ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES
The Relation Between Adsorption and Catalysis Centres of the Surface of a Platinum Sponge
The number of catalytic centres on Pt sponge (37.38 sample) was determined by studying the hydrogenation of C,H, at 75–245°C and 50–300 torr. The results show that the number of catalytic centres on the Pt sponge was (0.92±0.03) x 10^20 which is in good agreement with the number derived from adsorption experiments (1.03±0.03) x 10^20. This suggests that the adsorption and catalytic centres are of the same nature.

Study of Simultaneous Adsorption of Hydrogen Peroxide and Some Organic Acids on Platinum by Impulse Methods
The simultaneous adsorption of H,O, and organic acids (acetic, n- and iso-butyric, iso-valeric) on Pt was shown to occur on the same Pt centres. The acids have an inhibiting effect on the decomposition rate of H,O2.

Chemisorption of Nitrogen on Platinum (111): Reflection-Absorption Infrared Spectroscopy
Nitrogen adsorption on a (111) oriented Pt ribbon was studied under ultra-high vacuum conditions. The activation energy for desorption was found to be 40kJ/mole at 120K. The initial sticking probability at this temperature was found to be 0.15 and the maximum uptake was ~1.1 x 10^-14 molecule/cm².

Photoelectron Spectroscopic Studies of the Chemisorption of Ethylene and Halo-substituted Alkenes on the (100) and (111) Crystal Surfaces of Platinum and a General Model for the Dissociation of Unsaturated Molecules at Surfaces
X-ray and ultraviolet photoelectron spectroscopy were used to study the chemisorption of ethylene and halogen-substituted alkenes on the Pt(100) and Pt(111) surfaces. The results show that the initial dissociation of the vinyl halides at submonolayer coverage is followed by an associative mechanism at higher coverages. A statistical model explaining the differing reactivities of the alkenes on the two types of surfaces is proposed.

The Influence of Alloiying on the Heat Resistance of Platinum Alloys
The influence of Ru, Rh, Ir, Au and Pd alloying additions on the heat resistance of binary Pt alloys was studied by measuring their creep rate in air and in molten glass at a stress σ=0.5kg/mm² at 1200–1700°C. The results show that alloying Pt with Ru, Rh and Ir considerably lowers the creep rate and increases the time to failure. Alloying Pd does not give a strengthening effect. Alloying with 5% Au lowers the creep rate from 76 to 12.5%/h and increases the time to failure from 0.5 to 2.5h at 1400°C and stress σ=0.5kg/mm² in air.

Investigations of Metal Catalysts. X. Characterisation of Pt-M Catalysts (M=Fe, Co, Ni). XI. Investigations on Pt-γ-Al2O3 Catalysts Modified by Iron, Cobalt and Nickel
X-ray powder methods, magnetic studies and measurements of dispersity were used to characterise the phase structure and dispersity of carrier-free P-M bimetallic catalysts (M=Fe, Co, Ni) respectively. Pt-M/γ-Al2O3 catalysts were studied by magnetic investigations, reflectance spectra and determination of dispersity. The phase structure of Pt-rich catalysts was found to be of Pt,Fe superstructure to a high degree. All the Pt-Fe/γ-Al2O3 catalysts contained Fe⁷⁺ ions in octahedral symmetry. (54 Refs.)

Studies of the Properties of Calcium and Platinum Oxide Compounds
Studies of the properties of Pt and Ca oxide compounds formed on Ca sieves during recovery of Pt used in nitric acid production were carried out. The results showed a high instability of the bond between CaO and PtO₂ and a tendency to form compounds with a lower CaO content. Thermal stability of the compound was studied at 700–900°C. Further studies at pilot scale are suggested to ascertain losses from the above reaction during Pt recovery on the Ca filters.
Oxygen Penetration into the Bulk of Palladium


Studies of O₂ interaction with polycrystalline Pd showed that above 250°C a significant amount of O₂ penetrates into the bulk at pressures below the dissociation pressure of PdO. The uptake rate of O₂ began to decline after about 100 monolayers of O₂ were incorporated.

Thermodynamic Properties of Hydrogen in Palladium and Its Alloys under Conditions of Constant Volume


Thermodynamic properties of H/Pd and its alloys were studied experimentally under conditions of constant alloy volume. It is shown that the phase change a → P₂, which is characteristic of Pd/H no longer appears under condition of constant volume. This shows that long range dipole-dipole elastic interactions are predominant in this system.

Adsorption and Absorption of Hydrogen by Thin Palladium Layers

R. V. BUCUR, Surface Sci., 1977, 62, (2), 519-535

Kinetic analysis for the sorption mechanism of H₂ by a Pd layer is presented. Kinetic relationships describing the time dependence of the atomic fraction 0 during the sorption were obtained by direct integration of the differential balance equations.

Chemical Reactions on Palladium Surfaces Studied with Pd-MOS Structures

I. LUNDSTROM, M. S. SHIVARAMAN and C. SVENSSON, Surface Sci., 1977, 64, (2), 497-519

The catalytic reactions on Pd and Pt surfaces were successfully studied with metal-oxide-semiconductor structures. The hydrogen induces a flatband voltage shift at the metal-oxide interface, which is a measure of the amount of H₂ in the metal. The Pt film acts like a selective H₂ filter enabling the determination of participating species in the surface reaction in a very simple way.

A Conjecture on a Possible Relation Between the 55K Heat Capacity Anomaly in Palladium Hydride and the Modification of the Vibrational Spectrum of Palladium


The calorimetric measurements and lattice dynamics studies were used to explain the heat capacity anomaly at 55K in the Pd-H system. It is proposed that this anomaly may be caused by a displacement of the Pd atoms. This suggestion may have important consequences in the interpretation of superconductivity in these alloys.

Adsorption of NO and CO on a Ru(10\overline{1}0) Surface

R. KU, N. A. GJOESTEIN and H. P. BONZEL, Surface Sci., 1977, 64, (2), 465-483

The chemisorption of NO and CO on a (10\overline{1}0) Ru surface was studied by LEED, AES and thermal desorption spectroscopy. The results show that NO adsorbs and rapidly dissociates into separate N and O adsorbed phases with ordered C(2 × 4) and (2 × 1) structures, respectively. CO was found to adsorb in a molecular state and does not form an ordered structure. The results are discussed in terms of the catalytic reduction of NO by H₂ and CO.

CHEMICAL COMPOUNDS

A Structural Model for Barium Platinum Oxide, Ba₃Pt₂O₇


Crystal structure studies of Ba₃Pt₂O₇ show it to have a hexagonal cell of dimensions a = 10.109Å and c = 8.638Å, space group P6₃2c and Z = 4. Pt occupies mainly the face-sharing octahedra. The Pt-O bond length was found to be 2.00Å and the three long Pt-O distances 2.65Å.

Covalent Transition Metal, Lanthanide and Actinide Tetrahydroborate Complexes


A comprehensive review of synthetic methods and chemical properties of known tetrahydroborates, including Au and Pt group metal tetrahydroborates is presented. Structural studies of these compounds were carried out using vibrational spectroscopy and nuclear magnetic resonance. The geometric parameters associated with the metal-ligand interaction are derived and the bonding in covalent metal tetrahydroborates in relation to their physical and chemical properties is discussed. (213 Refs.)

The Addition of Alkyl Halides to Rhodium (I) Dithiolene Complexes. The Synthesis, Structure and Chemical Properties of Rhodium (III) Acyl Species


The synthesis and characterisation of a series of anionic and neutral Rh(III) acyl complexes by i.r. and ¹H NMR spectroscopy are presented. The structure of a representative member of the series (R = Et) was determined by single crystal X-ray diffraction. The complex (AsPh₃)Rh(COEt)₂(PPh₃)₃ crystallises in space group P2₁/a (C₁₆h) in a cell of dimensions a = 18.466, b = 13. 608, c = 19.088Å, β = 106.39° with four molecules/unit cell.
Stereospecific Exchange of Carbon Monoxide in Clusters of the Type Os(CO)\(_{10}\)X\(_2\)

Compounds of the type Os\(_8\)(10)\(_n\)X\(_2\), where X=Cl, Br, I and OEt, have been studied by \(^{13}\)CO NMR techniques. It was found that stereospecific exchange of labelled CO takes place on the nonunique Os atoms. Carbonyl bridging between the different types of Os atoms does not take place.

ELECTROCHEMISTRY

XPS Spectroscopic Study of Potentiostatic and Galvanostatic Oxidation of Pt Electrodes in H\(_2\)SO\(_4\) and HClO\(_4\)

X-ray photoelectron spectroscopic studies of the surface oxides produced by potentiostatic and galvanostatic oxidation of Pt electrodes in HClO\(_4\) and H\(_2\)SO\(_4\) were carried out. The oxide species produced as the initial oxidation product by successively more anodic potentiostatic oxidation in 0.2M HClO\(_4\) is found to have a Pt\(^{2+}\) oxidation state and a limiting thickness of 8A. Galvano-

The Analysis of Ru oxides observed on Ru supported graphitised C black and a comparison of both electrochemical and gas-phase chemi-

The anodic evolution of O\(_2\), on the Ir oxide electrode prepared by thermal decomposition of IrCl\(_4\) on a Ti substrate, was studied in acidic and alkaline solutions. The mechanistic parameters and the overall current densities for O\(_2\) generation were determined. It was shown that the rate-

The Electroformation up to a Monolayer Thickness at the Pt/KHSO\(_4\)(Melt) Interface and Its Relation with the Electrodereduction Process

The electrochemical reactions occurring at the Pt/KHSO\(_4\)(melt) interface were studied, and the the potentiodynamic E/I response of the interface under various O\(_2\) potentials and under different perturbation conditions. A reaction model involving different surface species gives a satisfactory explanation of the anodic and cathodic experimental results.

The Anodic Evolution of Oxygen on Iridium Oxide Electrode

The anodic evolution of O\(_2\) on the Ir oxide electrode prepared by thermal decomposition of IrCl\(_4\) on a Ti substrate, was studied in acidic and alkaline solutions. The mechanistic parameters and the overall current densities for O\(_2\) generation were determined. It was shown that the rate-

Oxide Stability and Chemisorption Properties of Supported Ruthenium Electrocatalysts

The analysis of Ru oxides observed on Ru supported graphitised C black and a comparison of both electrochemical and gas-phase chemi-

Catalysts in Action

A new technique, controlled atmosphere electron microscopy, was developed to study reactions between gases and solids at very high magnifications, while they are taking place. The technique was used to study the growth of Pt particles supported on \(\gamma\)-Al\(_2\)O\(_3\). It was found that the presence of Cl ions tends to suppress the growth of Pt on Al\(_2\)O\(_3\).

Determination of Platinum in Sands by Flameless Atomic Absorption Using the HGA-2100

A method for the determination of Pt in beach sands from the south of Chile, using atomic absorption and a graphite furnace is discussed. The use of the graphite furnace was found to improve the sensitivity of determination. It was shown that the concentration of HCl does not affect the results. The reproducibility and accuracy were found satisfactory for the studied range of 0.02\(\mu\)g Pt/ml-1.00\(\mu\)g Pt/ml.

Palladium and Titanium Thin Films as Probes for Determination of Hydrogen in Helium

Studies of the utility of a thin film of Pd in the detection and determination of H\(_2\) gas in a He atmosphere under ambient conditions showed that the response of Pd to H\(_2\) was different under unannealed and unannealed conditions. Un-

Platinum Metals Rev., 1977, 21, (4)
Heterogeneous Catalysis

New Hydrogenation Catalysts with Platinum Deposited on Polyamide-66. VI. Activity and Selectivity in the Hydrogenation of Styrene and Cyclopentadiene


Studies of the activity and selectivity of Pt/polyamide-66 catalysts were carried out during hydrogenation of styrene and cyclopentadiene using a reaction scheme of the "rake" type. The results showed that the adsorption-desorption equilibria of unsaturated hydrocarbons on Pt/polyamide catalysts are displaced towards the desorption thus favouring the production of an intermediate compound in successive hydrogenation reactions. The observed modifications of the catalytic properties of Pt/polyamide are explained by a partial electron transfer from the polyamide support acting as an electron donor, towards the incomplete inner electron shell of Pt.

The Catalytic Decomposition of Formaldehyde on Palladium

G. ERTL and J. TORNAI, Z. Phys. Chem. (Frankfurt), 1977, 104(4-6), 301-308

Spectroscopic studies of the decomposition of formaldehyde at a clean Pd surface by polycrystalline wire were carried out in a UHV flow system. The thermal desorption experiments showed that desorption takes place at higher temperatures than if present alone on the surface. The desorption energy of H₂ increased by the interactions between H₂ and CO₂. A reaction scheme is proposed whereafter desorption of the products is rate-determining.

Noble Metal Catalysis. IV. Products from Benzyl Alcohol Decomposition


Benzyl alcohol dihydrogenates to benzaldehyde and toluene in the presence of Pd, Rh or Ru chloride catalysts. The results show that the benzaldehyde can either carbonylate to benzene or disproportionate to benzyl benzoate. The order of catalyst activity is: Pd>Rh>Ru. Benzyl alcohol also dehydrogenates to benzaldehyde or dehydrates to dibenzyl ether. The order of catalyst activity is then: Ru>Rh>Pd.

Adsorption of Hydrogen on Skeleton Rhodium, Ruthenium and Rhodium-Ruthenium Catalysts


The adsorption of H₂ on skeleton Rh, Ru and 5-60 at.% Ru-Rh catalysts was studied using the charging curves method. It is shown that the adsorption ability of the catalysts with respect to H₂ in 1N H₂SO₄ decreases with increase in Ru.

Vapour Phase Carbynolation of Methanol at Atmospheric Pressure in the Presence of a Rhodium Catalyst. II. Rhodium Chloride on Alumina


Studies of the vapour phase carbynolation of methanol were carried out over Rh chloride supported on γ-Al₂O₃ at atmospheric pressure. The catalytic activity depended on the Rh concentration on the Al₂O₃ surface. Methyl iodide in the reacting mixture was found to affect the carbynolation of methanol only when its concentration was quite low.

Methane On-site as a Nuclear Power Station Spin-Off

H. WEBSTER, Processing, June 1977, 28, 30

Methane can be synthesised from carbon dioxide and hydrogen in the presence of a Ru/γ-Al₂O₃ catalyst. The stages in the development of such a methanation process, which resulted in the successful commissioning of four patented plants at Hinkley Point and Hunterston nuclear power stations, are outlined.

Study of the State and Behaviour of Hydrogen on Ru Catalysts


Adsorption, thermodesorption and isotopic methods were used to study the state of H₂ on the surface of Ru/Al₂O₃, Ru/SiO₂ and Ru-black catalysts. It was found that H₂ is adsorbed very strongly on the surface of these catalysts and can be removed only at high temperatures. The specific adsorption of H₂ is highest on the Ru/Al₂O₃ and lowest on the Ru-black catalyst. The H₂ adsorbed on Ru can migrate on its surface and exchange with the OH groups of the carrier.

The Activity of Supported Ruthenium-Palladium Catalysts in Hydrogenation and Isomerisation of Hexene-1


The hydrogenation and isomerisation of hexene-1 was carried out over 1% Pd, Ru and Ru-Pd catalysts supported on TiO₂, ThO₂ and activated C₁ in 96% ethanol at 20-40°C. It is shown that Ru-Pd catalysts are 1.5-2 times as active as Pd catalysts and 10-15 times as active as Ru catalysts. The Ru-Pd/TiO₂ and Ru-Pd/ThO₂ are 2-3 times as active as the Ru-Pd/C catalysts. The highest isomerisation activity was found for Pd catalysts.

Platinum Metals Rev., 1977, 21(4) 141
Homogeneous Catalytic Hydrogenation of Unsaturated Carboxylic Acid Esters with \( \text{H}_2\text{PtCl}_4 + \text{SnCl}_2 \) in isopropanol


Studies of the catalytic system, prepared from \( \text{H}_2\text{PtCl}_4 + \text{SnCl}_2 + \text{H}_2\text{O} \) and the additives HBr and H\(_2\)O in isopropanol showed it to be a very efficient catalyst for homogeneous hydrogenation of unsaturated esters under mild conditions. Reaction rates up to 40 m M\(_\text{ol}/\text{L} \cdot \text{min} \) and turnover numbers UZ higher than 1600 were observed.

Synthesis and Reactions of and Catalytic Homogeneous Hydrogenation by Chlorocarbonyl(o-(diphenylphosphino)-N,N-dimethylamine)iridium(I) and Chlorocarbonyl(o-(diphenylphosphino)-N,N-dimethylbenzylamine)iridium(I)


The preparation of complexes IrCl(CO)PCN and IrCl(CO)PN, where PN is o-(diphenylphosphino)-N,N-dimethylbenzylamine and PCN is o-(diphenylphosphino)-N,N-dimethylamine is described. The complexes react with HCl and with a mixture of MeI and iodide. They also catalyse the hydrogenation of hexene-1 with the following effectiveness: IrCl(CO)PCN > IrCl(CO)PN > IrCl(CO)(PPh\(_3\))₂.