

Multimetallic Catalysts in Synthesis and Transformation of Hydrocarbons

A REPORT FROM THE SECOND EUROPEAN SYMPOSIUM ON CATALYSIS BY METALS, BRUSSELS, SEPTEMBER 1983

Modification of the behaviour of a noble metal as a catalyst by the addition of a second metal has been practised for many years. The decade following the end of World War II witnessed the pioneering work of Eley, Schwab and Rienäcker, who were concerned primarily with the effects of adding Group IB metals on the catalysed reactions of simple molecules, and interpretation of the results in terms of a simple collective electron model which is now known to be not generally applicable. The later discovery that the performance of platinum reforming catalysts could be greatly improved by adding a second element, such as rhenium, germanium or tin, has stimulated renewed interest in bimetallic and multimetallic catalysts.

The papers presented at this conference demonstrated the variety of the still unsolved problems associated with these catalysts. It is impossible to try to summarise each one, as those concerned with structural studies were shown only as posters, while those submitted by Russian scientists were not in fact presented because the authors were absent. The following paragraphs therefore identify the principal themes of the discussions, and mention the names of authors making noteworthy contributions to them.

The problem of the *modus operandi* of the second element in reforming catalysts remains unsolved. Contradictory reports still appear on whether rhenium, for example, is chiefly in the zero-valent state and alloyed with platinum or whether it is in a +4 oxidation state and associated with the alumina support. Results presented by P. G. Menon and G. F. Froment, of Rijksuniversiteit Gent, on the effect of chloriding on catalytic properties were interpreted as supporting the former idea, while

EXAFS (extended X-ray absorption fine structure) measurements reported by P. Lagarde, H. Dexpert and G. Vlaic of L.U.R.E., Orsay, appear not to give evidence for alloying. Much probably depends upon the detailed pre-treatment which samples received, and on the conditions under which the measurements are made.

Another theme which was much debated concerns the so-called ligand effect in bimetallic catalysts. The question is this: to what extent if at all is the behaviour of a Group VIII metal atom modified by a neighbouring Group IB metal atom? Some progress was made towards an answer, in the following way. According to K. Christmann (Universität München) atoms such as hydrogen are susceptible to a ligand effect, while carbon monoxide molecules are less affected. In hydrocarbon reactions the initial chemisorption requires an ensemble of a critical size and geometry, the pattern of subsequent reactions not being much dependent on the amount of the second component. However, as the plenary lecturers W. M. H. Sachtler of Northwestern University, Evanston, and L. Guzzi of the Institute of Isotopes, Budapest, pointed out, the size of the ensemble determines the type of reaction undergone. Thus the necessary number of atoms in a site to achieve isomerisation is less than that for hydrogenolysis; this helps to explain the success of second element additions to reforming catalysts.

The Fischer-Tropsch synthesis continues to excite great interest, and a number of papers described the effect of a modifying element on the active one, which is usually iron or rhodium. The objectives were usually to achieve high yields of hydrocarbons in the gasoline range or of low molecular weight olefins or of oxygenates such as ethanol. Y. Murakami and

his colleagues at Nagoya University, Japan, examined the effect of alkali metal additions to palladium/alumina in terms of electron transfer to the palladium, while I. S. C. Hughes, J. O. H. Newman and G. C. Bond (Coal Research Establishment, Stoke Orchard, and Brunel University, Uxbridge) demonstrated a marked increase on the rate of olefin synthesis by iron/alumina brought about by the incorporation of platinum in the catalyst, even when only physically admixed as platinum/alumina.

These highlights do scant justice even to the few contributions selected for specific mention,

and they and the many other interesting papers will be read attentively when they appear in a forthcoming issue of the *Journal of Molecular Catalysis*. The conference was attended by some 150 scientists from twelve countries, Hungary and Poland being particularly well-represented. The fact that it took place at a time when public transport in the Belgian capital was at a standstill due to a strike can only help to fix it in the memory of those who attended. The banquet, and the quality of the papers, posters and discussions, alone would have made it a memorable occasion. G.C.B.

The Platinum Metals in C₁ Chemistry

Catalysis in C₁ Chemistry, EDITED BY WILHELM KEIM,

D. Reidel Publishing Company, Dordrecht/Boston/London, 1983, 312 pages, Dfl. 135.00, \$58.50.

Current interest in the chemistry of single carbon molecules, C₁ chemistry, has resulted in several reviews of the subject over the past few years, stimulated initially by the prospect of synthetic fuels in the late 1970s. This book is based on a series of lectures, given as part of a C₁ chemistry course at Aachen under the sponsorship of the European Community, concerned principally with homogeneous transition metal catalysed reactions of carbon monoxide, hydrogen cyanide, methane and carbenes.

Most of the chapters present interesting overviews of relevant industrial process chemistry, patent and general literature. They highlight the mechanistic chemistry involved and have a general data base up to 1981 with a few references to 1982 publications. Interest in the platinum group metals is covered in the previously well documented activity of rhodium and palladium complexes in hydrogenation, carbonylation and hydroformylation reactions. The Fischer-Tropsch section naturally refers extensively to data from the Sasol operation although the claimed versatility for diesel production of the Sasol 2 reactors is misleading. The activity of ruthenium catalysts for diesel fractions and methane under different operating conditions is detailed in addition to the activity of rhodium bimetallic catalysts for alcohol production. The chapter ends with a discussion of selectivity control and the conclusion that future exploitation of this chemistry will be based on selective production of olefins and alcohols rather than for transport fuels.

A review of methanol homologation reactions, especially the formation of ethanol, includes graphic details of recent data on cobalt from a dissertation by H. Loevenich at Aachen. It also highlights the activity of ruthenium co-catalysts for this reaction, patented by several petrochemical firms in 1981-82, and refers to the few detailed studies on other platinum group metals in this system. The major area of interest for platinum group metals chemists is likely to be the chapter by A. Behr on carbon dioxide activation where several platinum group metals and transition metal complexes with activity in this respect have recently been identified. This detailed review covering 312 references up to 1982 is subdivided into the insertion reactions of carbon dioxide in metal-ligand bonds. It includes specific reactions of carbon dioxide with hydrogen, alkenes and heterocyclic compounds and gives a valuable update in an expanding area of research. The author recommends the need for further work on the formation of carboxylic acids by this route, where the total functionality of the carbon dioxide is retained in the product.

The absence of a uniform chemical nomenclature system detracts from the overall quality of the text, but this book will provide a useful overview for those interested in a wide range of C₁ chemistry, particularly those without ready access to standard texts such as Kirk-Othmer's *Encyclopaedia of Chemical Technology* and *Comprehensive Organometallic Chemistry*. P.C.H.