

# CATALYSIS

## VOLUME V

Hydrogenation, Oxo-Synthesis, Hydrocracking, Hydro-  
desulfurization, Hydrogen Isotope Exchange and  
Related Catalytic Reactions

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## CHAPTER 3

# DIRECT CATALYTIC SYNTHESIS OF HIGHER ALCOHOLS FROM CARBON MONOXIDE AND HYDROGEN

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### INTRODUCTION

In Volume III Chapter 8 of this treatise the catalytic synthesis of higher alcohols from CO and H<sub>2</sub> with the use of modified methanol catalysts was not considered, although ordinarily this synthesis of higher alcohols is believed to be closely related to that of methanol. However, the difference in the mechanisms of the two reactions and the existence of several other processes for the synthesis of higher alcohols justify a separate treatment.

The problem of obtaining higher alcohols by a catalytic process has been approached by many authors from a number of different angles. The synthesis has been performed by several methods. This, and the lack in the literature, of a sufficient number of detailed research results which could have served as a basis for the clarification and the understanding of this matter, make it very difficult to review this field. The authors of this chapter have attempted a systematic treatment of the subject but wish to point out that the scarcity of experimental work has made it almost impossible to present a unified picture of the problems involved in the catalytic synthesis of higher alcohols.

The various processes for obtaining higher alcohols from CO and H<sub>2</sub> may be schematically divided into three groups:

- (1) Synthesis by processes and catalysts derived from those used in the synthesis of hydrocarbons (Fischer-Tropsch, Synthol, isosynthesis, Synol).
- (2) Synthesis with modified methanol catalysts.
- (3) Synthesis from CO, H<sub>2</sub> and olefins (oxosynthesis).

The processes belonging to the first group are closely connected with the Fischer-Tropsch process and with isosynthesis. This is clear particularly if the types of catalysts used, the reaction pressures, and the supposed reaction mechanisms are considered. It is obvious that a detailed discussion of higher alcohol synthesis by these processes cannot be separated from that of the synthesis of hydrocarbons from CO and H<sub>2</sub>. The authors are therefore referring the reader to the various chapters on Fischer-Tropsch synthesis and isosynthesis in Volume IV of this series of books on "Catalysis" for related information on the formation of higher alcohols.

The synthesis of higher alcohols in the presence of modified methanol catalysts is a more definite process, which therefore lends itself to a more complete treatment. In particular, this chapter will consider the catalysts containing:

- (1) a component which is selective for the synthesis of methyl alcohol;
- (2) one or more promoters or activating agents specific for the synthesis of higher alcohols and, possibly,
- (3) one or more stabilizing agents, whose presence in the catalyst structure increases the catalyst life.

The oxo synthesis was originated in Germany during World War II as a process for the production of higher alcohols<sup>60</sup>. The first catalysts used were similar to the cobalt-base catalysts commonly employed in the Fischer-Tropsch hydrocarbon synthesis. The process for the production of higher alcohols was practically divided into two consecutive stages, namely, the direct synthesis of aldehydes from CO, H<sub>2</sub> and olefins, and the hydrogenation of the aldehydes to alcohols<sup>60</sup>. Later, with the general use of catalysts composed of cobalt carbonyl compounds, oxosynthesis has been directed toward the production of many classes of organic compounds, and is actually such a fundamental process as to require a separate treatment. For a discussion of the synthesis of higher alcohols by this process, reference should be made to Chapter 2 of this volume.

Among the proposed methods for the synthesis of alcohols from olefins, the Ziegler process has assumed recently a considerable interest. This process<sup>65</sup> is based on the addition of oxygen by metal-alkyl compounds to form alcoholates<sup>59</sup>, which react with water to give the corresponding alcohols. Such alkyl-metallic compounds, and particularly alkyl-aluminum, may be prepared through exchange reactions between triethylaluminum or tri-isobutylaluminum and the olefins produced from CO and H<sub>2</sub> with the Fischer-Tropsch process. The alcohols obtainable with this process are

different from those obtained through the hydration of olefins in the presence of acid catalysts, because these latter are secondary alcohols, whereas the Ziegler process leads to primary alcohols.

This process for the production of alcohols is closely connected with the other Ziegler-type catalytic processes, and therefore will not be considered in this chapter.

#### HISTORICAL REVIEW

At the beginning of this century, Sabatier and Senderens published the results of their first experiments on the catalytic synthesis of methane from CO and H<sub>2</sub><sup>9</sup>. Several years later the Badische Anilin und Soda Fabrik patented its process of catalytic hydrogenation of carbon monoxide<sup>1</sup>. While Sabatier and Senderens had worked with reduced nickel or cobalt oxides as catalysts, the B.A.&S.F. catalysts consisted of alkalized oxides of cobalt or osmium. With these catalysts, in experiments performed at 100 to 200 atm. and 300 to 400°C, a prevalingly liquid product is obtained, which is a mixture of alcohols, aldehydes, ketones, acids and other organic compounds.

While the research work of the B.A.&S.F. was later developed toward the synthesis of methanol, progress in the synthesis of higher alcohols was noticeable in 1923-24 when Fischer and Tropsch developed their "Synthol" process<sup>13, 14, 15, 16</sup>. The reaction between CO and H<sub>2</sub> was performed at pressures ranging from 100 to 150 atm. and at temperatures of 400 to 450°C, in the presence of an alkalized iron oxide catalyst. The product was a mixture of alcohols, aldehydes, ketones, acids and other compounds.

These early results disclosed the wide field of the different organic syntheses from CO and H<sub>2</sub>. This subject was later developed along three distinct lines, namely, the synthesis of hydrocarbons, the synthesis of alcohols, and oxo synthesis.

The scientific and industrial importance of this matter was so clearly appreciated that in many laboratories experimental research on the subject was undertaken. Some interesting results have, accordingly, been achieved in the interpretation of the reaction mechanisms and in the understanding of this type of heterogeneous catalysis. The industrial development of the synthesis, however, initially proceeded rather slowly; significant progress could be achieved from the industrial point of view only after the solution of the many difficulties involved, such as the separation of the reaction products, and above all the preparation of highly selective and durable catalysts.

The discovery of the ZnO and Cr<sub>2</sub>O<sub>3</sub>-base catalysts represents a decisive step in the selective synthesis of alcohols from CO and H<sub>2</sub>. The first high yields in the synthesis of methanol from CO and H<sub>2</sub> were obtained at relatively high pressures in the presence of catalysts of this type<sup>2</sup>. It was soon

