

Heterogeneous Catalyst Preparation

CONTINUING INTEREST IN SUPPORTED PLATINUM METALS

The Fourth International Symposium on "Scientific Bases for the Preparation of Heterogeneous Catalysts" was held in Louvain-la-Neuve, Belgium, from 1st to 4th September 1986 under the chairmanship of Professor Bernard Delmon. It was attended by some 350 scientists from many different countries. These symposia, which are held at four-yearly intervals, are now well established as occasions for reviewing progress in the science underlying the preparation and manufacture of technical catalysts. The sixty-seven plenary lectures and contributed papers covered the whole range of catalysis, with some emphasis on newer applications such as amorphous metals and pillared clays. A significant number of the papers dealt with catalytic applications of the platinum group metals.

The ability to control the distribution of the noble metal through a catalyst pellet is a matter of great practical importance: picturesque terms such as egg-shell, egg-white and egg-yolk structures have been used to describe the various possible locations of the metal that can be produced, and empirical means of achieving these structures have been developed. The plenary lecture by J. A. Schwarz of Syracuse University, U.S.A., described systematic studies of the effect of competitive electrolytes on the adsorption of chloroplatinic acid by alumina pellets. Three types of effect were recognised: (i) on the electrostatics of the solution near the support surface; (ii) on the pH of the solution; and (iii) on competition for adsorption sites by the competing electrolyte.

Several other papers addressed fundamental questions concerning the preparation of supported metal catalysts. Controlled-porosity silicas were used as model supports for platinum by M. A. M. Luengo, P. A. Sermon and K. S. W. Sing, of Brunel University, to establish how experimental conditions affected metal dispersion and location. D. Richard and

P. Gallezot (Institut de Recherches sur la Catalyse, Lyon) studied the effect of oxidising graphite and carbon black with nitric acid, hydrogen peroxide and sodium hypochlorite in order to provide ion-exchange sites for the platinumous tetrammine ion. High dispersions were obtained after reduction at 300°C.

It has been known for some time that noble metals may be deposited on photoreactive supports such as titania by photolysis of the metal salt. This technique has been extended to most of the noble metals, including silver and gold, and to other supports such as zirconia, niobia, thoria, zinc oxide and cadmium sulphide by J.-M. Herrmann, J. Disdier, P. Pichat and C. Leclercq (Ecole Centrale de Lyon). The method can be used to make bimetallic catalysts. Materials made in this way are more active in photocatalysis than those made by conventional methods.

The phenomenon of strong metal-support interactions (SMSI) continues to excite interest. Most of the work in this area has employed titania as the support, but attention is gradually turning to the use of other transition metal oxides. Y. - J. Lin, R. J. Fenoglio, D. E. Resasco and G. L. Haller of Yale University described work with vanadium(III) oxide as support: dissolution and re-deposition of vanadyl ions during the aqueous impregnation led to the encapsulation of rhodium particles. This system is far more complex than that based on titania.

The preparation and use of bimetallic catalysts attracted considerable attention. Three groups described their work on the incorporation of the promoter element through specific chemical reaction either with the metal or the support. Thus for example J. Margitfalvi and colleagues at the Hungarian Academy of Sciences showed how tin complexes could be attached to an alumina surface by first lithiating the surface hydroxyl groups and then reacting them with tin(IV) chloride. Yang Yashu and

her co-workers at the Dalian Institute of Chemical Physics, China, applied molybdenum to alumina through the use of a molybdenum π -allyl compound. In both pieces of work, platinum was the active component.

It is also a well-established fact that the oxidation of supported metal particles, followed by their re-reduction, frequently leads to improved catalytic behaviour. L. D. Schmidt of the University of Minnesota has followed the changes that occur during these stages by X-ray photoelectron spectroscopy and by transmission electron microscopy, using rhodium on alumina. Startling changes in alkane hydrogenolysis rates were observed, not adequately explained by the higher dispersion obtained after the second reduction. Changes in particle morphology were invoked to account for the results.

Catalyst Normalisation

Particular interest was shown in the Minisymposium on Catalyst Normalisation organised by E. G. Derouane (Namur). Work presented by T. Hattori of Nagoya University, Japan, and carried out under the auspices of the Catalysis Society of Japan, focused on the use of the carbon monoxide pulse adsorption method for supported platinum group metals. This is a simple and rapid method, widely used in

industry: it has been in use within Johnson Matthey for some twenty years. The second paper by G.C. Bond and P.B. Wells (Brunel and Hull Universities, respectively) described work on EUROPT-1, a reference platinum on silica catalyst manufactured by Johnson Matthey Chemicals for the Council of Europe's Research Group on Catalysis. Penetrating studies of this material in a number of European laboratories have revealed previously unexpected problems in interpreting hydrogen adsorption isotherms and have raised important questions which only further research will answer.

In his concluding remarks, J. T. Richardson of the University of Houston, who had attended all the earlier symposia, commented on the changes he had noticed in the twelve years over which the meetings had been held. In the first meeting, most of the contributions had been made by workers in industry: now they were in a minority, and academic workers had submitted most of the papers. He was not clear whether this represented a growth of academic interest in the subject of catalyst preparation or whether industry was now more cautious in the amount of information it revealed.

This fourth symposium showed very clearly however that the platinum group metals continue to play a very important role in the field of catalysis.

G.C.B.

Corrosion Protection Conference

Some four hundred corrosion engineers from many countries assembled in Birmingham, England, during November for "UK Corrosion '86". The conference involved a varied programme of lectures and an exhibition, and not surprisingly cathodic protection was featured in both. While interest in cathodic protection for the North Sea oil industry is at a lower level than in previous years, undoubtedly there is an increased awareness of the opportunities for the cathodic protection of steel reinforcement bars in concrete.

A paper authored by B. S. Wyatt of Global Cathodic Protection Limited, Telford, and D. J. Irvine of Tarmac Construction Limited, Wolverhampton included descriptions of many of the presently available systems.

Much interest attaches to mesh anodes, in the

form of rolls of a wire netting-type material consisting of a fine titanium mesh coated with electrocatalyst. The electrocatalysts in use include ruthenium and iridium. Although the weight of iridium used per plan square metre may be as little as one gram, the likely area of concrete that may receive some form of cathodic protection of the underlying rebars suggests that this application is likely to require significant quantities of ruthenium and iridium.

In spite of the technical difficulties of applying cathodic protection to some concrete structures, and the need to prove durability and commercial viability of individual systems, there was a general air of optimism that the market for cathodic protection systems for reinforcement bars in concrete was just about to expand.

P.C.S.H.