ABSTRACTS

of current literature on the platinum metals and their alloys

PROPERTIES

The Heat of Adsorption of Hydrogen on Platinum

UHV adiabatic calorimetric studies of the heat of adsorption (q) of H on clean polycrystalline Pt determined as a function of the coverage (θ) and temperature showed that adsorption at 273 K resulted in a stepped shape q=0 curve with q (θ=0)=24.7 kcal/mole. At 77 K the form of the curve depends on the temperature of pre-adsorption.

Temperature-dependence of Resistivity of PtCr Alloys

Studies of the electrical resistivity of 5–12 at.%Cr-Pt alloys at 1.4–300 K showed that the spin-fluctuation temperature increased from 52.5 to 85 K as Cr concentration increased from 5 to 12 at.%. No magnetic ordering occurs above 1.4 K for concentration <12 at.%; a rough calculation performed which qualitatively accounts for the decreasing magnetic-ordering temperature across the series AuCr, PdCr and PtCr.

Magnetic Structure of Ordered Iron-Platinum Alloys

Elastic scattering of neutrons and magnetic measurements on 10–75 at.%Fe-Pt alloys revealed five magnetic structures corresponding to PtFe, PtFe, PtFe, PtFe, and FePt. Their magnetic properties vary from antiferromagnetic ordering in PtFe and PtFe to ferromagnetic in PtFe and FePt. FePt is believed to possess uncompensated antiferromagnetism, i.e. ferrimagnetism. Experimental and theoretical values are in best agreement for atomic moments of Fe (3.0–2.75)μB and Pt (0.2–0.3)μB.

The Reversible Martensite Transformation in Iron-Platinum Alloys near FePt

A series of 25–27 at.%Pt–Fe alloys with ordering of the γ phase varying from substantial disorder to nearly complete order were thermally cycled at 25–196°C. The kinetics of the γ→α transformation, the hysteresis revealed by electrical resistance/temperature plots, the thermoelastic growth and the reappearance of an identical microstructure after thermal cycling were studied as a function of the ordering of the γ-phase.

Localised Enhancement Effects in Pd-Ag Alloys

Low-temperature electrical resistivities of Pd-Ag alloys show a positive T2 temperature dependence in the concentration range above 60 at.%Ag. This behaviour supplements the well-known resistivity minima observed in alloys with lower concentrations of Ag, and strongly favours the model of scattering from localised exchange-enhanced Pd d states, as against s→d scattering in the rigid- or collective-band description of the alloys.

Surface Area Effects on the Sorption of Hydrogen by Palladium

Pressure–composition isotherms for dilute solutions of H2 in Pd were measured at 100–240°C and at up to 1000 Torr. For Pd foil the isotherms are consistent with data at lower temperatures, and with existing theoretical isotherms. With samples of appreciable surface area a higher sorptive capacity is found which may be due to the formation of a layer of adsorbed H2 on the metal surface; appropriate correction may be made for this. The variation of partial molar enthalpy of adsorbed H2 with H2-content is also affected by this surface phenomenon.

Electrical Resistivity of Some Palladium-Silver Alloys Containing Hydrogen at 4.2 K

The resistivities of the alloys of 50–90%Pd and 50–10%Ag measured as a function of absorbed H at 4.2 K showed minimum and maximum values, except for 10%Ag-Pd, which had only a maximum, and 50%Ag-Pd with only a minimum.

Effect of Pressure on the Curie Temperatures of PdFe, PdCo, PtFe and PtCo Alloys

The Curie temperatures of PdFe, PdCo, PtFe, and PtCo alloys with Fe or Co concentration of 1–10 at.% have been measured by thermal
scanning of the $^{57}$Fe Mössbauer resonance under pressures up to 170 kbar. The data are compared with models, which relate the variation of $T_c$ under pressure to changes in the impurity spin-conduction electron coupling parameter $J_1$ and to changes of the pure host susceptibility $X_h$. The differences between the experimental data and these models are discussed.

High Pressure Magnetic Behaviour of Low Nickel Content Pd-Ni Alloys
The magnetic properties of disordered Pd-Ni alloys, with low Ni content were studied at high magnetic fields and at high pressures. The variation of the saturation magnetisation and Curie temperature with the concentration and pressure are described.

Defects in Glassy Pd-Si Alloys
J. LOGAN, Scripta Metall., 1974, 8, (6), 727–732
X-ray diffraction and density studies on as-quenched and rolled $Pd_{60}Si_{40}$ showed that X-ray diffracted intensities were identical for both as-quenched and rolled foils but the density of the as-quenched foils is $\sim 5\%$ while the rolled foils vary by $\sim 0.3\%$. The increase in the density upon rolling is $0.5$–$5.8\%$.

The Glass Transition Temperature in Glassy Alloys: Effect of Atomic Sizes and the Heats of Mixing
The glass transition temperature $T_g$ of glassy systems ($Pd_{1-x}M_{x}$)$_y$($Si_{1-y}$$_4$) for $M$ = Cu, Ag, Au, Rh, Ni, Co and Fe and ($Pd_{1-x}M_{x}$)$_y$ for $N$ = Ni, Co and Fe was studied. The lowering of $T_g$ on admixture of metals with different atomic radii results in the non-linearity in $T_g$ vs $x$ curves (for small $x$) for ($Pd_{1-x}M_{x}$)$_y$ alloys and in the shift in peak positions of $T_g$ vs $x$ curves of ($Pd_{1-x}N_{x}$)$_y$ alloys.

Effect of Palladium on the Oxidation Behaviour of Sintered Tungsten-Chromium-Palladium Alloys
T. ITAGAKI and R. YODA, Nippon Kinzoku Gokkaishi, 1974, 38, (6), 486–492
The effect of Pd on sintering and oxidation behaviour of W-Cr alloys was studied on specimens containing 10–20%Cr, 0.1–2%Pd and 0.1–2%Ni and compared with that of Ni which is an effective activator for sintering of W. Both Pd and Ni accelerated the sintering of W-Cr as well as the sintering of W but Pd was more effective in activating the sintering than Ni.

Crystal Structure of the So-called R.E. Pd$_2$ Compounds
Single-crystal photographic data of the crystal structure of Dy$_2$Pd$_2$ show that this compound is cubic with $a=13.529\AA$, space group $Fd3m$, and the elementary cell containing 68 Dy and 28 Pd atoms. The R.E. Pd$_2$ compounds, where R.E. = Tb, Ho, Er, Tm, Lu, and Y, are isotypic with Dy$_2$Pd$_2$, and their lattice values are reported.

Oxidation of Iridium
Ir wires heated by self resistance at $1675$–$2260^\circ C$ were oxidised in naturally convected $O_2$ at $0.00132$–$1.32$ atm. The experimental results were correlated by a theoretical rate equation based on control of the oxidation rates by diffusion of Ir(g), IrO(g), and IrO(g) through the gaseous boundary layer. Standard-state free-energies of IrO(g) and IrO(g) formation were obtained.

Phase Diagram of the Iridium-Zirconium System
Studies of the Zr-Ir system detected the intermediate phases $ZrIr_2$, $ZrIr_3$, $ZrIr$, and $ZrIr$, $ZrIr_2$, $ZrIr_3$, $ZrIr_4$, and $ZrIr$ are formed by peritectic reactions. $ZrIr$ is formed directly and undergoes the polymorphic conversion $\beta \rightarrow z$.

Investigation of the Character of the Interatomic Interaction in Alloys of the Ruthenium-Vanadium System
The probability of stacking fault formation in Ru-V alloys in the V solid solution range was studied and a relation between stacking faults and alloy hardness was detected.

Density of Molten Palladium, Platinum, and Iridium at the Melting Point
Densities of molten Pd, Pt and Ir measured at the melting point were found to be $10.52$, $18.81$ and $19.39$ Mg/m$^3$ for Pd, Pt and Ir, respectively. The impurity contents of the metals were $0.050$%Pd, $0.021$%Pt and $0.030$%Ir.
CHEMICAL COMPOUNDS

Structure-Activity Relationships for Antitumour Active Platinum(II) Complexes
At least three new major classes of antitumour active Pt(II) complexes analogous to cis-Pt(NH₃)₂Cl₂ have been identified; [Pt(amine)₂X₂], X⁻ = malonates, oxalate; cis-[Pt₂Cl₄(A)₂], A = aliphatic amines; and the “Platinum Blues” – an uncharacterised class of Pt(NH₃)₂-pyrimidime complexes.

Chemistry and Antitumour Activity of “Platinum Blue” Complexes
The reaction of cis-diaquodiummine Pt(II) with 2,4-dihydroxypyrimidines and primary amines leads to the formation of highly coloured complexes of Pt which are different in type from the classic “Platinum Blue” complexes. The results of chemical and spectral studies on these complexes are given and are related to possible structures for these complexes.

Potential Anti-cancer Activity of Platinum and Palladium Amine Complexes
The preparation of Pd and Pt complexes with morpholine, piperazine and piperidine ligands, which show some biological activity but which do not exhibit anti-tumour activity in their own right, is reported. Complexes containing hydrazine as a ligand were also prepared and characterised before screening for anti-cancer activity.

Evidence for Ordered Layers of K⁺ in KCP (K₄[Pt(CN)₄]ClO₃·3H₂O)
The crystal structure of K₄[Pt(CN)₄]ClO₃·3H₂O was determined. It crystallises in space group P4mm, contrary to earlier assignments. The K⁺ ions occupy ordered positions in layers with a periodicity of c = 5.77 Å which are perpendicular to the c axis. The same kind of superstructure was found for K₄[Pt(CN)₄]BrO₃·3H₂O.

Observation of Electromagnetic Resonances in Crystals of K₄Pt(CN)₄BrO₃·3H₂O at Microwave Frequencies
Electromagnetic dielectric resonances in the range 8–11 GHz have been observed in 1 mm sized crystals of K₄Pt(CN)₄BrO₃·3H₂O. This observation results directly from the existence of large dielectric constants; values for the longitudinal and transverse dielectric constants at 4 K are ε₁ ≈ 3000 and ε₁ ≈ 4.

On Fluoropalladates(II) KPdF₅, RbPdF₅, TiPdF₅ and KPdF₅
RbPdF₅, TiPdF₅ and KPdF₅ were obtained by heating the binary fluorides in a closed system. lattice parameters and the colour of the compound in each case are given.

Composition and Stability of Osmium(IV)-Amino Acids Complexes
The interaction of Os(IV) with some amino acids using sodium chloroosmate in an aqueous medium was studied. pH measurement and potentiometric titrations were used to calculate the successive equilibrium constants, the overall stability constants, and the compositions.

ELECTROCHEMISTRY

Effect of Chemisorbed Carbon Monoxide on Hydrogen Adsorption at Platinum Electrodes
Studies of the effect of chemisorbed CO on H adsorption on Pt electrodes at room temperature showed that the potential-H coverage plots did not change their shape much on the three electrodes at CO coverages below 0.4. Theoretical predictions require a larger effect than that observed at θ₀c ≤ 0.4.

Clad Metal Anodes
Studies of the anodic polarisation behaviour and the stability of the clad metal electrodes (consisting mainly of Pt coatings on Ta, Nb and Ti) using Pt group metals and some of their alloys were conducted in HCl.

Chemisorptive and Catalytic Properties of Platinum-Rhodium Alloys
Studies of the electrocatalytic activity of Pt-Rh electrodes during methanol oxidation showed that at 0.58V the activity versus composition curve passes through a maximum at 34 %Rh-Pt. The catalytic behaviour is interpreted as a mechanism involving reaction between organic intermediates and hydroxyl radicals adsorbed on the alloy surface.

Platinum Metals Rev., 1975, 19, (1) 32
ELECTRODEPOSITION AND SURFACE COATINGS

Refractory Intermetallic Compound Coatings

P. J. Ficalora, V. Srikrishnan and L. Pecora, U.S. Rept. AD 77-4893/6GA, 1974; 20pp

Crystal structure, electronic configuration and thermodynamics of HfPt and ZrPt were studied. Films of HfPt and ZrPt are suitable for coatings for components subjected to high temperature oxidising atmospheres.

Electron Microscope Investigation of Mixed Stannous Chloride/Palladium Chloride Catalysts for Plating Dielectric Substrates


Electron microscopy and electron diffraction studies of surfaces treated by the catalysing system (SnCl2/PdCl2/HCl) in conjunction with various accelerating solutions show that the best plating results are obtained when PdSn is present on the treated surface prior to the metallisation step.

Kinetics of the Electrodeposition of Palladium


Surface area changes which occur when Pd is deposited on to Pd from chloro-complexes were studied electrochemically. A three-dimensional nucleation and growth model is used to evaluate the kinetics of the process.

HETEROGENEOUS CATALYSIS

Effect of Addition of Iridium on the Activity of Platinum/Alumina Catalysts in the Dehydrogenation of Cyclohexane


Studies of the effects of Ir additions to Pt/Al2O3 on catalyst activity, thermal stability and resistance to S poisoning during cyclohexane dehydrogenation showed that Pt-Ir/Al2O3 possesses greater thermal stability and resistance to the action of S compounds than does Pt/Al2O3.

Activity of Platinum Catalysts, Prepared on Supports of Type L Dealuminised Zeolites, in the Reactions of Isomerisation and Dehydroisomerisation


Isomerisation activity of Pt/type L dealuminised zeolites rises with increases in the amount of dealumination and reaches its maximum when SiO2:Al2O3 = 7.3. Increased dealumination of these zeolites leads to a decrease in the dehydrogenation activity of the Pt catalysts.

Conversion of Cyclic Hydrocarbons on Platinum/Alumina Catalyst

R. A. Bakulin, M. E. Levinter and F. G. Unger, Neftehimiya, 1974, 14, (5), 707-713

Diene condensation products tend to form on Pt/Al2O3 for diene, cyclo-olefin, indene, acenaphthene, phenanthrene, and anthracene hydrocarbons. Indane, indene, acenaphthene, phenanthrene, anthracene, and more condensed structures appear to form by C9- and C10-dehydrocyclisation of paraffins, alkylationary hydrocarbons and diene condensates of intermediate dienes and cyclo-olefins. Coke formation on Pt/Al2O3 tends to occur in the order: cyclopentadiene > indene > indane > methylcyclopentane > bis-butylbenzene > hexene > decalin > hexane > d-methylnaphthalene > styrene > tetralin.

Effect of Pore Diameter of Aluminium Oxide on the Activity, Stability and Selectivity of Platinum/Alumina Catalysts

V. G. Dyfrin, M. E. Levinter, S. V. Loginova and L. I. Vlasova, Neftehimiya, 1974, 14, (5), 714-719

Fine-pore catalysts have greater activity and stability for aromatisation, hydrocracking and coke formation of petroleum fractions but less selectivity because of increased Pt dispersion and filling of the pores by molecules of the reactants. Fine-pore catalysts have less selectivity than wide-pore catalysts because of secondary aromatisation, transposition of H2, hydrocracking, and destructur polycondensation with coke formation.

On a New Platinum on Alumina Catalyst. I. Preparation and Composition of the Catalyst


Finely divided Pt was deposited on Al2O3 without any change in the amorphous state of the support. The amounts of Pt and Cl contained in the samples were determined, as was their specific surface area by the adsorption of N2.

On the Activity of the Platinum Group Metals in the Demethylation of Toluene with Water Vapour


Pt metals on γ-Al2O3 catalyse demethylation of toluene with H2O vapour. Catalyst activity decreases in the order Rh > Pt > Pd > Ir, Ru, Os, as for demethylation in He. The catalysts are considered to be bifunctional, the metal possessing destructive activity and the support possessing hydrophilic properties.

Platinum Metals Rev., 1975, 19, (1) 33
Determination of the Surface of Dispersed Platinum Catalysts on Electrically Conducting Supports

The specific surface \( \sigma \) in \( \text{m}^2/\text{g} \) for Pt supported on active C, graphite and C black was determined by four independent methods. Supported Pt has 2–4 times the surface of Pt black; \( \sigma \) tends to increase as the Pt concentration decreases.

Adsorption of Hydrogen on Pt/Zelole Catalysts

Studies of the mechanism of \( \text{H}_2 \) chemisorption on various Pt/zelite catalysts with respect to Pt content, zelite type and method of application of Pt to the zeolites showed complexity of adsorption isotherms.

Crystallite Size Effects in the Low-temperature Oxidation of Ammonia over Supported Platinum

The effect of crystallite size on the specific catalytic activity of supported Pt catalysts in \( \text{N}_2 \) oxidation with \( \text{O}_2 \) was determined. Rates of \( \text{NH}_3 \) oxidation were measured in a differential, fixed bed, flow reactor at 393–473 K and catalysts with crystallite size of 20, 27 and 155 Å were used. The initial specific catalytic activity of the 155 Å catalyst was higher than those of the 20 and 27 Å catalysts by factors of 5.7 and 3.7, respectively.

Deactivation of a Platinum Monolithic Carbon Monoxide/Hydrocarbon Oxidation Catalyst

The effects of ageing on the CO/hydrocarbon oxidation activity and important physical properties of a Pt monolithic catalyst were determined. Catalyst samples were aged to 25,000 equivalent miles at a maximum temperature of 1450°F with unleaded fuel on an engine dynamometer. The activity for the oxidation of CO, \( \text{C}_2\text{H}_4 \), and engine exhaust gas hydrocarbons decreased rapidly during the first 1000–5000 miles with very little additional deactivation during further ageing. A large decrease in \( \text{C}_2\text{H}_4 \) oxidation activity continued through the 25,000 miles of ageing. The growth of very large Pt crystallites appeared to be a primary cause of catalyst deactivation. No significant changes in surface area or solid-state phase composition were noted. Small amounts of Pb were detected on aged catalyst samples.

Heats of Adsorption of Hydrogen on Skeleton Platinum, Rhodium and Platinum-Rhodium Catalysts in Hydrochloric Acid Solutions

The heats of adsorption of \( \text{H}_2 \) on skeleton Pt, Rh and Rh-Pt catalysts in \( 1\text{N} \) HCl solutions were determined and the bonding energies between the adsorbed \( \text{H}_2 \) and the surfaces were calculated.

Effect of Temperature on the Adsorption of Hydrogen by Skeleton Platinum-Rhodium Catalysts in Hydrochloric Acid Solutions

Galvanostatic and potentiodynamic studies of \( \text{H}_2 \) adsorption on Pt, Rh and Rh-Pt skeleton catalysts in \( 1\text{N} \) HCl at 10–70°C showed that the adsorption capacity for \( \text{H}_2 \) on heating is significantly diminished on Rh and Rh-rich alloys.

Effect of the Composition and Conditions of Heat Treatment of Palladium-Rhodium Alloys on Their Catalytic Activity in the Dehydrogenation of Cyclohexane

Catalytic activity for cyclohexane dehydrogenation of 7–20%,Rh-Pd alloys decreases as \( \text{H}_2 \) is removed from them and is completely reduced after treatment by \( \text{H}_2 \). The activity increases with the temperature for treatment in air from 350 to 750°C. Activity increased after tests at 450–470°C in a stream of Ar, presumably due to the removal of firmly adsorbed \( \text{H}_2 \).

The Catalytic Chemistry of Nitric Oxide. II. Reduction of Nitric Oxide over Noble Metal Catalysts

The reduction studies of NO with \( \text{H}_2 \), \( \text{CO} \), and equimolar mixture of \( \text{H}_2/\text{CO} \) over supported Pt, Pd, Rh, and Ru catalysts showed that when \( \text{H}_2 \) was used the activity of the catalyst was \( \text{Pt} > \text{Pd} > \text{Rh} > \text{Ru} \). When CO or CO/\( \text{H}_2 \) mixtures were used, this activity sequence was reversed. The results show that CO inhibits NO reduction strongly over Pt and Pd, the presence of CO over Ru catalyst accelerates the reaction and the reduction of NO in the presence of Pt and Pd gives \( \text{NH}_3 \) as major product.

Hydrogenation of Allyl Alcohol on Rhodium

The rate of hydrogenation of allyl alcohol on Rh
black is high because of weakly adsorbed H₂ on the Rh surface. Greatest yield (93%) of propanol occurred at 20°C, 20 atm H₂; greatest yield of propanol occurred at 20°C and 80°C, 60 atm.

**Hydrogenation of Aliphatic Ketones under Pressure of Hydrogen**


1 wt.% Ru/γ-Al₂O₃ in H₂O at 20-100 atm H₂ supports a high rate of conversion of acetone and methylethylketone to saturated secondary alcohols. To increase the rate of ketone hydrogenation the H₂ is stabilised by Ru using an alkaline solvent. Hydrogenation takes place by the formation of free radicals not exposed to condensation.

**Hydrogenation of Epoxycyclododecadiene over Group VIII Metals**


Hydrogenation of epoxycyclododecadiene (trans-epoxy-cis,trans-cyclododecadiene) on Group VIII metals takes place at the double bonds in two stages; first to the cis and trans forms of epoxycyclododecene, which is then reduced to epoxycyclodecanone. Yield of the latter is 87-96% on Pd, Ru, Rh, or Pt. Oxirane rings are not reduced on these catalysts. Hydrogenation of the cis and trans double bonds of epoxyclodecadiene and epoxycyclodecene on Pd and Rh proceeds at similar rates.

**Catalytic Transfer Hydrogenation**


Studies of the catalytic transfer hydrogenation with an organic molecule as H donor, using Pd but occasionally also Raney Ni showed that this reaction permits the reduction of olefins, nitriles and nitro compounds, as well as hydrogenolysis of benzylc and allylic functional groups and the replacement of aromatic halogen. The reaction is more selective than regular hydrogenation and in special cases, such as the reduction of polyn saturated steroids, has proved superior.

**HOMOGENEOUS CATALYSIS**

**Investigation of the Catalytic Action of Pt-Sn(II) Complexes in Hydrogenations of Acetylene Hydrocarbons**


Pt-Sn complexes catalyse a higher rate of hydrogenation for mono-substituted C=CH bonds than for dissubstituted, irrespective of the length of the substituted alkyl chain. The amount of hydrogenation of pentyne-i and phenylacetylene is closely connected with catalyst concentration and with the pressure of H₂. Monoalkylacetylenes and phenylacetylene are hydrogenated in stages, and diphenylacetylene adds two moles of H₂ via the intermediate stage of diphenylethylen.

**Tetraakis(triphenylphosphine) palladium(0) — Homogeneous Catalyst for the Hydrogenation of Acetylene and Ethylene**


Tetraakis(triphenylphosphine) palladium(0) in o-xylene effectively catalyses hydrogenation of C₃H₆ and C₅H₈ at 100°C, 1 atm. Butene in the product is formed by hydrodimerisation of C₅H₈ and C₇H₁₄. The reducing agent may be toluene sulphate and formamide.

**Polymerisation of Some Cycloolefins with Palladium-π-complexes**


Studies of the Pd π-allylic complexes prepared by the reaction of PdCl₂ with pinenes at high temperature showed them to be very active catalysts for the polymerisation of bicyclohepta-(2,5)-diene at 130-200°C. The polymerisation pattern revealed that only one double bond of the diene was opened by this reaction.

**Catalysis by Supported Transition Metal Complexes. II. Hydrogenation of Allyl Alcohol on a Palladium Resin**


The liquid phase hydrogenation of allyl alcohol in the presence of a catalyst obtained by ion exchange with a basic resin having a PdCl₂ anion gives a mixture of propanol and the corresponding aldehyde. The activity and selectivity of the catalyst was studied as a function of solvent, temperature (25-28°C), H₂ pressure (1-100 bar), and was compared with those of the usual Pd catalysts. Differences in results indicate the presence on the resin of active centres, with markedly different properties to highly dispersed Pd.

**The Selectivity of Palladium(II) in Substitution Reactions of Their Chloro-complexes with Diamines**

R. Ernst and R. Roulet, Chimia, 1974, 28, (7), 347-349

The rate constants of the substitution reactions of Cl⁻ and H₂O by various diamines in Pd(II) chloro-complexes were determined spectrophotometrically. The substitution mechanism is associative, and comparison with the corresponding Pt (II) complexes shows the selectivity of Pd(II) to be smaller than that of Pt(II).
Rhodium Carbonyl Chloride Anion, [Rh (CO)₃Cl]⁻: a True Catalyst in the Reduction of NO by CO

Studies of the RhCl₅/EtOH catalyst during reduction of NO by CO showed that addition of HCl to the catalyst system shortens an induction period, during which Rh(CO)₂Cl⁻ is formed, and acid accelerates the reaction between NO and CO. The interaction of Rh(CO)₂Cl⁻ with NO has been examined and i.r. spectroscopy reveals the presence of several nitrosyl species.

Preparation of Hydridometallocarboranes and Their Use as Homogeneous Catalysts

Methanol solution of the tris(triphenylphosphine) rhodium(I) cation was reacted at 60°C with a yield of Rh(CO)₂Cl⁻. Further reactions with terminal boron- and acid accelerates the reaction between NO and CO. The interaction of Rh(CO)₂Cl⁻ with NO has been examined and i.r. spectroscopy reveals the presence of several nitrosyl species.

Transition Metal Catalysed Exchange of Deuterium Gas with Terminal Boron- Hydrogen Bonds in Carboranes, Metallo-carboranes, and Other Boron Compounds

Studies of the RhCl₅/EtOH catalyst during reduction of NO by CO showed that addition of HCl to the catalyst system shortens an induction period, during which Rh(CO)₂Cl⁻ is formed, and acid accelerates the reaction between NO and CO. The interaction of Rh(CO)₂Cl⁻ with NO has been examined and i.r. spectroscopy reveals the presence of several nitrosyl species.

Homogeneous Catalysis of Hydrogen Isotope Exchange between D₂ and Ethanol by Chlorotris(triphenylphosphine)rhodium(I), II. In Chloroform-Ethanol

The kinetics and mechanism of D₂ exchange catalyzed by RhCl₅(P₅)₃ was studied in CHCl₃ –C₆H₆OH solutions. The D₂ exchange reaction rate is strongly dependent on solvent composition and decreased 30 times between 6-96 mol.% C₆H₆OH. The activation energy for D₂ exchange = 101 ± 9 kJ/mol at 58 mol.% C₆H₆OH, and 86 ± 8 kJ/mol at 6 mol.% C₆H₆OH. Results thus indicate solvent-catalyst bonding interactions to be important in this respect.

Homogeneous Catalysis of Olefin Isomerisation. Part IV. The Isomerisation of Pent-1-ene Catalysed by Solutions of Ir(CO)(P₄H₁₃) and of PtH(SnCl₅)(P₅H₁₃) in benzene.

The isomerisation of pent-1-ene to pent-2-ene at 80°C is catalysed by solutions of (1) Ir(CO)(P₅H₁₃); (2) IrCl₂(P₅H₁₃); (3) IrCl₂(P₅H₁₃) or IrCl₂(CO)(P₅H₁₃) each in the presence of O source; and (4) PtH(SnCl₅)(P₅H₁₃) in benzene. System (1), (2), and (4) catalyse the preferential formation of cis-pent-2-ene whereas (3) provides preferential formation of trans-pent-2-ene.

Part V. Pent-1-ene Isomerisation Catalysed by Solutions of RuHCl(CP₆)₃ and of RuHCl(CO)(P₅H₁₃); Variation of the Iso-meric Composition of Pent-2-ene and Its Attribution to Steric Factors

Isomerisation of pent-1-ene to pent-2-ene at 35-80°C is catalysed by solutions of RuHCl(CP₆)₃ and RuHCl(CO)(P₅H₁₃) in benzene. Preferential formation of cis-olefin occurs at higher catalyst concentrations but a change to preferential trans-olefin formation is observed as catalyst concentration is reduced.

Part VI. Pent-1-ene Isomerisation Catalysed by Solutions of Dodeca-carbonyl-tri-iron(0) and of Bis(benzonitrile)dichloropalladium (II) in Benzene

Isomerisation of pent-1-ene to cis- and trans-pent-2-ene is catalysed at 50°C and above by solutions in benzene of Fe₆(CO)₁₈ and of PdCl₃...
In both cases, preferential formation of trans-pent-2-ene occurs. The reaction mechanisms involve \( \pi \)-allylic intermediates; for the Pd-catalysed reaction bis-\( \pi \)-allyl complexes may also participate.

**Homogeneous Hydrogenation of Buta-1,3-diene and Ethylene Catalysed by Carbonylhydridotris(triphenylphosphine)iridium(I) and by Carbonyltrihydridobis(triphenylphosphine)iridium(III)**


Spectrophotometric and kinetic studies of the individual steps in the catalytic cycle of buta-1,3-diene hydrogenated to a mixture of butenes and butane by IrH(CO)(PPh\(_3\))\(_2\) and IrH\(_3\)(CO)(PPh\(_3\))\(_2\) at 50°C in dimethylformamide, were quantitatively interpreted in terms of a mechanism based on the reductive elimination of butenes by Ir(\( \tau \)-C\(_3\)H\(_5\))(CO)(PPh\(_3\))\(_2\). The intermediate Ir(\( \tau \)-C\(_3\)H\(_5\))(CO)(PPh\(_3\))\(_2\) was also isolated and characterised.

**Complex Metal–Polymer Catalysts for Benzene Hydrogenation**


Studies of Rh, Ir and Pd catalysts complexed with nylon showed how conditions of their preparation affect their properties in \( \text{C}_6\text{H}_6 \) hydrogenation. Cyclohexene is formed as well as cyclohexane. The order of activity of these complexes is Ir>Pt>Rh>Pd.

**NEW PATENTS**

**METALS AND ALLOYS**

**Palladium Alloy for Hydrogen Membranes**

URALSKY ORYDENA TRUDORAGA KRAJSNOGO ZNAMEI POLITEKHNICHESKY INSTITUT

*British Patent* 1,365,271

Alloys for H diffusion contain 1–26% Ag, 1–26% Au, 0.1–0.9% Ru, 0.1–2% Al and 0.1–2.5% Pt, remainder Pd. In one example an alloy contains 75% Pd, 20% Ag, 2.5% Au, 0.5% Ru, 1% Al and 1% Pt.

**CHEMICAL COMPOUNDS**

**Synthesis of Silyl Metal Complexes**

DOW CORNING CORP.  

*British Patent* 1,363,158

Silyl Pt and Pd complexes are formed by reacting disilanes or hydrosilanes with Pt or Pd phosphine complexes. Thus Si\(_2\)Cl\(_4\) with Pd(PPh\(_3\)_Me)\(_2\)Cl\(_2\) gives Pd(PPh\(_3\)_Me)\(_2\)(SiCl\(_4\))Cl.

**CHEMICAL TECHNOLOGY**

**Morphology of Dimensionally Stable Anodes**


X-ray studies of 2:1 molar ratio solutions of Ti and Ru painted on a clean Ti substrate and fired at 100–700°C showed that below 300°C they are amorphous and above 700°C they are fully crystalline with extremely small crystals of 100–500Å. Electrical conductivity of fully crystalline solid solutions falls between the insulator TiO\(_2\) and metallic conductor RuO\(_2\).

**ELECTRICAL AND ELECTRONIC ENGINEERING**

**Reliability Studies of the PtSi-Ta-Au Metalisation System for Microwav Power Transistors**


X-ray and electron diffractometry studies of the Si-Ta-Pt-Au and Si-Pt layers showed formation of TaSi, TaSi\(_2\) and TaPt compounds at > 450°C, while PtSi formed at the Si-Pt interface at 200°C in 20 min. The ion backscattering data indicate that no further reaction takes place at the Si-Pt interface when annealed in vacuum at 700°C. Auger electron data on the Si-Ta-Pt-Au system are also obtained and discussed.