

Homogeneous and Heterogeneous Catalytic Phenomena

A REVIEW OF THE SECOND INTERNATIONAL COLLOQUIUM

At an international colloquium sponsored by the Centre National de la Recherche and held at Lyon in November 1977 the four principal lectures, and several of the supporting ones, featured the use of platinum group metals as catalysts. The main objective of this meeting was to bring together chemists working with heterogeneous catalytic reactions and others specialising in inorganic and organometallic chemistry in order that they could together consider the relations between homogeneous and heterogeneous catalytic phenomena.

Throughout the conference the theme was to explore that intermediate area of catalytic behaviour which lies between the homogeneous systems on the one hand and the heterogeneous systems on the other. There were four plenary lectures. The first, Homogeneous and Heterogeneous Catalysis—Kinetic and Mechanistic Aspects, by Professor J. Halpern, of the University of Chicago, provided a detailed analysis of Wilkinson's catalyst $(\text{Ph}_3\text{P})_3\text{RhCl}$. The enormous complexity of catalytic hydrogenation of alkenes by this complex was explored. Halpern, in his summary, drew attention to the problem of making realistic comparisons between the truly homogeneous and truly heterogeneous, or supported homogeneous, catalysts.

The second plenary lecture—Cluster Compounds and their possible relation to Heterogeneous Catalysts—was given by Dr. B. F. G. Johnson, of the University of Cambridge, who summarised the contribution that studies of cluster complexes have made to the understanding of the chemistry occurring on macroscopic crystal surfaces. He took as his examples the cluster carbonyls of osmium for which a series of derivatives based on Os_3 , Os_4 , Os_5 , Os_6 , Os_7 and Os_8 units has been established. The structural relationship between small groups of metals and the bulk

metal structure was examined. Bonding modes adopted by small molecules such as CO, H, alkenes and alkynes with triangular, square planar, and butterfly arrangements of metal atoms were described as possible models for the binding of such molecules to the bulk metal.

Professor C. U. Pittman, University of Alabama, took as his subject the chemistry of supported homogeneous catalysts, in particular those based on rhodium and platinum compounds. In his lecture, Catalytic Reactions over Anchored Complexes on Polymers, he developed the theme that many of the problems associated with homogeneous catalysts, such as loss of catalyst due to difficulty in retrieving precious metal salts, may be resolved by the fixation of the catalyst to a rigid support. He was able to demonstrate that variation in support design could be used to modify or regulate catalyst activity but conceded that, in general, anchored catalysts were less efficient than their strictly homogeneous counterparts.

The final plenary lecture—Oxidation Reactions in Homogeneous and Heterogeneous Phases: Oxygen Activation—by Professor R. Ugo, of the Instituto di Chimica Generale, Milan, was devoted to catalytic oxidation. In a wide-ranging lecture Professor Ugo first discussed the role of silver in the catalytic

oxygenation of ethylene to ethylene epoxide by oxygen. He continued with a summary of the work by Sharpless and the study of the stoichiometric oxidation of olefins by metallo-oxygen and seleno-oxygen compounds. He reported on stoichiometric oxygenation by the oxygen complexes of the platinum metals. The role such complexes might play as catalysts in the homogeneous phase was appraised. Throughout considerable emphasis was placed on the mechanisms by which these various oxidation reactions might occur.

These lectures will be published in full in a future volume of the *Journal of Catalysis*. Many of the supporting lectures, some briefly mentioned below, have been published in the same journal.

In a supporting lecture Dr. M. Bartholin, L.M.O., Villeurbanne, France, described the fixation and evolution of organometallic rhodium complexes supported on modified polyphenylsiloxane and silica. Oxidative-

additions with C-H fission at triosmium clusters was reported by Dr. A. J. Deeming, of University College, London, and asymmetric synthesis via polymer attached optically active platinum catalysts by Dr. J. Stille, of Colorado State University. Dr. Z. M. Michalsha, Institute of Polymers Technical University, Lodz, Poland, presented a paper on the catalytic activity of supported rhodium (I) and platinum(0) complexes in hydrosilylation reactions, and A. Guyot a paper on the influence of the texture of phosphinated polystyrene resins on the stability and catalytic activity of supported rhodium complexes. Papers by G. Sbrana and Dr. R. H. Grubbs considered the catalytic activity of ruthenium (II) and rhodium (I) catalysts bound to polycarbonylate and poly-B-diketone matrices, and hybrid catalyst-metathesis catalysts attached to polystyrene copolymer, respectively.

B. F. G. J.

Platinum Metal Co-ordination Compounds

SPECIALISED PRODUCTS FOR INDUSTRIAL OR DEVELOPMENT USE

Strictly speaking most compounds of the platinum group metals can be classified as co-ordination compounds although most of the commercially available materials comprise relatively simple species such as oxides and chlorides. In recent years other platinum group metal co-ordination compounds, particularly organometallic complexes, have begun to find increasing applications in various fields. To meet the existing demand and to stimulate the development of additional applications Johnson Matthey Chemicals have considerably extended the range of platinum group metal compounds commercially available. This expanded range is possible as a result of extensive research and development work in the Johnson Matthey laboratories, where all the compounds are produced and fully characterised. A new publication entitled "JMC Co-ordination Compounds of Platinum Group Metals", which is available from Johnson Matthey offices and associated companies, lists over one hundred of these compounds, many of which are organometallic in nature. Information on infra-red

spectra, colour and form, solubility and stability are provided for each compound together with comments on the possible applications which have been reported to date.

The major types of compounds available are carbonyl, carbonyl halide, carbonyl phosphine, ammine (amine), β -diketone, phosphine and nitrosyl, although a variety of other individual species is included. Potential applications are likely to occur in the petrochemical, heavy organic, pharmaceutical, photographic, scent and cosmetic industries among many others.

Most of the applications researched on these compounds to date are concentrated on homogeneous catalysis and several large plants are now in operation using platinum metal co-ordination complexes as catalysts.

The aim of the new catalogue is to stimulate research into these and other applications of platinum group metal complexes and all the compounds listed can be supplied in development quantities. In addition enquiries for complexes not mentioned in the publication are welcomed.

M. J. C.