Ru(III) and Ru(IV). The rates of the chemical step are discussed.
ELECTRODEPOSITION AND SURFACE COATINGS

The Effect of the Substrate on the Electrical Resistance of Polymer Films


A comparative study has been made of the effect of mild steel and Pt substrates on the electrical resistance of polymer films. Pt and mild steel samples coated with three different varnishes were exposed to 3.5M KCl. It was found that the resistance of films supported on Pt was one or two orders of magnitude higher than those supported on mild steel. It is suggested that this was due to the fact that ionic diffusion occurred from only one side of the Pt substrate.

HETERGENEOUS CATALYSIS

Laboratory Experiments Evaluating the Effects of S and Ca on a Pt-Al₂O₃ Auto Exhaust Oxidation Catalysts

J. T. KUMMER, J. Catalysis, 1975, 38, (1-3), 166-171

Cu impregnation of Pt/Al₂O₃ increases its ethylene oxidation activity in a laboratory gas stream but decreases its CO oxidation activity. SO₂ decreases the activity of untreated Pt/Al₂O₃ catalyst for both CO and CO₂ oxidation. The Cu-treated Pt/Al₂O₃ catalyst showed decreases in C₂H₄ and CO oxidation activity due to SO₂ comparing with the untreated one. Reduction of the Cu-treated catalyst greatly increased the CO activity and decreased the C₂H₄ activity.

Infra-red Study of the Interactions between Aromatic Hydrocarbons and Alumina Supported Platinum


I.R. spectroscopy shows that aromatic hydrocarbons are chemisorbed on Pt/Al₂O₃ with the formation of a π-complex. The electronic transfer between the ring and the metal is dependent on the number of methyl groups in the compound. The hydrogenation of adsorbed species destroys this complex.

The Influence of Nitrogen Compounds on the Properties of Alumina-Platinum Catalysts with Rare Earth Element Additions


The influence of nitrogen compounds on the activity of a 0.5% Pt/Al₂O₃ catalyst with 0.5, 1.0 and 2.0% additions of H₂O was studied in the reactions of hydrocracking and isomerisation of n-hexane. The results show a higher stability of the catalysts with H₂O additions in relation to nitrogen compounds.

Platinum-Rhenium/Alumina Catalysts. I. Investigation of Reduction by Hydrogen


Reduction to metallic Re occurred below 200°C when Re₂O₃ was mixed with Pt powder. A strong activation by Pt of the reduction of Re₂O₃ also occurred on Al₂O₃ samples co-impregnated with H₂PtCl₄ and Re₂O₃. The results showed that the reduction of Re₂O₃ to metallic Re under 1 atm of H₂ was completed at a low temperature.

Characterisation of Pt-Sn-Al₂O₃ Catalysts by Mössbauer Spectrometry


A large amount of Sn in PtSn/Al₂O₃ catalysts is lost during their preparative thermal treatments. The remaining part is present as SnO₂. For the same number of Pt atoms only 2/3 of this oxide is reduced by H₂. A quantitative reduction occurs in solids with three times larger Pt content.

Interaction between Components in Supported Mo-Pt Catalysts Studied by X-ray Electron Spectroscopy


The influence of Mo ions on the catalytic activity of 5.5%Pt-4.9%Mo/SiO₂, 4.4%Pt-1.9%Mo/SiO₂, 3.9%Pt/SiO₂, 1.5%Mo/SiO₂ catalysts was studied using electron spectroscopy method. The results indicate a direct interaction between the Pt atoms and Mo ions.

New Hydrogenation Catalysts with Platinum Deposited on Polyamide 66. II. Activation of Catalysts


Catalytic activity of polyamide 66 supported Pt catalysts in the partial hydrogenation of styrene is observed when the samples are previously activated by H₂ at 80°C. The activity remains constant over the activation temperature range between 120-220°C. Activation of the catalysts can also be produced, in the absence of H₂, by the support itself. The presence of Pt crystallites is revealed by X-ray diffraction.

Reactions of Alkanes on Supported Pt-Au Alloys


Studies of isomerisation, dehydrocyclisation and hydrogenolysis of n-pentane and n-hexane over supported Pt and Pt-Au alloys showed that 1-4% Pt-Pt alloyed catalysts isomerisation, 10% Pt-Au alloys favoured dehydro-
cyclisation and pure Pt catalysts mainly isomerisation. Self-consistent picture of the mechanisms involved is explained by comparison of the \( n \)-pentane and \( n \)-hexane reactions.

On the Mechanism of the Catalytic Effect of Palladium during the Reduction of Molybdenum Oxide with Hydrogen


The effect of 0.1% Pd addition on the reduction process of MoO\(_3\) with molecular and atomic H was studied. It is shown that the highest reaction rates are obtained when atomic H and catalytic additions of Pd are used simultaneously at 450°C. Both Pd and atomic H lower the starting temperature of the reduction.

Changes in the Catalytic Activity of Cold-worked Platinum during the Oxidation of Carbon Monoxide


The rate of oxidation of CO was measured on cold-worked Pt to study the influence of annealing on the catalytic behaviour. The presence of lattice defects (dislocations) in the crystal plays a role in initiating the reaction and serves to create new active sites during an acceleration period of the reaction.

Catalytic Hydrogenation of Nitroethane on Skeleton Platinum-Rhodium Catalysts in the Solutions of Sulphuric and Hydrochloric Acids


Studies of nitroethane hydrogenation on skeleton Pt, Rh and 10-90% Rh-Pt catalysts in 1N HCl and 1N H\(_2\)SO\(_4\) show a decrease of catalytic activity with an increase of Rh content. The rate of reaction in 1N H\(_2\)SO\(_4\) is found to be higher than in 1N HCl. This is explained in terms of specific adsorption of Cl\(^-\) ions in preference to H. The reaction rate constants at 10-50°C and activation energies are given.

Differential Determination of Composite Catalyst Surface Areas by Chromatography. VI, Supported Rhodium


The chemisorption of O\(_2\) and CO on Rh blacks, Rh/Al\(_2\)O\(_3\), Rh/FeO\(_2\), Rh/Al\(_2\)O\(_3\), SiO\(_2\), Rh/C and also on pure supports was studied using chromatography and static methods to obtain adsorption isotherms at room temperature. From these, the degree of dispersion and specific surface of Rh were calculated. It is shown that the dispersion changes in the following order: Rh/C > Rh/Al\(_2\)O\(_3\) > Rh/Al\(_2\)O\(_3\) SiO\(_2\) > Rh/SiO\(_2\) and depends on the nature of the support and the method of preparation of the catalysts.

On the State of Rhodium in Alumina-Rhodium Catalysts


The state of Rh in Rh/\( \gamma \)-Al\(_2\)O\(_3\) catalysts containing 0.15, 0.3 and 0.6% Rh was investigated using magnetic susceptibility and chemisorption measurements. The results show that a proportion of Rh in catalysts containing 0.15 and 0.3% Rh remains in an ionic form even after reducing treatment in H at 500°C.

Reduction of Nitric Oxide with Carbon Monoxide and Hydrogen over Ruthenium Catalysts


Studies of the reduction of NO with a mixture of CO and H\(_2\) in the presence of H\(_2\)O and CO\(_2\) over Ru/Al\(_2\)O\(_3\) showed two peaks in the NH\(_3\) yield; a CO-assisted NH\(_3\) maximum at \(-270°C\) and a H\(_2\)-assisted NH\(_3\) maximum at \(-350°C\). The low temperature NH\(_3\) maximum increased with decreasing the particle size of Ru.

Electron Spin Resonance Study of Supported Ruthenium Catalysts Promoted by Alkali Metal Salts in Dehydrogenation of Cyclohexane

M. Kobayashi and T. Shirasaki, J. Catalysis, 1975, 38, (1-3), 394-401

Studies of the dehydrogenation of cyclohexane over Ru/SiO\(_2\) and Ru/graphite catalysts promoted by alkali metal salts showed that additions of KCN LiCN and KCl increased the activity of the Ru/SiO\(_2\) catalyst but NaCN, RbCN and CsCN had no effect. The ESR spectra of the Ru/SiO\(_2\) catalysts which absorbed cyclohexane and benzene at 500°C were observed. There were three signals in these spectra of the catalysts promoted by KCl; a main singlet spectrum (\( g = 2.009 \)) and two spectra of small intensity (splitting 58.63 gauss).

Supported Metal Complex Catalysts


Isomerisation catalyst RhCl\(_3\) and hydroformylation catalysts (P\(_2\)O\(_5\))\(_3\)RhCOC\(_3\) (AsO\(_2\))\(_3\)RhCOC\(_3\) and CO\(_2\)(CO\(_3\))\(_2\)(PBU\(_3\)) on support were found to be more active when dissolved in a liquid phase. The hydrogenation catalyst (P\(_2\)O\(_5\))\(_3\)RhCl was more active as the supported solid catalyst than its supported liquid-phase counterpart. The results showed that the shape of the conversion versus liquid-loading curve is diagnostic of the intrinsic activity of the dispersed catalyst solution.
On the Catalytic and Asymmetrising Activity of Ruthenium Catalysis. V. On the Mechanism of Asymmetric Hydrogenation


Hydrogenation of acetooacetate ester on a Ru/SiO₂ catalyst modified by D(-)-tartaric acid was studied at different temperatures and H₂ pressures. The results show that increasing the pressure of H₂ increases the reaction output from 0% to 5.4% at 80 atm. Increasing the temperature has a similar effect.

HOMOGENEOUS CATALYSIS

Carboxymethylation of Organic Halides by Palladium Complexes under Mild Conditions


The complexes Pd(CO)(PPh₃)₂, Pd₃(CO)₄(PPh₃)₂, Pd₁(CO)₅(PPh₃)₂ and PdCl₄(PPh₃)₂ are excellent catalysts for the carboxymethylation of various organic halides under very mild conditions. The reaction is believed to proceed via acyl complexes as the intermediates.

Kinetic Studies of n-Butene Isomerisation Catalysed by Methanolic Rhodium Trichloride


The isomerisation of n-butene catalysed by methanolic RhCl₃·3H₂O on its own and in the presence of SnCl₂, HCl, NH₄Cl or an alkali chloride as co-catalysts was studied. An induction period was observed only in the presence of SnCl₂ or in the absence of any co-catalyst. Carbon-14 tracer studies suggest the existence of a common intermediate for all three paths which interconnect the three n-butene isomers. A structure of the common intermediate and a model for the isomerisation path are proposed.

Reactions of Amines and Active Methylene Compounds with Buta-1,3-diene and Isoprene: Catalysis by Nickel, Cobalt, Rhodium, and Iridium Complexes


Studies of the reaction of buta-1,3-diene with morpholine and di-ni-propylamine in the presence of NiCl₂·Ph₃·NaBN₄, CoCl₂·Ph₃·NaBH₄·Al(OP₃)₂ and IrCl₃ showed the yield of two isomeric 2:1 and 1:1 adducts. In the presence of RhCl₃ and CoCl₂·Ph₃·NaBN₄, mainly 1:1 adducts were obtained. When the Ph₃P and arsine were added to the RhCl₃ catalyst the 2:1 adduct was formed.

Catalytic Asymmetric Hydrogenation Using Ruthenium(II) Chiral Phosphine Complexes


The hydrogenation of unsaturated carboxylic acids was catalysed, under mild conditions, by Ru(II) complexes [RuX₂((+)-diop)]₃ [X = Cl, Br; diop = 2,2dimethyl-1,3-dioxolan-4,5-bis(methylene)bis(diphenylphosphine)], containing a bridging bidentate phosphine ligand, and gave products of high optical yields (ca.60%).

Kinetics and Mechanism of the Osmium Tetroxide Catalysed Oxidation of 2-Propanol and 1-Propanol by the Hexacyanoferrate(III) Ion in Aqueous Alkaline Medium


Kinetic studies of OsO₄ catalysed oxidation of 2-propanol and 1-propanol by [K₃Fe(CN)₆]₄ showed that the oxidation goes through the formation of an intermediate complex between the alcohol molecule and OsO₄ which decomposes to an intermediate product and Os(VI) species. Os(IV) is then rapidly oxidised to Os(VIII) with [K₃Fe(CN)₆]₄.

ELECTRICAL AND ELECTRONIC ENGINEERING

Reaction of Sputtered Pt Films on GaAs


X-ray diffraction, spectroscopic and backscattering studies of Pt/GaAs interface reaction at 250–500°C showed a rapid diffusion and dissolution of Ga in Pt at the beginning of the reaction; it was then slowed down by the formation of PtAs₂ at the interface. Five different Pt-Ga phases were identified; PtAs₂ and GaPt were the final reaction products. The reaction was self-limited (up to 500°C) for Pt films thicker than 200Å, probably due to a slow diffusion of Ga through the interfacial PtAs₂.

Reactions between the Ta-Pt-Ta-Au Metalisation and PtSi Ohmic Contacts


Reactions between Si substrates and a stabilised (Ta-Au metalisation with and without an intervening PtSi layer were studied as a function of annealing temperatures up to 785°C. The contact resistance of small area PtSi ohmic contacts, with geometries representative of microwave power transistors overlaid with the Ta-Pt-Ta-Au system, remained constant during anneals up to 400°C for 24h. Thermochemical reactions and diffusion at higher temperatures are discussed.