

Chemisorption and Catalysis on the Platinum Metals

A SELECTIVE REVIEW OF THE RIDEAL CONFERENCE

The Rideal Conference takes its name from the late Sir Eric Rideal who was one of the leading contributors to the understanding of chemisorption and catalysis in the present century. The conference is held every three years and brings together scientists from both industrial and academic backgrounds to present and discuss their work in the area of chemisorption and catalysis. The most recent Rideal Conference was held at the University of Bradford in March and was attended by 84 people. A total of 17 papers was presented, covering a wide range of topics from the characterisation of catalysts by surface analysis techniques to classical chemisorption experiments, representing interest in metal-support interactions, reaction intermediates and industrial processes such as methanation and emission control.

Metal-Support Interactions

A strong feature of the papers presented at the conference was the use of modern analytical techniques in the characterisation of catalysts and adsorbed species. These techniques included infrared spectroscopy, X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), high resolution vibrational spectroscopy and extended X-ray absorption fine structure (EXAFS). EXAFS can provide information about the nearest neighbour atoms of a particular element and was applied to highly dispersed rhodium catalysts by R. Prins of the Laboratory for Inorganic Chemistry and Catalysis, Eindhoven. Two support materials, alumina and titania, were studied, and the results gave an indication of rhodium particle size as well as of particle shape in the case of the titania support. Additional peaks in the EXAFS spectrum of well dispersed rhodium/alumina were thought to represent Rh^{3+} -Rh distances, which led to the

postulation that metal cations exist in the interface between the metal particles and the support, a factor which may be responsible for an increased metal-support interaction.

A number of techniques were used by G. Munuera of the University of Sevilla, Spain to investigate strong metal-support interactions (SMSI) in rhodium/titania catalysts which had shown high activity and selectivity for the Fischer-Tropsch synthesis. Carbon monoxide adsorption on a rhodium/titania catalyst resulted in oxidation of the metal to $\text{Rh}(\text{I})$, leaving carbon on the surface, while hydrogen adsorption on a similar SMSI system was characterised by two forms of adsorbed hydrogen, one of these being weakly bound.

It was concluded that the heterolytic dissociation of the weakly adsorbed hydrogen at the rhodium/titania interface, together with the dissociative adsorption of carbon monoxide were the main factors responsible for the high catalytic activity observed in Fischer-Tropsch synthesis. It was considered that $\text{Rh}(\text{O})$, $\text{Rh}(\text{I})$ and the titania support were acting as a multifunctional catalyst, and that SMSI was assisting in the carbon monoxide/hydrogen reaction.

Adsorbed Reaction Intermediates

The study of molecular adsorbates on single crystal platinum surfaces was reviewed in two papers, one by A. Bhattacharya, N. D. S. Canning and M. A. Chesters of the University of East Anglia who characterised ethylene adsorption on a $\text{Pt}(\text{I}11)$ surface, and the other by M. Surman, F. Solymosi, P. Hofmann, R. Diehl and D. A. King of the University of Liverpool who investigated isocyanates adsorbed on $\text{Pt}(\text{I}10)$. At temperatures above $\sim 155\text{K}$ HNCO adsorption on $\text{Pt}(\text{I}10)$ led to the formation of a surface isocyanate species. This species was found to decompose as the temperature was

raised, although oxygen stabilised the -NCO intermediate, retarding decomposition until 350K. Studies of ethylene adsorption on Pt(III) showed that the species on the surface changed with increasing temperature and a $\text{CH}_3\text{C-}$ species was detected under certain conditions. Although both of these papers presented work carried out under conditions divorced from those used in real life, they nevertheless give a valuable insight into the processes occurring on precious metal surfaces. The adsorption of -NCO species on platinum is particularly relevant to vehicle exhaust catalysts since this has been implicated in ammonia formation on such catalysts under reducing conditions.

A detailed study of the adsorption and interaction of carbon monoxide and nitric oxide on rhodium/alumina catalysts was made by E. A. Hyde and R. Rudham of Nottingham University and C. H. Rochester of Dundee University. Using thermogravimetric analysis, hydrogen and carbon monoxide adsorption isotherms and infrared spectroscopy of adsorbed carbon monoxide it was found that rhodium/alumina samples prepared by reduction of rhodium(III) nitrate gave superior dispersions to those prepared from rhodium(III) sulphite or chloropentaamminerhodium(III) chloride. The spectroscopic results gave evidence of isocyanate (-NCO) formation when carbon monoxide and nitric oxide were admitted to the catalyst, although the quantity varied according to the order in which the gases were admitted to the reactor. This work was

again relevant to vehicle exhaust catalysts and had formed part of a Science and Engineering Research Council CASE award sponsored by Johnson Matthey.

Methanation Activity

A useful screening technique for determining relative activities of catalysts for the methanation reaction was described by I. J. Kitchener, C. Komodromos, C. W. Lam and N. D. Parkyns of the British Gas Corporation. This technique, known as Temperature Programmed Methanation, was used to study monolith supported nickel/alumina and ruthenium/alumina catalysts. Of the catalysts tested a co-precipitated nickel/alumina catalyst showed highest activity. Despite the inherent problems in this type of approach to catalyst activity testing, particularly with regard to accurate temperature monitoring, useful kinetic data were obtained from the results as well as information on relative activities.

Although few of the papers presented at the Rideal Conference described work directly relevant to the commercial applications of the platinum metals, it was encouraging that a significant amount of research is being undertaken with the aim of gaining a basic understanding of the mode of adsorption of gases on such metal surfaces and the mechanism of reactions between adsorbed species. The pioneering of new surface analytical techniques will undoubtedly produce benefits in the characterisation of platinum metal catalysts. L.S.

The Chemistry of the Platinum Group Metals

Following the very successful meeting held in Bristol in 1981, a second international conference on this topic is to be held in Edinburgh from July 1-6, 1984, organised by the Royal Society of Chemistry. The chemistry of the six platinum group metals will be discussed in sessions devoted to aspects of photochemistry, electrochemistry, kinetics and mechanisms, industrial applications of thermochemistry, homogeneous and heterogeneous catalysis, and organometallic and cluster chemistry. In addition the use of platinum group metal compounds in organic synthesis and in medicine,

and current developments in physical techniques such as EXAFS, resonance Raman spectroscopy, and solid state NMR will be considered.

Among distinguished scientists who have already agreed to contribute are Bosnich, Brown, Calvert, Chatt, Clark, Drury, Fyfe, Graham, Halpern, Porter, Sheppard, and Werner; anyone wishing to contribute to the poster sessions, or to receive further information should contact the organising secretary, Dr. T. A. Stephenson, Department of Chemistry, University of Edinburgh, Scotland.