Platinum Group Metals in Catalysis

A REPORT FROM THE EIGHTH INTERNATIONAL CONGRESS

The International Congress on Catalysis is held every four years, and the eighth of the series took place at the International Congress Center in West Berlin from 2 to 6 July 1984. It was attended by over a thousand research workers from many countries, including a notable delegation from China. In addition to six plenary lectures and seventy-two orally presented papers, some forty posters were displayed each day. Conscientious participants had their work cut out to do justice to this rich fare. All accepted papers have appeared in four stout volumes, and the texts of the plenary lectures in a slimmer one, all published by Verlag Chemie, Weinheim. A further volume containing the discussion is promised.

As judged simply from the titles, about one-quarter of both the oral and poster presentations made explicit reference to one or other of the platinum group metals, which bearing in mind the state of current interest in zeolites, in selective oxidation and in base metal catalysts for hydrotreating, is an eloquent testimony to the predominant place which these metals continue to occupy on the catalytic scene. It would be pointless to attempt any kind of review of all the relevant papers. However, some of the most popular and important themes are surveyed below, and one or two papers of outstanding quality are highlighted.

Bimetallic Catalysts and Petroleum Reforming

For some thirty-five years, platinum on alumina catalysts have been used to upgrade naphtha fractions by effecting skeletal isomerisation and aromatisation, with a consequential increase in octane number. The discovery that bimetallic systems, such as platinum-rhenium and platinum-tin, deactivated less rapidly has stimulated much research into the role of the second component, but many questions still remain unanswered. The number of papers presented at the 8th International Congress on Catalysis devoted to bimetallic catalysts and petroleum reforming reflects the continuing interest in this important field.

Work by Russian and East German scientists has greatly extended the range of second components; elements selected from Groups IB to VIB of the Periodic Classification have been systematically examined, and antimony and bismuth have been found effective in high-temperature operation. Tin, which particularly promotes dehydrocyclisation, does not appear to be completely reduced in the working catalyst, and may play its role through modification of the metal-support interaction.

Much more is now understood about the intermediates existing during the preparation and re-activation of platinum on alumina catalysts. Although sintering occurs more readily in oxidising than in reducing atmospheres, its rate increases as oxygen concentration decreases, and Pt^{4+} is implicated in the sintering process. Conversely Pt^{4+} is formed as a chloro-complex during re-activation, and this is responsible for redispersion of the metal.

Reports were presented on the kinetics of coking, and its effect on product distributions. Other systems have been studied for various reactions; ruthenium-copper and ruthenium-gold for alkane hydrogenolysis, and rhodium-tin for hydrogenation of esters to alcohols.

Reactions of Synthesis Gas

A mixture of carbon monoxide and hydrogen can afford almost any molecule containing carbon, hydrogen and oxygen providing the necessary catalyst is to hand. Current research into the application of the platinum metals as catalysts for these reactions is focused on ruthenium as a possible catalyst for making diesel fuel or alkenes, and on palladium and rhodium for the synthesis of methanol or

higher alcohols including ethylene glycol.

Several papers given at this Congress were concerned with the mechanism of oxygenate formation, and the role of the additives (usually oxides having basic character). The formation of methanol is now definitely associated with ions in positive oxidation states, for example Rh^{2+}, and it is thought that these may play a part in the synthesis of ethanol and acetaldehyde over rhodium catalysts.

Strong Metal-Support Interactions

The discovery by workers at Exxon some years ago that noble metals supported on titania and other transition metal oxides lost their ability to chemisorb hydrogen when reduced at about 500°C has stimulated research into the structural chemistry of supported metals. The effect was named Strong-Metal Support Interaction (SMSI). In a few instances only this is accompanied by an improvement in catalytic performance, the Fischer-Tropsch synthesis being one. The phenomenon continues to excite catalytic chemists, although it is now reasonably certain that it is caused by a simple blocking of the metal surface by the partially-reduced support.

Two of the papers presented highlight the fact that the unexpected in catalysis often occurs. The oxide supports previously found to give SMSI were all more or less easily reducible, and this has been held to be an essential property if SMSI is to take place. However, similar effects have now been discovered with platinum on magnesia, the reduction of which is notoriously difficult. It was also reported that palladium on titania was capable of selectively reducing non-conjugated dienes; palladium on normal supports can only achieve this after prior isomerisation to the conjugated form.

Platinum and Cancer Chemotherapy

There may at first sight be no obvious connection between catalysis and cancer, but the link was forged in a masterly paper presented by John Turkevich of Princeton University. He showed that Cisplatin and other therapeutic complexes react with the component bases of DNA to form adducts having greatly different catalytic activities for decomposition of hydrogen peroxide. From this he was able to conclude that the miscoded DNA responsible for uncontrolled cell growth probably contained a string of cytosine molecules, and he was thus for the first time able to offer an explanation of the phenomenon of cancer in molecular terms. It will be surprising if this work does not have a profound effect on cancer research for many years to come.

In conclusion, the 8th International Congress on Catalysis may be said to have been a worthy successor to its antecedents in providing a marked stimulus for all research workers in the field. Excellently organised by Dechema, it will long be remembered by all who attended as a source of great intellectual nourishment and a further demonstration of the key role which the platinum group metals continue to play in catalysis. G.C.B.

A Compilation of Catalysts

What is probably the first-ever comprehensive survey of the many catalysts used in the refining industry has recently been published in the U.S.A. ("OGJ Catalyst Report: '84", *Oil Gas J.*, 1984, **82**, (41), 55, 56, 58, 60–65, 68–72, 74–82, 84–86). The compilation which identifies some 700 different catalysts will be of considerable benefit to the refiner or design engineer requiring a clear picture of the many catalyst suppliers, manufacturers and licensors.

This interesting and useful survey demonstrates the high degree of specialisation in the catalyst supply and refining industries. The catalysts, many of which contain a platinum group metal, have been categorised into 18 specific process areas and over 20 pages of tables are required to present the assembled information. Legitimate concern about proprietary matters has been respected and where a contributor had reservations about identifying some aspect of a catalyst, most frequently the composition of the carrier/support or the active agents, this has been indicated in the tables. Nevertheless it is clear that platinum group metal-containing catalysts dominate several of the processing categories and make important contributions to others.