

Chemistry of the Platinum Metals

A REVIEW OF THE AMERICAN CHEMICAL SOCIETY MEETING

As part of the 158th National Meeting of the American Chemical Society, held in New York in September, a Symposium on the Platinum Group Metals was organised. This review outlines the papers presented, and deals also with a number of other papers given during the remainder of the meeting.

At this meeting the great interest that at present exists in the chemistry of the platinum group metals and their use in a wide range of applications was clearly demonstrated by the fact that some fifty papers concerned with this group of elements were read.

The Division of Inorganic Chemistry included a Symposium on Platinum Group Metals, organised by Dr U. V. Rao, of Matthey Bishop. This was divided into four sessions: (1) synthesis, structure determination, and the study of magnetic and thermodynamic properties of some platinum group metal compounds; (2) chemistry of σ - and π -bonded complexes of platinum group metals; (3) spectroscopic properties of platinum group metal compounds; and (4) newer industrial aspects of platinum group metals.

In the first session a paper entitled 'Magnetic Properties of Platinum Group Metal Alloys', by H. J. Albert, *et al.* (Engelhard Industries) reviewed the work done on investigating the magnetic properties of platinum metals alloyed with iron, nickel and cobalt. Particular reference was made to the extraordinary magnetic properties of cobalt-platinum. G. Parravano (University of Michigan) considered 'Surface Activity of Platinum Group Metals towards Hydrogen'. The chemical reactivity of the metals dispersed on alumina and silica substrates was studied by a method which enabled differentiation to be made between the thermodynamic and kinetic contribution to the reactivity of the surface. A potentially interesting field for

usage of the platinum metals was indicated by A. Wold (Brown University) in 'Platinum Group Metal Chalcogenides'. The structure and electrical and magnetic properties of the sulphides, selenides and tellurides and some ternary compounds were theoretically considered, and theory was compared with experiment. The ability to predict whether or not the compounds are diamagnetic semi-conductors or metallic was demonstrated. Simple and complex oxides of platinum and palladium were described in papers by O. Muller and Rustum Roy (Pennsylvania State University) and H. R. Hoekstra, *et al.* (Argonne National Laboratory) entitled respectively 'Recent Studies on Simple and Complex Oxides of Platinum and Palladium' and 'Reactions of Platinum Dioxide with some Metal Oxides'. In the first paper a study of the systems Pt-O and Pd-O up to 900°C and 3,500 atmospheres oxygen pressure was described and complex oxides with alkaline earths, magnesium and zinc oxide were noted. In the second, an investigation into the reactions between platinum dioxide and di-, tri-, and tetra-valent oxides at 40 kilobars pressure and 750 to 1250°C was considered and the reaction products were characterised.

'Nitrido Complexes of the Platinum Group Metals', by M. J. Cleare, F. M. Lever (Johnson Matthey) and W. P. Griffith (Imperial College) reviewed terminal and bridged nitrido complexes with particular reference to new μ -nitrido bridged complexes of Os (IV) and Ru (IV). Trinuclear iridium nitrido complexes, only at present under

investigation, were briefly considered. A. D. Allen and F. Bottomley (Toronto University) dealt with nitrogen complexes with emphasis on the possibility of atmospheric nitrogen fixation using Group VIII metal complexes. Preparation, properties and interesting features of complexes containing molecular nitrogen were surveyed. 'Activation of Covalent Molecules by Platinum Group Metal Complexes', by L. Vaska (Clarkson College of Technology) enquired into the governing factors of reversible reactions of complexes with molecular hydrogen, oxygen, carbon monoxide, sulphur dioxide and ethylene and related molecules, discussing the biological and catalytic implications of the results. L. M. Venanzi (State University of New York) in 'Hydrido-complexes of Platinum Group Metals' reviewed the subject stressing the considerable interest of iridium in this field. The nature of the bonding of small inorganic and organic molecules, particularly acetylene and ethylene, to the derivatives of platinum metals, usually in low valency state, was considered by C. D. Cook and K. Y. Wan (Toronto University) in the paper 'Organometallic Compounds of the Platinum Group Metals'.

The application of physical, particularly spectral, techniques to the elucidation of the structures of platinum metal complexes was considered in a group of five papers.

The opening paper of the final session of the symposium, 'The Availability of the Platinum Group Metals', by L. B. Hunt and F. M. Lever (Johnson Matthey) outlined the considerable resources of the metals and related their production to applications in industry. (This was published in full in the October 1969 issue of *Platinum Metals Review*.) The potential source of rhodium and palladium arising from nuclear reactors was considered by C. A. Rohrmann (Battelle-Northwest) in his paper 'Nuclear Power Contribution to the Resources of Platinum Group Metals'. It should be commented that even though they are theoretically available, tremendous problems are associated with

their extraction from highly active fission products, while the fact that the rhodium and palladium isotopes, even if 100 per cent pure, are radioactive, seems to make their economic recovery unlikely and their usage undesirable.

C. E. Tirrell (Electrodecs Inc.) in 'Use of Platinum Group Metals in Electroplating' indicated an increasing usage of platinum plated titanium as auxiliary anodes particularly in the copper-nickel-chrome finishing of automobile trim. The various types of fuel cell, their performance and limitations, were reviewed by J. Giner (Tyco Laboratories) and the possibility of platinum continuing to be used as the catalyst in acid cells using reformer gases or hydrocarbons and unscrubbed air was discussed. P. M. Rylander (Engelhard Industries) in 'Double Bond Isomerisation as a Product Controlling Factor in Hydrogenation over Platinum Group Metals' considered the facile migration of olefinic double bonds in the presence of platinum group metals and hydrogen and stressed its importance in product composition.

Fuel Cell Symposium

In the Sixth Biennial Fuel Cell Symposium, which was held under the auspices of the Division of Fuel Chemistry, a number of papers considered the catalytic properties and usage of platinum. A. J. Appleby (Institute of Gas Technology) reviewed the theoretical factors influencing electrocatalysis, particularly for the oxygen electrode, on noble metals and oxides. S. Gilman and L. D. Sangeramo (NASA/Electronics Research Centre) pointed out the sensitivity of oxygen reduction to adsorbed anions and organic substances in acid cells and to heavy metal ions in alkaline cells.

Problems associated with separating the effects of the electrode structure from the intrinsic activity of a particular catalyst and means of overcoming them were discussed by W. M. Vogel and J. T. Lundquist (Pratt & Whitney Aircraft). The results of an investigation into the influence of structural factors

on the activity of platinum catalysts for different reactions were reported by V. S. Bagotzky, *et al.* (Institute of Electrochemistry, Academy of Sciences, U.S.S.R.) while in a paper by S. Schuldiner and B. J. Piersma (Naval Research Laboratory) it was shown that the free radicals generated when formic acid or sodium formate dehydrogenate on a clean platinum surface react with each other and the surface to form organic residues which hinder further hydrogenation. The factors involved in the mechanism of the direct oxidation of hydrocarbons at a platinum electrode were studied and the methods employed were described by M. Bonnemay, *et al.* (Laboratoire d'Electrolyse du C.N.R.S.).

Petroleum Chemistry

In the Division of Petroleum Chemistry there were presented a number of papers concerning the use of platinum metals in processes associated with the petrochemicals industry. 'A New Process for the Hydroformylation of Olefins', by K. L. Olivier and F. B. Booth (Union Oil of California) described the use of hydridocarbonyltrisphenylphosphinerhodium as a homogeneous catalyst for the hydroformylation of olefins to aldehydes. E. J. Eisenbraun, J. M. Springer and C. W. Himan (Oklahoma State University) considered the reaction of methyl substituted 1-tetralones with heated Pd/C catalyst in absence of solvent and showed the products to be the expected naphthalene and naphthol.

Milder conditions for the hydrocracking of various hydrocarbons were shown to be required if platinum-alumina catalysts are reacted first with hydrochloric acid, then with a sulphur chloride or sulphur dioxide and chlorine, and finally again with hydrochloric acid. This work was described by J. P. Giannetti and R. T. Sebulsky (Gulf Research & Development Co.) in 'Hydrocracking with Chlorinated Platinum-Alumina Catalysts'. A. W. Ritchie, *et al.* (Shell Development) showed that, in the dehydrogenation of methylcyclohexane and decalin, the catalyst

stability was inversely proportional to catalyst pore size and that the more stable catalysts had smaller pore diameters. In 'The Chemistry of Aromatics Production via Catalytic Reforming', by E. L. Pollitzer, *et al.* (Universal Oil Products) work was described designed to elucidate the mechanism of reforming with platinum-acidic alumina catalysts, using the pure compounds cyclohexane, cyclopentane and a number of aliphatic paraffins.

Two papers by N. W. Cant, *et al.* (Mellon Institute), 'Catalytic Oxidation. (1) The Reaction of Ethylene over Palladium and Palladium-gold alloys. (2) Silica-supported Noble Metals for the Oxidation of Ethylene and Propylene' described the products of these reactions and applied the results to a kinetic and theoretical study of the processes. Results of an investigation into the activation of molecular oxygen and oxidation of carbon monoxide at surfaces of iron, cobalt, ruthenium, nickel, platinum, silver and gold and their theoretical treatment were described by D. Y. Cha (Upjohn Co.) and G. Parravano (Michigan University). In 'The Oxidative Carbonylation of Ethylene to Acrylic Acid', by D. M. Fenton, *et al.* (Union Oil of California) it was stated that, in stirred autoclaves, ethylene reacts with carbon monoxide and oxygen in presence of palladium chloride and a redox system in acetic acid solution to yield acrylic acid and β -acetoxy-propionic acid, which thermally cracks to acrylic and acetic acids. An investigation into hydrocarbon autoxidation using chlorocarbonylbis(triphenylphosphinerhodium) and related compounds as homogeneous catalysts using diphenylmethane both as solvent and substrate was described by L. W. Fine, *et al.* (American Cyanamid).

Inorganic Chemistry

Several papers concerning platinum metals related to a wide field of interests, including complex compounds, were presented to this Division.

F. M. L.