INDUSTRIAL APPLICATIONS OF HOMOGENEOUS CATALYSIS

Edited by

A. MORTREUX AND F. PETIT

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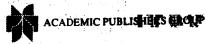
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PREFACE

Catalysts are now widely used in both laboratory and industrial-scale chemistry. Indeed, it is hard to find any complex synthesis or industrial process that does not, at some stage, utilize a catalytic reaction.

The development of homogeneous transition metal catalysts on the laboratory scale has demonstrated that these systems can be far superior to the equivalent heterogeneous systems, at least in terms of selectivity. Thus, there is an increasing interest in this field of research from both an academic and industrial point of view.

In connection with the rapid developments in this area, four universities from the E.E.C (Aachen, FRG; Liège, Belgium; Milan, Italy; and Lille, France) have collaborated to organise a series of seminars for high-level students and researchers. These meetings have been sponsored by the Commission of the E.E.C and state organizations.

The most recent of these meetings was held in Lille in September 1985 and this book contains updated and expanded presentations of most of the lectures given there.

These lectures are concerned with the field of homogeneous transition metal catalysis and its application to the synthesis of organic intermediates and fine chemicals from an academic and industrial viewpoint.

The continuing petroleum crisis which began in the early 1970s has given rise to the need to develop new feedstocks for the chemical industry. Up to the present, interest has focussed on carbon monoxide and methanol, the latter now being available at the competitive price of \$100 per ton. Thus, the opening chapter of this book is concerned with new catalytic processes for the synthesis of chemical building blocks from these feedstocks.

The second part of this book describes the use of coordination catalysts for the activation of small molecules like CO, H₂, etc. and fine chemical synthesis.

The next section contains lectures given on the chemistry of processes already used by the chemical industry. For example, alkene oligomerization and polymerization, together with new findings in this field. Included

in this section is a treatment of hydrocarbon activation in the alkene metathesis reaction, and is concluded by a report of recent work in the important and challenging Fold of alkane activation.

The last section contains two unusual examples of catalytic processes, namely photochemically induced catalysis and supported molecular cluster catalysis. The latter is a new and promising area of research, since it combines the advantages of both heterogeneous and homogeneous catalysis.

Professor Keim, who organized the first of these meetings in Aachen in 1982, concludes this book by an overview of homogeneous catalysis and discusses its future: a future in which changing raw material supply, engineering requirements and environmental considerations are all important.

Lille, September 1987.

A. M.ORTREUX F. PETIT

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M. RÖPER*

CHEMICALS FROM METHANOL AND CARBON MONOXIDE

1. Introduction

Methanol is a versatile, readily available C₁-compound made from synthesis gas. Large scale industrial methanol production from CO/H₂ was started up in 1925 by BASF using ZnO/Cr₂O₃ catalysts. The present methanol production capacity has been reported to be 21 mio t/a, while the actual demand is only in the range of 12 mio t/a. This overcapacity is mainly due to the build-up of new plants in the Midde East, Eastern Europe, New Zealand and Latin America, where surplus natural gas is available at a very low price [1, 2]. The ready supply as well as the low raw material costs will keep the price of methanol low in the near future. This will stimulate methanol demand and will help to introduce new methanol-based processes for motor fuels as well as for organic base chemicals [3].

The present industrial uses of methanol include the syntheses of formaldehyde, methyl esters, methyl animes and methyl halides. In addition, methanol or its derivatives find increasing interest as a substrate for carbonylation and dehydration reactions, which are summarized in Scheme 1. Some of these processes have already been commercialized, such as the synthesis of acetic acid, of acetic anhydride, or of methyl formate. The feasibility of the MTG (methanol-to-gasoline) process has been proved by pilot plant operation and a commercial unit of a capacity of 560 000 t/a of hydrocarbons had started up operation in New Zealand by 1985. In addition there is a variety of carbon monoxide-based reactions, which convert methanol mainly into C₂-oxygenated compounds.

These can potentially replace ethylene-based routes, e.g. in the case of ethanol, acetaldehyde, vinyl acetate, and ethylene glycol. With methanol from cheap natural gas becoming available in the near future, these processes, although uneconomic today, might become industrially attractive.

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