# 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 $H_2$ 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 $H_2$ may be schematically divided into three groups:

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(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, $H_2$ 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 $H_2$. 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[60]. 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, $H_2$ and olefins, and the hydrogenation of the aldehydes to alcohols[60]. 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[65] is based on the addition of oxygen by metal-alkyl compounds to form alcoholates[59], 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 $H_2$ 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 $H_2$[49]. Several years later the Badische Anilin und Soda Fabrik patented its process of catalytic hydrogenation of carbon monoxide[1]. While Sabatier and Sanderens 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 prevailingly 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[13, 14, 15, 16]. The reaction between CO and $H_2$ 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 $H_2$. 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 $Cr_2O_3$-base catalysts represents a decisive step in the selective synthesis of alcohols from CO and $H_2$. The first high yields in the synthesis of methanol from CO and $H_2$ were obtained at relatively high pressures in the presence of catalysts of this type[2]. It was soon

learned that these catalysts, when modified through the addition of salts or oxides of alkaline metals, brought about the formation of liquid end-products, consisting mainly of aliphatic alcohols[8, 17, 18, 30]. From this point on, the industrial synthesis of higher alcohols from CO and $H_2$ and that of methanol have followed two different paths, with the latter assuming a more important position than the synthesis of higher alcohols.

The direct synthesis of higher alcohols assumed considerable importance in Europe in the period 1935–1945. In fact, while with the more frequently used process of olefin hydration only secondary alcohols are obtained, the direct synthesis from CO and $H_2$ gives a mixture of primary alcohols, most of which are of the non-linear type. Primary isobutylalcohol, which is the main product of the synthesis, has been used in Germany for the production of pure isobutylene, which in turn is an interesting intermediate of the syntheses of isooctane and of *Oppanol* elastomers[60].

Recently, the extensive development of oxo synthesis has brought to the front the industrial synthesis of alcohols through the hydrogenation of aldehydes. The direct catalytic synthesis of alcohols from CO and $H_2$ has thus lost much of its original interest. A reason for this is to be found in the fact that, while the products of the reaction of oxo synthesis from olefinic hydrocarbons are mainly the isomeric aldehydes containing one carbon atom more than the original hydrocarbon, the synthesis of alcohols from CO and $H_2$ leads to complex mixtures of alcohols and it is very difficult to direct the reaction toward the formation of a few special end-products. Therefore it may be concluded that the high cost of the separation and purification processes has been responsible for the slowness of the industrial development of the direct synthesis of higher alcohols from CO and $H_2$, after the development of oxo synthesis. Nevertheless in the last part of World War II and in the years which followed, the I.G. Farbenindustrie and the Ruhrchemie in Germany succeeded in the realization of the "Synol" process[63], which substantially represents a last stage in the evolution of the synthesis of primary linear higher alcohols from CO and $H_2$[60]. However, it must be pointed out that the low pressures of synthesis and the type of catalysts used for the synol process place it closer to the Fischer-Tropsch hydrocarbon synthesis than to the classical high pressure synthesis of alcohols from CO and $H_2$ with zinc or chromium-base catalysts.

### THERMODYNAMIC CONSIDERATIONS

The following over-all reactions may be considered, which lead to the formation of alcohols starting from CO and $H_2$ :

$$2nH_2 + nCO = C_nH_{2n+1}OH + (n - 1)H_2O \qquad (1)$$

$$(n + 1)H_2 + (2n - 1)CO = C_nH_{2n+1}OH + (n - 1)CO_2 \qquad (2)$$
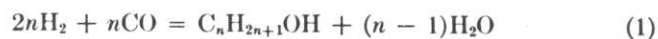
The free energy variation of Eq. (1) in the temperature range of 600 to 150J°K may be calculated from the following equation:

$$\Delta G_1^\circ = -38.386n + 11.098 + \frac{(5.982n - 0.144)}{100} \; T \; \text{Kcal/mole} \quad (3)$$

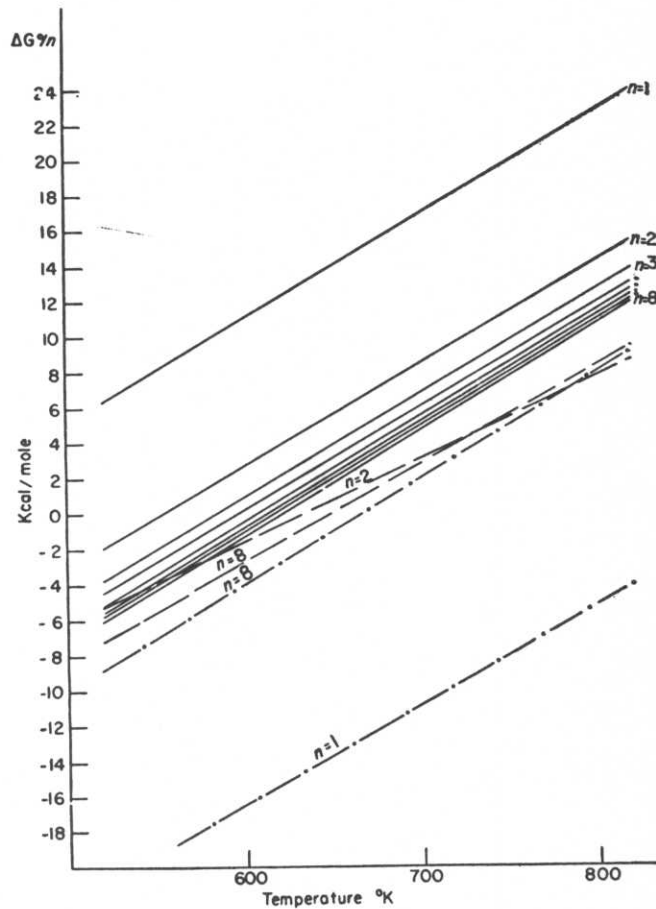In Figure 1 the values of $\Delta G^\circ/n$ are reported as functions of the absolute



Figure 1. Free energy variation with temperature for the synthesis of alcohols, $\alpha n$-olefins, and $n$-paraffins from hydrogen and carbon monoxide.

| | | | | |
|---|---|---|---|---|
| ——— reactions leading to alcohols | | | | $nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$ |
| — — — — " " " $\alpha n$ olefins | | | | $nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$ |
| — . — . — " " " $n$ paraffins | | | | $nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$ |

temperature, for several fixed values of $n$. The calculation of such values for $n > 1$, has been made according to the group contributions method, using the values reported by van Krevelen and Chermin[61]. The results which are generally obtained with this method are accurate within $\pm 0.6$ Kcal/mole. The degree of accuracy in our specific reactions is certainly much higher.

The free energy variations for reaction (2) may be readily calculated from Eq. (3), adding to the $\Delta G^\circ$ of reaction (1), for any given value of $n$, the $\Delta G^\circ$ of the conversion reaction (4), multiplied by $(n - 1)$:

$$CO + H_2O = CO_2 + H_2 \tag{4}$$

$$\Delta G^\circ_{(4)} = -8.514 + 0.771T \times 10^{-2} \text{ Kcal/mole}$$

for $600°K < T < 1500°K$.

Since the free energy of reaction (4) is negative in the temperature range of the higher alcohols synthesis, reaction (2) is thermodynamically favored with respect to reaction (1) (Figure 2).

It may be deduced from the curves of Figures 1 and 2 that at a given temperature the stability of higher alcohols increases with the number of carbon atoms in their molecules. From the above reported data it may be calculated that the temperatures at which the free energies are zero, range respectively from 555 to 620°K for reaction (1), and from 590 to 700°K for reaction (2) for each value of $n$ higher than 1.

With alkalized methanol catalysts the synthesis of higher alcohols occurs generally at temperatures above 400°C. It is therefore necessary in view of the considerable volume contractions of reactions (1) and (2) to operate the synthesis under high pressure.

Such simple considerations are obviously not sufficient to justify the experimental conditions under which the synthesis of higher alcohols is performed. In fact, several possible reactions between CO and $H_2$, competitive to the synthesis of higher alcohols, have lower $\Delta G^\circ$ values in the temperature range of interest. This is particularly true for the Fischer-Tropsch synthesis:

$$2nH_2 + nCO = C_nH_{2n} + nH_2O \tag{5}$$

$$(2n + 1)H_2 + nCO = C_nH_{2n+2} + nH_2O \tag{6}$$
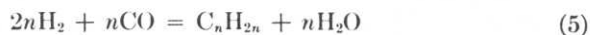
In fact, from the data given by van Krevelen and Chermin, the following formula may be deduced in the case of reaction (5) leading to $\alpha$-$n$-olefins:

$$\frac{\Delta G^\circ_{(5)}}{n} - \frac{\Delta G^\circ_{(1)}}{n} \text{ Kcal/mole} = \frac{6.547}{n} - \frac{3.290}{n} T.10^{-2}$$

This difference becomes zero for T = 200°K, while for temperatures above 200°K, $-\Delta G^{\circ}_{(5)}/n$ is higher than $-\Delta G^{\circ}_{(1)}/n$.

Similarly, it may be calculated, for reaction (6) leading to $n$-paraffins:

$$\frac{\Delta G^{\circ}_{(6)}}{n} - \frac{\Delta G^{\circ}_{(1)}}{n} = \frac{24.06}{n} + \frac{0.03}{n} T \cdot 10^{-2}$$

These considerations are sufficient to make necessary the use of highly selective catalysts in the synthesis of higher alcohols.

It should be pointed out that reactions (1) and (2), which lead to higher alcohols, occur with volume contractions which are slightly higher than
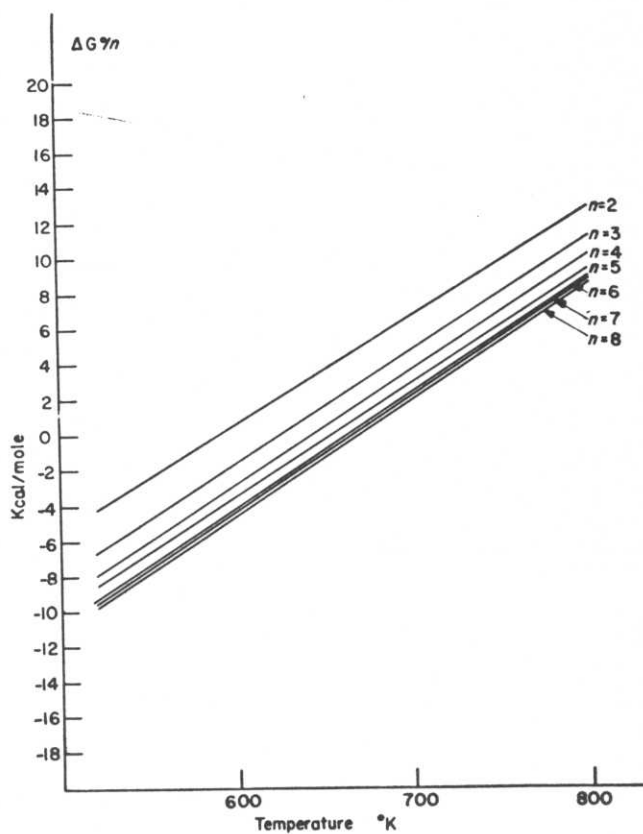


Figure 2. Variation with temperature of $\dfrac{\Delta G^0}{n}$ for the reaction

$(n + 1)H_2 + (2n - 1)CO \rightarrow C_nH_{2n+1}OH + (n - 1)CO_2$

those of reaction (5) and (6), leading to hydrocarbons. In fact the volume contraction for reactions (1) and (2), expressed as volume ratio between the reactants and products, is equal to 3, while those of reactions (5) and (6) are respectively equal to $3n/(n + 1)$ and $(3n + 1)/(n + 1)$, which are both lower than 3.

As will be shown in the following paragraph, the various processes for the synthesis of higher alcohols lead to the exclusive formation of certain types of alcohols with linear or branched structures. Not even in this respect may any conclusion from general thermodynamic considerations be drawn. It is, in fact, known that the variations of standard free energy for a typical isomerization reaction (7) have very low values:

$$CH_3 - (CH_2)_{n-2} - CH_2OH = (CH_3)_2CH - (CH_2)_{n-4} - CH_2OH \quad (7)$$

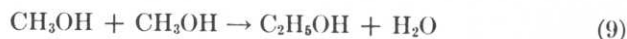$$\Delta G^\circ_{(7)} = -1.355 + 0.258 \cdot T \cdot 10^{-2} \, *$$

The $\Delta G^\circ$ of reaction (7) assume the following values: $T = 525°K$, $\Delta G^\circ = 0$; $T = 600°K$, $\Delta G^\circ = +0.195$; $T = 700°K$, $\Delta G^\circ = +0.455$; $T = 800°K$, $\Delta G^\circ = +0.705$ Kcal/mole.

The low value of the slope $d(\Delta G^\circ)/dT$ for reaction (7) prevents one from calculating with sufficient precision the temperature at which one isomer becomes stable with respect to another, until very accurate data become available.

As far as the other possible reactions are concerned between CO, $H_2$ and their reaction products, we shall consider in this paragraph only those that will be involved in the reaction mechanisms proposed†.

$$CH_3OH + CO \rightarrow CH_2COOH \qquad (8)$$

$$\Delta G^\circ_{(8)} = -33.23 + 3.69 \cdot T \cdot 10^{-2}$$

$$CH_3OH + CH_3OH \rightarrow C_2H_5OH + H_2O \qquad (9)$$

$$\Delta G^\circ_{(9)} = -16.18 - 0.014 \cdot T \cdot 10^{-2}$$

$$CH_2O + CH_2O \rightarrow CH_2(OH) - CHO \qquad (10)$$

$$\Delta G^\circ_{(10)} = -16.88 + 2.95 \cdot T \cdot 10^{-2}$$

* This formula is approximate. In this respect it is sufficient to point out that such a formula may be applied to any isomerization reaction of the following type:

$$CH_3-CH_2-CH_2-\ldots-CH_2-X \rightarrow CH_3-CH_2-\ldots-CH(CH_3)-\ldots-CH_2-X$$

or also:

$$CH_3-CH_2-CH_2-\ldots-CH_2-X \rightarrow CH_3-CH_2-\ldots-CH(X)-\ldots CH_2-CH_3$$
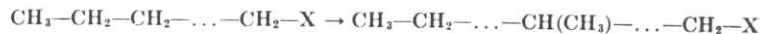
† The $\Delta G^\circ$ values for methanol have been calculated from references 25, 51, and 66.

$$CH_3(CH_2)_{n-2} - CHO + H_2 \rightarrow CH_3(CH_2)_{n-2} - CH_2OH \qquad (11)$$

$$\Delta G^{\circ}_{(11)} = -17.24 + 2.99 . T . 10^{-2}$$

In Figure 3 the values of $\Delta G^{\circ}$ for these various reactions are plotted as a function of absolute temperature.

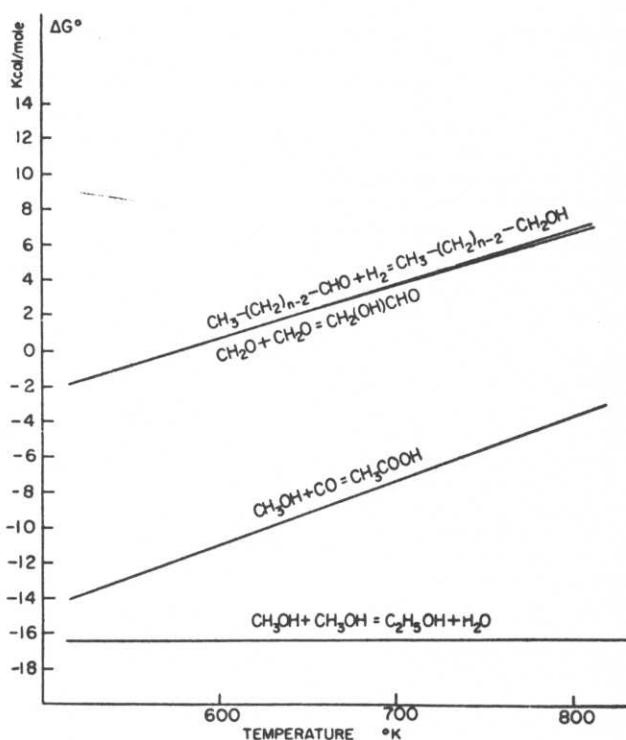In the temperature range 600 to 800°K the reaction free energies are



Figure 3. Variation with temperature of $\triangle G^{0}$ for some reactions involved with or competitive to the synthesis of higher alcohols.

negative for reactions (8) and (9), and slightly positive for reactions (10) and (11). However, since the latter reactions occur with volume contractions, these too may be considered as possible when operations are carried out at high pressure.

As a conclusion, it may be stated that both the nature and distribution of products obtained in the synthesis of higher alcohols depend mainly upon the particular characteristics of the catalysts employed and upon kinetic factors. Therefore, these general thermodynamic considerations are not sufficient to establish the possible steps of this synthesis.

### Remarks on the Catalytic Synthesis of Higher Alcohols from CO and H$_2$

When the synthesis of methanol from CO and H$_2$ is performed with a normal selective catalyst, the formation of low quantities of higher alcohol may be noticed. The concentration of these higher alcohols varies according to the type of catalyst used and to the physicochemical conditions under which the reaction is operated. Means for inhibiting the formation of higher alcohols include the use of very pure ZnO catalysts (as, for example, ZnO from zinc acetate obtained by solution of pure Zn in acetic acid) and operation at low temperatures and high space velocities. Under such conditions the formation of higher alcohols is negligible[40]. If, instead, the catalyst is prepared by precipitation with alkali of zinc hydroxide or of basic zinc and chromium carbonates, the formation of much higher quantities of higher alcohols is noticed. This is probably to be attributed to the promoting action of the traces of alkaline ions adsorbed on the surface of the catalyst and not entirely eliminated in the filtration and in the washing of the precipitates[54].

Another way of enhancing the formation of higher alcohols is the use of substantial amounts of strongly basic substances. If, for example, ZnO is treated with a solution of potassium dichromate, a catalyst is obtained after reduction of chromium to Cr$^{+++}$ containing potassium zincate and potassium chromite which promote the synthesis of higher alcohols[33].

A considerable production of higher alcohols is obtained as a rule when a catalyst selective for the synthesis of methanol is activated with a promoter containing cations of strongly basic character. Also, the alkalization of certain catalysts originally non-selective for the synthesis of methanol leads to the formation of higher alcohols from CO and H$_2$. This is shown in the synthesis of higher alcohols with alkalized iron or iron oxide catalysts, which are initially selective for the synthesis of hydrocarbons[52]. In the synthesis of hydrocarbons with the Fischer-Tropsch process, during operations at temperatures over 200°C and at high or medium pressures with iron-base catalysts, small amounts of oxygenated compounds, including higher alcohols, are obtained[52].

The formation of higher alcohols, mainly of the branched type, is observed when the high-pressure synthesis of hydrocarbons is performed at relatively low temperatures with thorium oxide-base catalysts (isosynthesis)[43, 44]. More recently the Badische Anilin and Soda Fabrick has introduced the use of a catalyst consisting of a mixture of alkalized titanium and zirconium oxides[3]. With this latter catalyst a liquid reaction product is obtained, containing 20 to 25 per cent isobutyl alcohol together with other higher alcohols. Other types of catalysts employed in the synthesis of higher alcohols from CO and H$_2$ will be considered in the following paragraphs.

The mechanism of the synthesis of higher alcohols appears to be extremely complicated, and possibly connected with a series of reactions consecutive to the synthesis of methanol. This side of the synthesis will be discussed in detail in the course of this chapter.

## EFFECT OF THE NATURE OF PROMOTERS

From the consideration of the data available in the literature, concerning the influence of the alkaline promoters upon the activity of the catalysts used for the synthesis of higher alcohols, it may be concluded that the relative influence of the various promoters is practically independent of the type of the catalysts used. The activating character of such promoters appears to be rather a function of their basicity*. This behavior is shown particularly by the cations of the metals belonging to the first semigroup of group 1 of the periodic system; their promoting activity is closely related with their basicity, which increases with an increase in the atomic weight.

Fischer and Tropsch[10, 11, 14] were probably the first authors who pointed out that the yield of higher alcohols in the synthesis from CO and $H_2$, performed with alkali-activated iron-base catalysts, increases with the basic character of the promoters. In the following years Natta and Strada[31] obtained similar results in the higher alcohols synthesis with ZnO-base catalysts, and found that the highest yields of alcohols were obtained by the use of catalysts containing potassium, rubidium or cesium ions[32]. A few years later Morgan and his co-workers performed a systematic investigation of the quantitative influence of the addition of five different alkali ions to a chromium oxide-manganese oxide catalyst employed in the synthesis of alcohols[28]. The results obtained by these workers are shown in Table 1. It may be observed that the presence of $Li^+$, $Na^+$ or $K^+$ (added as hydroxides) leads to a decrease of the over-all reaction yield (expressed as per cent of converted gas in each passage through the catalyst), whereas this is not observed when $Rb^+$ or $Cs^+$ are present.

A consideration of the content, in the reaction product, of compounds insoluble in $CaCl_2$ solutions indicates that the concentration of higher alcohols, in the liquid end products, increases with the addition of alkaline promoters in the order: Li, Na, K, Rb, Cs. The best catalyst among those tested by Morgan and his co-workers contains 9.8 per cent $Rb^+$. A further increase in the rubidium content of this catalyst does not appear to bring a substantial variation of the yield. These results were confirmed later by Taylor[58], who worked with a $Cr_2O_3$-MnO catalyst, and found that the best yields in higher alcohols were obtained when the catalyst was pretreated with RbOH.

* It is therefore obvious that the cations used as promoters should not be easily reducible to metals, because such reduction would destroy their basic character.

Table 2 shows some recent interesting results obtained by Runge and Zepf, who studied the effects of alkaline promoters upon the performance of a ZnO-Cr$_2$O$_3$ catalyst[48]. The data reported in Table 2 were obtained, with each catalyst under the best tested conditions of pressure and temperature. According to these authors, the sodium-activated catalyst appears to be slightly superior to that containing potassium. This apparent

TABLE 1. INFLUENCE OF THE ADDITION OF ALKALI IONS UPON THE PERFORMANCE OF A CHROMIUM OXIDE-MANGANESE OXIDE CATALYST[28]

| Alkali added as oxide | Weight per cent of added alkali | Per cent gas conversion at each passage through catalyst | Over-all conversion yield (g/h) | Methanol in reaction product (%) | Per cent carbon converted into compounds other than MeOH | Amount of carbon in compounds other than MeOH (g%) | Volume percentage of material insoluble in CaCl$_2$ soln. (cc/100 g) | Yield material insoluble in CaCl$_2$ soln. (cc/h) |
|---|---|---|---|---|---|---|---|---|
| — | — | 3.5 | 6.2 | 80.5 | 2.8 | 13.0 | 0.3 | 0.2 |
| Li | 3.4 | 2.7 | 47 | 76.9 | 3.8 | 21.7 | 3.55 | 1.7 |
| | 6.7 | 2.6 | 45 | 73.7 | 3.2 | 20.3 | 6.26 | 2.8 |
| | 10.1 | 2.3 | 40 | 71.7 | 3.6 | 24.9 | 4.42 | 1.8 |
| Na | 2.8 | 2.4 | 43 | 63.9 | 5.0 | 32.9 | 12.8 | 5.5 |
| | 6.3 | 1.2 | 21 | 55.0 | 2.6 | 37.9 | 14.4 | 3.0 |
| | 9.8 | 1.0 | 17 | 50.1 | 2.1 | 39.4 | 14.05 | 2.4 |
| K | 1.5 | 2.7 | 47 | 81.8 | 2.8 | 16.4 | 0.63 | 0.3 |
| | 3.9 | 2.2 | 39 | 60.8 | 5.5 | 38.4 | 12.80 | 5 |
| | 4.9 | 1.9 | 33 | 50.7 | 5.9 | 48.6 | 21.50 | 7.1 |
| | 5.7 | 1.6 | 29 | 53.0 | 4.3 | 42.9 | 18.60 | 5.4 |
| | 8.4 | 1.4 | 24 | 52.2 | 3.6 | 43.4 | 17.50 | 4.2 |
| | 11.9 | 1.5 | 27 | 49.0 | 4.3 | 46.3 | 23.00 | 6.2 |
| Rb | 2.3 | 3.4 | 61 | 75.5 | 5.2 | 23.1 | 4.65 | 2.8 |
| | 4.4 | 3.5 | 62 | 67.2 | 7.7 | 33.1 | 17.8 | 8.8 |
| | 9.8 | 3.0 | 53 | 49.7 | 8.4 | 46.0 | 28.7 | 15.2 |
| Cs | 1.8 | 3.5 | 62 | 79.5 | 3.6 | 16.2 | 1.53 | 1.0 |
| | 3.8 | 3.0 | 53 | 82.1 | 3.8 | 18.8 | 1.58 | 0.8 |
| | 8.9 | 3.3 | 58 | 63.7 | 8.3 | 37.5 | 16.4 | 9.5 |

discordance with the above mentioned alkalinity rule is probably to be related to the higher water content in the product obtained with the sodium activated catalyst.
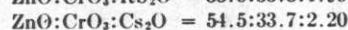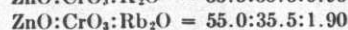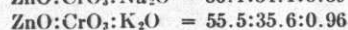
As has already been pointed out, the various investigators who studied this field agree substantially in concluding that the most active promoters for the production of higher alcohols are Cs$^+$, Rb$^+$, K$^+$. From a practical point of view, the high cost of rubidium and cesium has prevented their employment in the industrial processes: therefore almost all the catalysts used for the industrial synthesis of higher alcohols from CO and H$_2$ contain potassium.

A generalization of the basicity rule could lead to useful conclusions concerning the possible employment of other metals as promoters for the higher alcohol synthesis. In these reactions for which dry catalysts are used, it is preferable to refer the basic strength to the dissociation heat of

TABLE 2. EFFECT OF ALKALINE PROMOTERS UPON THE PERFORMANCE OF A $ZnO-Cr_2O_3$ CATALYST EMPLOYED IN THE SYNTHESIS OF ALCOHOLS[18]

| Fractions Obtained in the Distillation of Product** | Catalyst activated with* | | | | |
|---|---|---|---|---|---|
| | Li | Na | K | Rb | Cs |
| Tops<br>$CH_3OH$<br>$C_2$ | 0.9⎫<br>10.4⎬45.9<br>4.6⎭ | 0.6⎫<br>44.6⎬49.8<br>4.6⎭ | 0.4⎫<br>53.5⎬57.4<br>3.5⎭ | 0.5⎫<br>46.6⎬50.9<br>3.8⎭ | 0.8⎫<br>47.4⎬52.2<br>4.0⎭ |
| $C_3$ | 0.5 | 0.9 | 0.8 | 1.6 | 1.0 |
| Isobutylalcohol (primary) | 8.1 | 12.5 | 10.3 | 15.2 | 15.6 |
| $C_5$ (amyl alcohols) | 0.6 | 0.9 | 1.1 | 1.7 | 1.3 |
| Intermediates<br>$C_6$<br>$C_7$<br>Residue | 0.3⎫<br>0.5⎬2.1<br>0.8⎪<br>0.5⎭ | 0.5⎫<br>1.2⎬5.5<br>1.3⎪<br>2.5⎭ | 0.9⎫<br>1.0⎬5.4<br>1.2⎪<br>2.3⎭ | 1.6⎫<br>1.3⎬9.3<br>2.3⎪<br>4.1⎭ | 1.1⎫<br>1.6⎬9.2<br>2.0⎪<br>4.5⎭ |
| Intermediates 2,4 + distillation loss | 1.7 | 1.7 | 1.7 | 2.5 | 2.4 |
| $H_2O$ | 41.1 | 28.7 | 23.3 | 18.8 | 18.3 |
| Yield, expressed in liters per hour per liter of catalyst | 0.585 | 0.985 | 0.882 | 0.980 | 1.102 |

* The compositions of the catalysts, expressed in weight percentages, before the reduction of $CrO_3$ to $Cr_2O_3$, were the following:

$$ZnO:CrO_3:Li_2O = 55.0:36.1:0.32$$
$$ZnO:CrO_3:Na_2O = 56.1:34.1:0.59$$
$$ZnO:CrO_3:K_2O = 55.5:35.6:0.96$$
$$ZnO:CrO_3:Rb_2O = 55.0:35.5:1.90$$
$$ZnO:CrO_3:Cs_2O = 54.5:33.7:2.20$$
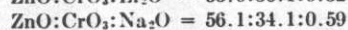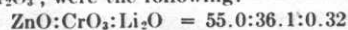
As it may be noticed, the alkali contents are equal in all catalysts, if measured in moles.

** The concentrations of reaction products are expressed in weight per cent.

the carbonates into $CO_2$ + oxides. This criterion is justified considering that in the conditions of the synthesis of higher alcohols, uncombined hydroxides are certainly not present in the catalysts. In Table 3 the ionization potentials of the corresponding metals are also indicated. These values are closely related with the reducibilities of the oxides.

A more complete and correct comparison of the activities of catalysts activated with the different promoters should take into consideration the differences in reducibility of metal oxides and their selectivities for the various reactions (dehydrogenation, dehydration, hydrocarbon synthesis,

TABLE 3

| Metals | Ionization Potentials (Electron-Volts)* | Carbonates | Dissociation Heat (Kcal/mole) |
|---|---|---|---|
| Li | 5.36 | $Li_2CO_3$ | 54.1 |
| Na | 5.12 | $Na_2CO_3$ | 76.9 |
| K | 4.32 | $K_2CO_3$ | 93.5 |
| Rb | 4.16 | $Rb_2CO_3$ | 96.7 |
| Cs | 3.87 | $Cs_2CO_3$ | 99.5 |
| Mg | 7.61 | $MgCO_3$ | 29.0 |
| Ca | 6.09 | $CaCO_3$ | 42.5 |
| Ba | 5.19 | $BaCO_3$ | 63.9 |
| Cu | 7.68 | $CuCO_3$ | 11.1 |
| Zn | 9.36 | $ZnCO_3$ | 17.1 |
| Mn | 7.41 | $MnCO_3$ | 27.9 |
| Fe | 7.83 | $FeCO_3$ | 21.0 |
| Co | 7.81 | $CoCO_3$ | 21.5 |
| Cr | 6.74 | — | — |

* The ionization potential values were taken from the book "Spectrochemical Procedures" by C. E. Harvey (A. R. L. Glendale, Calif. 1953)—The values of dissociation heats were taken from reference 47.

etc.). However, if only the alkaline and alkaline earth metals are considered, their promoting activity for the synthesis of higher alcohols may be considered as closely connected with their basic strength. The low basic strength of ZnO and $Cr_2O_3$ is probably the cause of the almost complete absence of higher alcohols in the synthesis of methanol with ZnO or ZnO-$Cr_2O_3$ base catalysts free from alkali. It can be assumed that chromium oxide, $Cr_2O_3$, presents a lower basic strength than ZnO, since the neutral chromium carbonate, $Cr_2(CO_3)_3$, is not known. The other metal oxides listed in Table 3 exert a relatively favorable influence for the formation of higher alcohols. From a qualitative point of view, this influence seems to depend upon their basic strength. This assumption is corroborated by the conclusion of Strada[53, 54] that magnesium oxide is a more effective promoter for a zinc-oxide catalyst than manganese oxide.

A differentiation of the various promoters according to their basic strength does not appear to be valid for certain catalysts of slightly basic character which, however, favor the formation of higher alcohols without the aid of alkaline promoters. A striking example of this kind of catalyst is offered by thorium oxide, the well known catalyst of isosynthesis[43, 44, 45]. The basic strength of $ThO_2$ is very low: the corresponding neutral carbonate is not stable and only the acid carbonate is known[20]. It may be convenient to note at this point that the activating influence of alkaline metals in the synthesis of higher alcohols is probably associated with an analogous promoting action upon the conversion of water gas[16]:

$$CO + H_2O \rightleftharpoons H_2 + CO_2 .$$

Activated zinc oxide (particularly if obtained by decomposition of the neutral zinc carbonate, smithsonite) can also be considered a catalyst for the conversion of water gas. However, its activity for this reaction grows when it is pretreated with alkali (particularly with $K_2CO_3$)[35].

From the data given by Morgan and his co-workers[28] with an alkali-activated $Cr_2O_3$-$MnO$ catalyst, it may be concluded that the yield in higher alcohols increases, up to a certain limit, with the amount of alkali present in the catalyst. This is particularly true with a rubidium or cesium-activated catalyst. The results of Morgan and co-workers were substantially confirmed by other authors who tested different catalysts. For example, the already mentioned catalysts tested by Natta and Strada show yields of higher alcohols increasing with the content of the alkali acting as promoter.

Frolich and Lewis[18], working with potassium-activated chromium steel catalysts, have reached conclusions in disagreement with those of the above mentioned authors. In Figure 4 the production curves obtained by Frolich and Lewis are reported as functions of the $K_2O$ content in the catalysts. It may be seen that the yields of higher alcohols present a minimum for a $K_2O$ content of 5 per cent, and that the best yields are obtained with catalysts containing small amounts of $K_2O$. The apparent singularity in the behavior of these catalysts may be considered as due to differences of constitution and probably differences in the mechanisms of the reactions.

In conclusion, it has to be pointed out that the method of preparation of the catalysts appears to be very important for their evaluation in the synthesis of alcohols. Therefore the results obtained by different investigators cannot be strictly correlated. This limitation has to be kept in mind when, for example, the relatively high yields of higher alcohols obtained by Runge and Zepf[48] with $ZnO$-$Cr_2O_3$ catalysts containing small amounts of alkali oxides are considered.
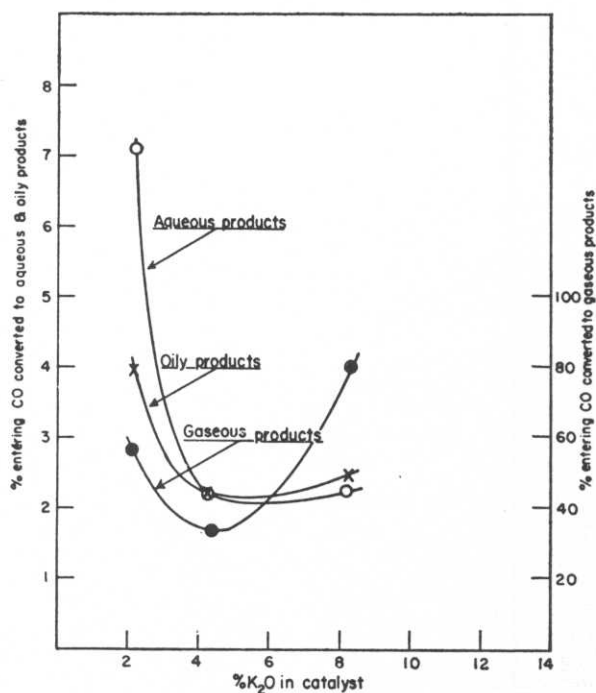
Figure 4. Influence of the amount of promoter ($K_2O$) present in a catalyst upon the yields in gaseous, aqueous, and oily products (From Ref. 18).

Catalyst = chromium steel turnings
Temperature of synthesis: 330°C
Pressure of synthesis: 254 atm.
Gas composition: $CO/H_2$ = 40:60
Space velocity: 400–2000

## REVIEW OF THE CATALYSTS PROPOSED FOR THE SYNTHESIS OF HIGHER ALCOHOLS

The data available in the literature are indeed very scarce. Furthermore, it has to be pointed out that all the experiments reported in the literature, and particularly those published before 1950, were performed in apparatus in which probably a good constancy of the temperature in all the parts of the catalyst was not obtainable because of the difficulty of obtaining isothermal conditions for highly exothermic reactions operated under pressure. As may be seen from the work of Natta and co-workers[38] a constancy of temperature (within 2°C) along all the catalyst is obtainable only with relatively limited space velocities and with very low ratios of catalyst volume to the area of the surface of the surrounding thermostat walls.

## ZnO-Base Catalysts with Alkaline Promoters

Pure zinc oxide, with the addition of only alkaline compounds, is not suitable for the preparation of durable catalysts for the synthesis of higher alcohols. The reasons for this are quite obvious when one bears in mind what is already known on the aging of ZnO employed for methanol synthesis[40]. This oxide, however, being a base for most of the catalysts used in alcohol synthesis, has a paramount importance in this field.

Natta and Strada[33], examining some ZnO catalysts, found that those obtained from calcined smithsonite* were very active catalysts, both in the synthesis of methyl alcohol and higher alcohols. Calcined iron-free smithsonite, when operating at high pressures and at temperatures not exceeding 380 to 390°C, on mixtures of CO and $H_2$, produces by itself only MeOH. If, however, the synthesis is operated at temperatures over 400°C, this catalyst also produces small amounts of water and of methyl ether, resulting from the dehydration of methanol. When the reaction is performed in the same experimental conditions, but at slightly higher temperature (t = 390 to 420°C), after the catalyst has been impregnated either with alkali hydroxide or with other salts of alkaline metals, a mixture of alcohol is obtained. Impregnation of the catalyst is carried out very easily by soaking the calcined smithsonite, whose porosity is very high, with a solution of the alkaline salt.

As already stated, Natta and Strada[33, 53] have studied the activity of zinc oxide from smithsonite, impregnated with variable amounts of some potassium salts (Figure 5). From the careful examination of the products obtained with the use of such catalysts, these authors concluded that the average composition of the reaction product after the first few hours of performance does not substantially depend upon the kind of tested anion combined to the alkali metal (hydroxide, carbonate, organic salts). Operation with such a catalyst at 400°C, 250 atm. with a CO:$H_2$ ratio of 1:2 yielded a raw product with about 20 per cent of higher alcohols, the principal component of which was isobutanol.

## ZnO and Cr$_2$O$_3$ Base Catalysts with Alkaline Promoters

In this group may be found the catalysts which have been mostly applied not only for the synthesis of methanol from CO and $H_2$ but also for the synthesis of higher alcohols. Frolich and Lewis[18] studied several catalysts, composed of oxides of the following elements: Cr-K; Fe-Cr-K; Zn-Cr-K, Ba-Cu. These authors noticed that the best results are obtained with Zn-Cr-K catalysts; in particular they have found that the best yields of higher alcohols were obtained with a catalyst prepared by reduction of a

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* Smithsonite is neutral $ZnCO_3$ mineral, containing other divalent metal oxides as impurities in solid solution.

mixture of zinc oxide, ammonium dichromate, and potassium carbonate. Operating with such a catalyst at 490°C, 240 atm. with a space velocity of 2000, they reported obtaining a raw product having the following volume composition: methanol 17.8%, ethanol 2.3%, propionic alcohols 33.4%, butyl alcohols 2.5%, amyl alcohols 9.0%, and water 35.6%. However, owing to the fractionation method used by these authors, the above data should not be considered as completely reliable.
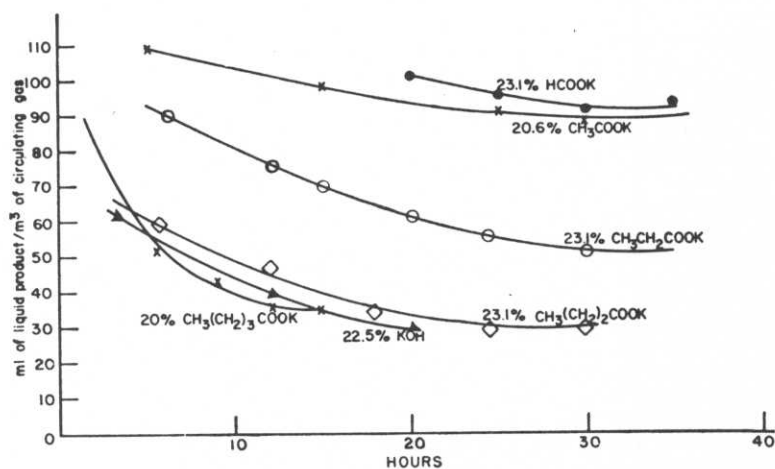


Figure 5. Influence of the anion bonded to the alkaline promoter upon the conversion of carbon monoxide and upon the stability of the catalysts employed in the synthesis of higher alcohols. (From Refs. 33 and 53)

Catalyst: ZnO from calcined smithsonite
Temperature of synthesis: 400°C
Pressure of synthesis: 250 atm.
Gas composition: $CO/H_2 = 1/2.2$

The data obtained by Runge and Zepf[48] who experimented with catalysts impregnated with the different alkaline components, have already been mentioned. The best results (see Table 2) were obtained by these authors in experiments carried out at a temperature of 440 to 445°C, with a pressure of 250 atm. and a space velocity of 20,000. The composition of the input gas was approximately 5:1 $H_2$:CO.

It is to be noticed that such experimental conditions correspond closely to those which may be deduced from the operating data of an industrial plant set up in Germany by the I.G. Farbenindustrie for the synthesis of isobutanol[50].

## Catalysts Containing Oxides of Zinc, Manganese, Chromium Activated with Alkaline Promoters

From the examination of seventeen types of catalysts, Frolich and Cryder[19] noticed that the best performances were given by catalysts obtained through reduction of mixtures of basic carbonates of zinc, chromium, and manganese containing potassium carbonate. The molar composition of such catalysts was as follows:

$$Zn:Mn:Cr = 1.00:1.10:1.03.$$

The activity of such catalysts was very high and uniform even in long tests and the products obtained contained low amounts of acids and aldehydes. The composition of the products obtained varied considerably according to the space velocity of the feed gas. The values for the individual productions of $C_1$-$C_4$ alcohols are not reported here because of the very low separating power of the fractionation methods then used.

## Catalysts Containing Cu, ZnO, $Cr_2O_3$ Activated with Alkaline Promoters

The presence of Cu requires, for maintaining the life of the catalyst, that the synthesis be operated at temperatures lower than when $ZnO$-$Cr_2O_2$ catalysts are employed. Pospechov[16] has studied a catalyst having the following molar composition: 82% Cu, 16% ZnO, 2% $Cr_2O_3$. Such a catalyst was prepared through the reduction of a mixture of the hydroxides, obtained by reaction of the nitrates with NaOH. The addition of 0.1 to 5.0 mole per cent of $K_2O$ imparts to the catalyst a very remarkable activity. Pospechov has obtained at a temperature of 200°C and a pressure of 100 atms. with a catalyst of this type activated with 0.1 mole per cent of $K_2O$ a mixture of alcohols containing up to 22.3 per cent by weight of ethanol. It should be pointed out that, contrary to what occurs for the catalysts so far examined, in this case the production of relatively high amounts of ethanol is observed. This result may be connected with the relatively low temperature of synthesis. A similar result is reached with the use of a CuO-MgO (or ZnO) catalyst[9] when employed at temperatures above 100°C and pressures above 10 atm.

Another catalyst of this type, prepared by slowly heating (from 100 to 400°C) an equimolecular mixture of $Zn(OH)_2$, $Cu(OH)_2$ and $K_2[Cr(C_2O_4)_3]$. $3H_2O$ was reported to be very durable and active for the synthesis of isobutanol[11]. The yield of isobutanol obtained with this catalyst was 30 per cent, while the over-all yield of other higher alcohols was 15 per cent, when it was operated at 400°C and at 150 atm. According to Sueta and Niwa[55]

the activity and durability of this catalyst may be considerably improved through the addition of small amounts of CaO.

### Catalysts Containing Copper and Oxides (or Salts) of Zinc, Chromium, Manganese, Calcium, Lead, Aluminum, Thorium, etc. Activated with Alkaline Metals

Several types of catalysts were proposed, containing two or more of the above listed metallic oxides. One such catalyst may be prepared by adding $CaC_2$ to a mixture of $ZnO$ and $Cr_2O_3$. Such a catalyst was employed by Nagishi[29] who obtained a liquid product containing higher alcohols. The addition of small quantities of $ThO_2$ increases the yield of butanol up to values over 18 per cent of the total liquid product, without, however, varying the amount of methanol obtained. A catalyst having essentially the same properties may be conveniently prepared by melting a mixture of $ZnO$ and $CaCr_2O_7$[23].

As was previously mentioned, the $Cr_2O_3$-$MnO$-base catalysts, which were also proposed by the I.G. Farbenindustrie[24], were particularly studied by Morgan and his co-workers[28]. These authors determined experimentally the influence of the five alkaline metals upon a catalyst of this type. The best results were obtained when the catalyst was activated with 9.8 per cent or more rubidium. In particular, the product obtained with the catalyst containing 15 per cent Rb had the following composition (expressed in percentage, as referred to the initial carbon): 42% methanol; 38% higher alcohols; 15% aldehydes, acetals (and probably ketones); 1% acids; 2% methane; 2% carbon dioxide.

A catalyst containing Cu, Cr, K, whose composition was $Cu:Cr:K = 1:4:1.97$, examined by Tahara and co-workers[56, 57], who operated at 490°C and 180 atm., with gases having a $CO:H_2$ volume ratio of 1:2 flowing at the rate of 700 l/h over 80 ml of catalyst, was reported to give yields of isobutanol as high as 37 per cent of the total liquid reaction product. This appears to be amazingly high. However, due to the high temperature of synthesis, the catalysts of this type show a poor resistance to aging.

Bocherova, Dolgov and co-workers[4, 5, 6] have studied the influence of the presence, in $ZnO$-base catalysts, of the oxides of lead, aluminum, vanadium, etc. These authors operated, in general, in the following experimental conditions: temperature, 350 to 450°C; pressure, 150 to 250 atm.; gas composition, $CO:H_2 = 1:1$; space velocity, 5–6000. They operated with the following catalysts:

(1) $4ZnO.PbO$; $PbO.Zn(OH)_2$; $4ZnO.PbO.0.2Zn(OK)_2$; $4ZnO.PbO$ $0.2Zn(OK)_2CdO$

(2) $4ZnO.V_2O_5.KOH$; $8ZnO.V_2O_5.KOH$

(3) $ZnO.Al_2O_3.KOH$

(4) Alkali zincate with the addition of $Sb_2O_5$ ; $V_2O_5$ ; $Ca(OH)_2$ ; $MnO_2$

(5) $8ZnO.Al(OK)_3.0.1V_2O_5$

(6) $Ca(OH)_2 + KOH$

(7) $8ZnO.Al(OH)_3.0.1V_2O_5.0.1MoO_3.3KOH$.

The catalysts of group (1), containing PbO, have given very low yields of higher alcohols, at all the temperatures tested, as could be predicted from the ease with which the lead oxides reduce.

The alkali vanadates of group (2) have given higher yields than the catalysts of groups (3), (4) and (6), but lower than those of groups (5) and (7). The catalyst $8ZnO.Al(OK)_2.0.1V_2O_5$ has given a production of 225 ml of liquid compounds per cubic meter of gas. The total yield in alcohols is 60 per cent, with a concentration of 35 per cent of higher alcohols in the condensate product, along with 60 per cent of methanol. The condensate was, as usual, present in two strata, one of which was aqueous, the other, oily. Qualitatively the aqueous condensate consisted of MeOH, EtOH, and isopropanol, while the oily condensate contained a mixture of propanol with butanols (mainly with primary isobutanol).

Among the several other catalysts which have been proposed by the various investigators for the synthesis of higher alcohols from CO and $H_2$, the following should be mentioned:

(1) The catalysts containing $ZnO$-$CuO$-$K_2O$ proposed by Patart[42]

(2) A catalyst consisting of equal weights of $K_2CO_3$, $V_2O_5$, and CuO, which has yielded at 480°C a product containing 40% MeOH, 25% isobutanol, 20% $H_2O$, and 15% other higher alcohols and esters[23].

(3) The catalysts containing large amounts of one or more components which act as hydration catalysts rather than as hydrogenation catalysts. An example of this class of catalysts is the catalyst $CdO$-$Cr_2O_3$[24].

## Catalysts Containing Cobalt

Such catalysts differ from those mentioned above because they contain a metal of the iron group and because of the fundamentally different nature of the products obtained. While the modified methanol catalysts lead mainly to the formation, among the other higher alcohols, of primary isobutanol, the catalysts containing Co give rise to the formation of high amounts of ethanol, even if the synthesis is operated at high temperatures. Taylor[58] was probably the first investigator who observed the formation of substantial amounts of ethanol when using a catalyst containing Cu, Mn and Co. The highest yields in ethyl alcohol (up to 22 per cent with respect to the condensate product) were obtained by Taylor with a catalyst prepared by adding 0.1 g eq. of CoS to a mixture of 1 g eq. CuO + 1 g eq. MnO. The reaction was operated at 40°C and 200 atm. with a space velocity of 200,000.

High yields in ethanol (20 per cent of the total condensate product) were also obtained with the use of a catalyst prepared from $Co(NO_3)_2$, $Zn(MnO_4)_2$ and $KMnO_4$. With this group of catalysts the higher alcohols obtained are prevailingly of the linear type, whereas with modified methanol catalysts they appear to have mainly branched molecules.

Klyukvin and his co-workers[26] have obtained very high yields of ethanol operating with a catalyst composed of $ZnO:CoO = 3:1$. In fact, when the reaction was performed at 320 to 330°C and 120 atm., yields of ethyl alcohol were obtained up to 39 per cent of the condensate products.

TABLE 4. PERFORMANCE OF AN ALKALI-ACTIVATED* ZnO-Cr₂O₃
CATALYST AS A FUNCTION OF TIME

Temperature of synthesis: 400°C
Pressure of synthesis: 400 atm
Space velocity: 29,000
Feed gas composition: $CO = 15$-$20\%$; $H_2 = 52$-$60\%$; $CH_4 = 18$-$22\%$; $CO_2 = 2$-$4\%$

|  | Total Production (kg per 100 liters catalyst) | Density of Production | Per cent Alcohols in Product | Per cent Acids in Product | Per cent Esters in Product | Per cent Water in Product |
|---|---|---|---|---|---|---|
| 1st Day of performance | 1630 | 0.850 | 78.0 | 0.4 | 2.2 | 18.5 |
| 16th " " " | 1580 | 0.855 | 75.0 | 0.4 | 1.8 | 21.0 |
| 31st " " " | 1420 | 0.865 | 72.6 | 0.2 | 1.7 | 24.0 |

* The catalyst was impregnated with 12% by weight of potassium acetate.

### RESISTANCE OF THE CATALYSTS TO AGING AND POISONS

While the catalysts employed in the industrial synthesis of methanol have a life which may reach one year or more of actual performance, those employed for the synthesis of higher alcohols are not very resistant to aging, and their activity decreases rapidly with time. Natta tested several alkali-activated methanol catalysts for the synthesis of higher alcohols, and noticed that their activity decreased remarkably with time. A typical example of this behavior is given by a ZnO-Cr₂O₃ catalyst activated with 12 per cent by weight of potassium acetate. This catalyst has shown a higher resistance to aging with respect to analogous catalysts activated by different potassium compounds ($K_2CO_3$ or $KOH$); however, its activity decreased considerably with working time.

In Table 4 some unpublished data obtained by Natta are given, concerning the performance of a plant which had been designed for the synthesis of methyl alcohol, but which for a certain period was used for the synthesis of higher alcohols. In such experiments the production of methanol was still as high as $\frac{2}{3}$ of the over-all alcohol production. The amount of

isobutanol produced was about 50 per cent of the total production of higher alcohols.

The low resistance to aging of certain catalysts which have been employed[56, 57] for the synthesis of higher alcohols in a rather high temperature range has already been pointed out.

Natta and Strada[33, 53] have studied the influence of the type of anion bonded to the promoting alkaline metals upon the resistance to aging of the catalysts for higher alcohol synthesis. These authors have tested in particular a series of ZnO catalysts prepared from calcined smithsonite, activated with different potassium salts, such as KOH, $K_2CO_3$, HCOOK, $CH_3COOK$, $C_2H_5COOK$, $C_3H_7COOK$, $C_4H_9COOK$. The experimental results obtained by these authors are reported in Figure 5. It is clear that the

TABLE 5. AMOUNTS OF FATTY ACIDS CONTAINED IN HIGHER ALCOHOL CATALYSTS FROM CALCINED SMITHSONITE, REFERRED TO THE CATALYSTS' WEIGHTS.

Working temperature: 400-420°C

| Type of Promoter | Per cent Promoter in Catalyst | Carbonic Acid | Formic Acid | Higher Fatty Acids | Nature of Most Abundant Fatty Acids |
|---|---|---|---|---|---|
| KOH | 17.5 | 3.34 | 3.91 | 4.24 | acetic, propionic |
| $K_2CO_3$ | 28.5 | 6.65 | 1.92 | 7.89 | acetic, propionic |
| HCOOK | 23.1 | 5.70 | 0.51 | 4.77 | acetic, propionic |
| $CH_3COOK$ | 20.6 | 1.59 | 2.40 | 10.90 | propionic |
| $C_2H_5COOK$ | 23.1 | 2.55 | 0.62 | 13.05 | propionic, butyric |
| $C_3H_7COOK$ | 32.1 | 4.50 | 0.31 | 2.32 | butyric, valeric |

resistance to aging is not uniform for the catalysts having different promoters. The catalysts activated with potassium formate or acetate are more durable than those activated with potassium hydroxide or carbonate. We shall consider later on the possible causes for this lower resistance of the catalysts activated with KOH or $K_2CO_3$. The catalysts activated with either $C_2H_5COOK$, $C_3H_7COOK$, $C_4H_9COOK$ show a limited resistance to aging; their durability is lower the longer the carbon atom chain.

In general, it may be stated that the low melting points of most of the alkaline salts favor the recrystallization of the ZnO. This appears to be one of the causes of the generally low aging resistance of the higher alcohol catalysts. Another factor which seems to contribute to the low durability of higher alcohol catalysts is the filling of the catalyst pores by high molecular weight reaction products.

Natta and Strada[33] have reported that ZnO catalysts contained, after a normal performance, relatively high amounts of fatty acids. In Table 5 are indicated the amounts of the different fatty acids contained in a series of

higher alcohol catalysts prepared from calcined smithsonite impregnated with different potassium salts.

It may be of some interest to point out that Natta and Strada did not notice the presence of fatty acids in catalysts that had operated at 430 to 450°C.

Other authors[12, 50] reported the gradual elimination by thermal decomposition of formic acid from the catalysts activated with alkaline formates.

In catalysts activated with alkaline salts of fatty acids, the formation of fatty acids with higher molecular weights than the starting ones has been noticed. The formation of such acids on the catalyst is probably one of the main reasons for the aging of the catalysts activated with KOH or $K_2CO_3$. Let us consider for example a typical KOH-activated methanol catalyst. Owing to the reaction

$$ZnO + 2KOH \rightarrow ZnO_2K_2 + H_2O$$

the ZnO at its surface is transformed into potassium zincate. The consecutive formation of the organic potassium salt takes place through the zincate, with the formation of ZnO.

The transformation of $K_2O$ into organic potassium salts is accompanied by a volume increase of about 156 per cent. The organic salts thus formed have, on an average, the molecular weight of the potassium acetate; their formation results in a reduction of the pore volume. The activation of ZnO with $K_2CO_3$ leads to catalysts which are more active and resistant than those activated with KOH. According to Natta and Strada[33], a similar cause is responsible for the stronger promoter action of the potassium acetate when used as activator for ZnO catalysts.

Several factors may influence this effect: the type of ZnO used, the possible presence of other promoters, the pore size distribution and the mechanical behavior of the catalyst.

It has already been mentioned that the copper-containing catalysts have a lower resistance to aging than ZnO catalysts.

Tahara and his co-workers[56, 57] have tested a copper-chromium catalyst activated with $K_2CO_3$, and having the composition:

$$CuO:Cr_2O_3:K_2CO_3 = 1:4.72:2.80.$$

At 490°C they noticed a considerable reduction with time of the amount of liquid reaction products obtained. After 48 hours of performance such volume was only 43 per cent as large as initially. In the same test, the isobutyl alcohol concentration in the liquid dropped from 37 to 30 per cent after 10 hours, and to 24 per cent after 100 hours, with a corresponding increase of the methanol concentration.

## EFFECT OF THE COMPOSITION OF REACTING GASES

Stoichiometrically, the synthesis of higher alcohols requires two volumes of hydrogen for one volume of carbon monoxide, according to the reaction:

$$nCO + 2nH_2 = C_nH_{2n+1}OH + (n + 1)H_2O \tag{1}$$

It is, however, obvious that the volume ratio $CO/H_2 = \frac{1}{2}$ must not be presumed to be the optimum, either for the input gas or the circulating gas. During the reaction the concentration of $H_2$ in the gas increases as a result of the carbon monoxide conversion reaction brought about by the water formed in reaction (1):

$$CO + H_2O = CO_2 + H_2 \tag{2}$$
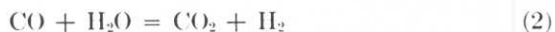
The occurrence of reaction (2) is particularly evident when the reaction is performed continuously with recycle of the reacting gases.

If reactions (1) and (2) are combined, the following equation is obtained for the higher alcohol synthesis:

$$(2n - 1)CO + (n + 1)H_2 = C_nH_{2n+1}OH + (n - 1)CO_2 \tag{3}$$

The carbon dioxide formed in reaction (3) is very soluble in the liquid reaction products; therefore, the hydrogen concentration in the gaseous phase increases. This is shown, for example, by the performance data of an I.G. Farbenindustrie isobutanol plant, in which the $H_2/CO$ ratio varies from 1.8 in the input gas to 2.6 in the circulating gas[60].

While in the above mentioned isobutanol plant the input gas composition corresponds to a $H_2/CO$ ratio of 1.8, in the Synol process the same ratio is approximately 1.0. Since the reaction is heterogeneous, the rate of the over-all process of higher alcohol formation depends mainly on the concentration of the reactants adsorbed by the catalyst. It is obvious that the concentrations in the adsorbed phase do not necessarily follow the stoichiometric ratios of the reactants in the gas phase.

Only few data are available concerning the influence of the $CO:H_2$ ratio upon the higher alcohols synthesis with modified methanol catalysts. On the contrary extensive studies have been reported for the synthesis of methanol[38, 39]. Bocharova and co-workers[5] studied the synthesis of higher alcohols with a catalyst of the following composition: $8ZnO.Al(OK)_2.0.1V_2O_5$. They reported that the $CO-H_2$ ratio of 1:1 is the most satisfactory. Such a conclusion is, from a qualitative point of view, in agreement with the results obtained by Natta and Rigamonti[34], who reported that the best yields of higher alcohols are found when the $CO:H_2$ ratio in circulating gases is higher than the stoichiometric ratio.

It appears clear that a high partial pressure of carbon monoxide favors the formation of high molecular weight compounds. This matter will be

discussed more thoroughly in the paragraph concerning the mechanism of the synthesis of higher alcohols.

The presence of inert gases exerts an influence due to the decrease in the partial pressures of the gases participating in the reaction.

A more remarkable influence is ascribed to the presence in the synthesis gas of compounds which may take part in the reaction. One such compound is, of course, water, which inhibits the formation of higher alcohols. An excess of CO, which removes the water with the formation of $CO_2$, is very favorable to the reaction. On the other hand, it should be noted that the synthesis of higher alcohols may be also performed starting from hydrogen and carbon dioxide[6, 27].

When the synthesis of higher alcohols is performed with the preliminary addition of methanol, the results are practically identical to those obtained when the reaction is operated with only CO and $H_2$. This is true also when the synthesis of higher alcohols is realized by the use of CO and methanol as the sole components of the starting gas. In the aforementioned I.G. plant, methanol is recycled and is computed in the balance as $CO + 2H_2$[60]. Such a way of operating the higher alcohol synthesis makes it possible to direct the reaction toward the formation of larger amounts of higher alcohols with respect to methanol, as a consequence of the mass action effect of this compound. It is possible to work under such conditions that the amount of methanol produced is equal to that which is converted to higher alcohols in the consecutive reactions.

An analogous influence is exerted by the presence of higher alcohols in the starting gas used for their synthesis. For example, the presence of propyl alcohol in the input gas increases considerably the yield of isobutanol[3]. The presence of olefins in the reaction gas has a favorable effect on the formation of higher alcohols. This seems to be attributed to the following factors:

(1) A mass-action effect, as olefins are produced in the secondary dehydration reaction of higher alcohols;

(2) A more direct effect, because olefins may participate in the mechanism of the higher alcohol formation.

In this connection, it has been claimed[7] that the yields of higher alcohols can be increased up to 145 per cent by the addition of as little as 1.2 per cent (by volume) of ethylene to the input gas, when the synthesis is performed with cobalt-base catalysts.

The presence, in the reaction gas, of other compounds, such as propionic aldehyde or acid, seems to lead to a higher yield of isobutanol. This has been noticed with the use of alkalized $ZnO$-$Cr_2O_3$ catalysts, operating in the usual conditions of reaction (300 atm., 430°C)[3].

## EFFECT OF SPACE VELOCITY

In the synthesis of methanol, the purity of the product may be increased by operating the reaction with increased space velocities. This is to be attributed to a negative effect on possible consecutive reactions which lead to products other than methanol. The synthesis of higher alcohols has to be operated with lower space velocities, in order to obtain sufficiently high concentrations of the desired products. This is due to the fact that the for-
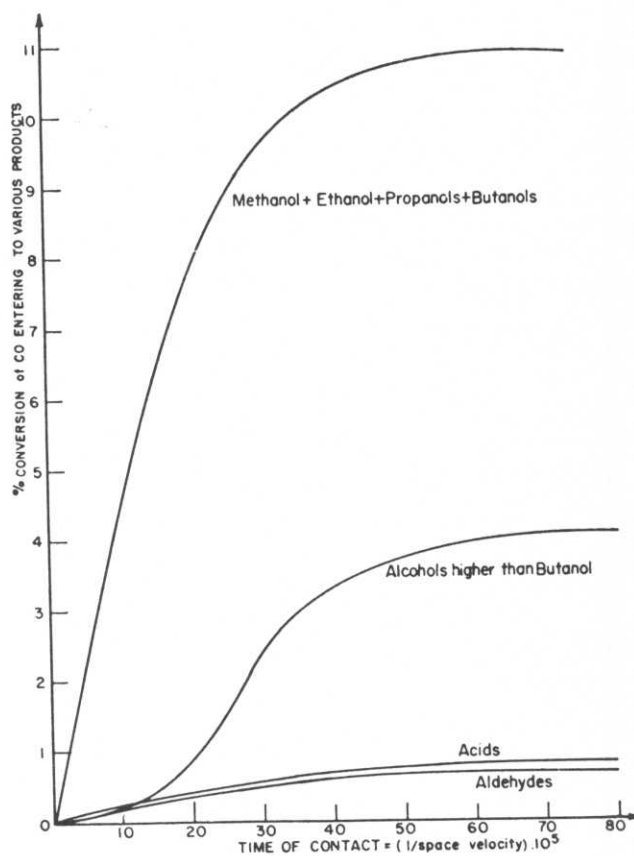
Figure 6. Effect of contact time upon the conversion of carbon monoxide to alcohols, acids and aldehydes. (From Ref. 19)

Catalyst: ZnO-MnO-Cr₂O₃-K₂O
Temperature of synthesis: 400°C
Pressure of synthesis: 204 atm.
Gas composition: CO/H₂ = 0.84

mation of higher alcohols takes place through reactions consecutive to the synthesis of methanol.

The results obtained by Frolich and Cryder[19] are shown as an example in Figure 6. These authors worked with a $ZnO$-$MnO$-$Cr_2O_3$-$K_2O$ catalyst and with a $H_2$:$CO$ ratio in the circulating gas of 1.18. It may be further observed that the concentration ratio between higher alcohols and methanol in the reaction product increases with the contact time, although the yield in methanol is higher than the yields of its homologs.

However, considerations of a different nature have played an important role in the choice of the space velocity for the synthesis of higher alcohols. We have already mentioned the experiments of Runge and Zepf[48] who operated with a space velocity as high as 20,000. In the most recent industrial plants[69] the space velocities employed are of this order.

### EFFECTS OF TEMPERATURE AND PRESSURE

The synthesis of methanol from $CO$ and $H_2$ is ordinarily operated at temperatures of the order of 350 to 400°C with the most active catalysts, and at even lower temperatures with such catalysts as $CuO$ or $CuO$-$ZnO$.

The synthesis of higher alcohols with modified methanol catalysts takes place to an appreciable extent only when the reaction is operated at higher temperatures. Some temperature data concerning the synthesis of higher alcohols with modified methanol catalysts have already been reported in this chapter. It may be here pointed out that, from a practical point of view, the synthesis has to be performed at temperatures higher than 400°C, owing to the increase, with an increase in temperature, of the yield of higher alcohols with respect to methanol. The catalytic synthesis of alcohols from $CO$ and $H_2$ leads mainly to methanol when temperature is maintained below a certain limit; above this limit there is a sharp increase with temperature of the concentration of higher alcohols in the reaction products. For example, for alkalized $ZnO$-$Cr_2O_3$ catalysts, this characteristic temperature at which the concentration of higher alcohols is sharply increased is about 390°C[19].

### COMPOSITION OF THE PRODUCT OF THE DIRECT SYNTHESIS OF HIGHER ALCOHOLS

It may be stated that, when the synthesis is operated with alkalized methanol catalysts, the production of a relatively high amount of methyl alcohol cannot be avoided. In general, primary isobutanol is predominant among the higher alcohols, while the concentrations of ethanol, propanols, and other higher alcohols, are much lower.

Detailed analyses of the product of this synthesis were performed by

several authors, but in most of the cases the complexity of the reaction product was such as to prevent the obtaining of precise, complete results. The problem is further complicated by the influence upon the nature and distribution of reaction products exerted by the type of catalyst, and by the type and the amount of promoters employed. The composition of the reaction products obtained with a given catalyst varies with the physico-chemical conditions of the synthesis, particularly with temperature, space velocity and gas composition.

Natta and Rigamonti[34, 35] have reported the analytical data for the raw product obtained on industrial tests performed with the use of a catalyst prepared from calcined smithsonite activated by impregnation with potassium acetate. The following higher alcohols were found in this product:

Normal alcohols: methanol, ethanol, 1 propanol, 1 amyl alcohol

Branched alcohols: isobutanol, 2-methylbutanol, 2-methylpentanol, 2-methylhexanol, 3-methylpentanol, isoamyl alcohol, 2,3-dimethylbutanol

Secondary alcohols: isopropanol, ethyl isopropylmethanol, diisopropyl-butanol, propyl-isopropylcarbinol

Tertiary alcohols: tertiary butyric and amyl alcohols.

As far as the relative amounts of alcohols produced, the analysis of Natta and Rigamonti shows that methanol is the most abundant, and that isobutanol is the principal higher alcohol, followed by *n*-propanol, 2 methylbutanol, ethanol, isopropanol, *n*-butanol, 2-methylpentanol.

The amount of isobutanol plus *n*-propanol is as high as 65 per cent of the over-all higher alcohols production.

In Table 6 the relative amounts of the individual higher alcohols produced are shown, referred to the total production of higher alcohols, as reported by Natta and Rigamonti[35].

The relative amounts of alcohols produced in the two different tests are substantially identical. It should be further observed that among the branched alcohols those with a methyl group in the 2-position are predominant. The higher content of this type of branched alcohols had also been observed by Morgan and co-workers[28] and by other investigators.

Tertiary alcohols seem to be present in extremely low amounts in the synthesis product. In fact, Natta and Rigamonti have noticed only qualitatively the presence of tertiary butyl and amyl alcohols.

The data found by the above mentioned authors are in good agreement with the results obtained by Morgan and co-workers[28], who operated the synthesis of higher alcohols with catalysts containing only oxides of manganese, chromium, and alkaline metals. The following alcohols were identified by these investigators: methanol, ethanol (traces), propanol, isobutanol, 2-methylbutanol, 2-methylpentanol, 2,4-dimethylpentanol.

The analytical data concerning the product obtained by Graves[21] show the presence of an amazingly high amount of secondary alcohols (Table 7).

*CATALYSIS*

However, Graves does not indicate the nature of catalyst, the apparatus used for the synthesis nor the concentration of lower alcohols (methanol, ethanol, propanol).

TABLE 6. COMPARATIVE PRODUCTIONS OF INDIVIDUAL HIGHER ALCOHOLS[35] WITH ALKALIZED ZnO CATALYSTS*

| Alcohols | Production | |
|---|---|---|
| | Test 1 | Test 2 |
| Ethanol | 4.16% | 3.33% |
| *n*-propanol | 11.59% | 13.12% |
| isopropanol | 3.69% | 2.62% |
| *n*-butanol | 1.99% | 1.78% |
| isobutanol | 46.65% | 51.37% |
| 2 methylbutanol | 4.79% | 4.93% |
| higher alcohols (b.p. <107°C) | 4.25% | 3.61% |
| higher alcohols (107°C < b.p. < 180°C) | 15.10% | 14.98% |
| higher alochols (b.p. > 180°C) | 7.78% | 4.26% |

* These tests were performed under the following conditions:

*Test 1:* Catalyst, calcined smithsonite, activated with potassium acetate (9.3% $K_2O$); space velocity, 17,000; gas composition, $CO/H_2 = 4$; temperature, 400–420°C; pressure, 400 atm.

*Test 2:* Catalyst, calcined smithsonite, activated with potassium acetate (13.7% $K_2O$); space velocity, 10,000; gas composition, $CO/H_2 = 4$; temperature, 400–420°C; pressure, 350–400 atm.

TABLE 7. HIGHER ALCOHOLS IDENTIFIED BY GRAVES[21] IN THE REACTION PRODUCT

| Primary alcohols: 48.5% | Secondary alcohols: 51.5% |
|---|---|
| Propanol | Isopropanol |
| Isobutanol | |
| 2-methylbutanol | |
| 2-methylpentanol | 3-methyl-2-butanol |
| 2,4-dimethylpentanol | 2,4-dimethyl-3-pentanol |
| 2-methylhexanol | 3-pentanol* |
| 2,4-dimethylhexanol* | 2-pentanol* |
| 2-methylheptanol* | 2-methyl-3-pentanol* |

* Products whose identification was uncertain.

The results obtained by the various investigators show clearly that both the nature and the amount of secondary reaction product depend upon the type of catalyst employed in the synthesis and upon the physicochemical conditions of the reaction.

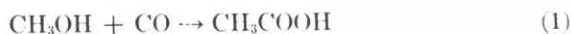In general, several types of oxygenated compounds are present among

the reaction products: water, aldehydes, ketones, esters, acids. However, while Morgan and co-workers[25] obtained over 13 per cent of aldehydes plus ketones with an alkalized Mn-Cr catalyst, Natta and Rigamonti[35] found only 1 per cent of such compounds, with traces of ethers and hydrocarbons and with higher concentration of esterified fatty acids.

Morgan and co-workers have identified in the reaction products formaldehyde, propionic aldehyde, and both hydroxyaldehydes and unsaturated aldehydes.

Strada[54] has obtained in the higher alcohol synthesis a raw product with 1.08 per cent of free acidity and 1.58 per cent of fixed acidity (expressed as propionic acid). This investigator has separated a continuous series of fractions boiling up to 285°C. His results show that acetic acid was present in a lower concentration (2.20 per cent of total acids) than butyric acid (9.20 per cent of total acids).

### MECHANISM OF THE SYNTHESIS OF HIGHER ALCOHOLS

Several hypotheses have been proposed to explain the mechanism of this synthesis. The first of them is probably that of Fischer and Tropsch[13], who suggested that higher alcohols are formed from methanol through the following consecutive reactions:

$$CH_3OH + CO \rightarrow CH_3COOH \qquad (1)$$

$$CH_3COOH + H_2 \rightarrow CH_3CHO + H_2O \qquad (2)$$

$$CH_3CHO + H_2 \rightarrow C_2H_5OH \qquad (3)$$

and so forth for primary linear higher alcohols.

The acetic acid produced from methanol in reaction (1) is partly transformed into acetone, which in turn undergoes reduction to isopropylalcohol:

$$2CH_3COOH \rightarrow (CH_3)_2CO + H_2O + CO_2 \qquad (4)$$

$$(CH_3)_2CO + H_2 \rightarrow (CH_3)_2CHOH. \qquad (5)$$
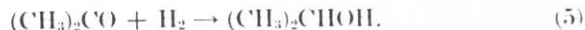
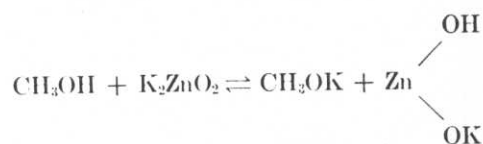A further addition of CO and $H_2$ to isopropylalcohol leads to the formation of isobutylalcohol.

Another interesting hypothesis was formulated by Natta[32, 36], whose starting point was the consideration that the formation of alkali salts of fatty acids on the catalysts may be explained by their direct participation in the mechanism of the synthesis. This hypothesis differs from that given by Fischer and Tropsch because it implies that the catalysts play a fundamental role in the formation of these intermediate fatty acid salts.

According to Natta, the synthesis of higher alcohols takes place in the following consecutive steps:
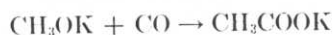
(1) Synthesis of methanol, catalyzed by ZnO:

$$CO + 2H_2 \rightarrow CH_3OH$$
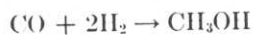
(2) Formation of potassium methylate, by reaction of methanol with alkali or with alkali zincate*:

$$CH_3OH + KOH \leftrightharpoons CH_3OK + H_2O$$

$$CH_3OH + K_2ZnO_2 \rightleftharpoons CH_3OK + Zn\begin{array}{c} \diagup OH \\ \diagdown OK \end{array}$$
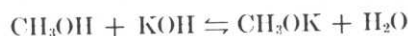
(3) Reaction of alkali methylate and CO with the formation of alkali acetate:

$$CH_3OK + CO \rightarrow CH_3COOK$$

(4) Hydrogenation of alkali acetate to alkali ethylate:

$$CH_3COOK + 2H_2 \rightarrow H_2O + C_2H_5OK.$$
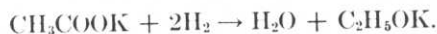
The water formed in the above written reactions provokes the hydrolysis of the alcoholates, thus regenerating potassium hydroxide and giving rise to the formation of ethanol. The portion of potassium ethylate which is not hydrolized may react with carbon monoxide and give rise to the formation of potassium propionate, which in turn is easily reduced to potassium propylate, by a reaction analogous to reaction (4). The formation of isopropyl alcohol is explained by admitting a thermal decomposition of potassium acetate to give acetone, the reduction of which then leads to isopropyl alcohol. The formation of acetone is catalyzed by zinc oxide.

Several authors have noticed the presence of acetone, which is found in higher concentrations when the reaction is performed with an excess of carbon monoxide. Similarly, the formation of secondary butylalcohol is assumed to take place through that of methyl-ethylketone.

According to this mechanism, primary linear higher alcohols could be

---

* The formation of alkali zincate takes place in the temperature range of the synthesis, in the reaction between ZnO and KOH or $K_2CO_3$ :

$$ZnO + 2KOH \rightarrow K_2ZnO_2 + H_2O$$

$$2ZnO + K_2CO_3 \rightarrow K_2ZnO_2 + ZnCO_3 \text{ (or } ZnO + CO_2\text{)}$$
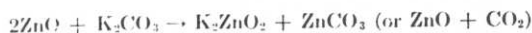
formed by the direct hydrogenation of the salts of the corresponding fatty acids. However, the slowness with which these salts are reduced makes it possible that primary linear alcohols be formed at least partially by the reduction of aldehydes, which are produced in the thermal decomposition of mixtures of alkali formate and alkali salts of fatty acids:

$$HCOOK + C_nH_{2n+1}COOK \rightarrow C_nH_{2n+1}CHO + K_2CO_3 \qquad (1)$$

$$C_nH_{2n+1}CHO + H_2 \rightarrow C_nH_{2n+1}CH_2OH \qquad (2)$$
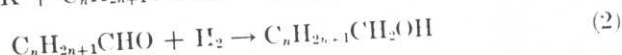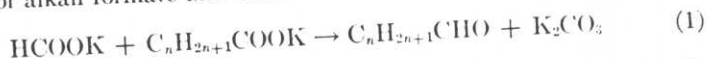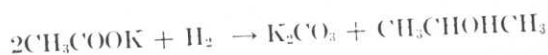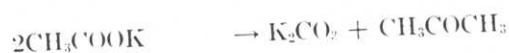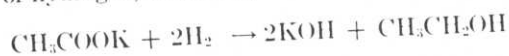
The hypothesis proposed by Natta is corroborated by the following experimental data:

(1) When the higher alcohol synthesis is performed with ZnO catalysts activated with potassium formate or potassium acetate, the formation of considerable amounts of methyl, ethyl and isopropyl alcohols is noticed. Much smaller amounts of isopropyl alcohol are formed when the synthesis is performed with ZnO catalysts activated with potassium carbonate[32].

(2) At temperatures lower than 400°C and at high pressures, carbon monoxide and hydrogen may be fixed by alkali activated ZnO-base catalysts containing alcoholate, to give salts of fatty acids[32].

(3) Above 400°C, alkali salts of fatty acids are rapidly decomposed, in the presence of hydrogen, according to the following reactions:

$$CH_3COOK + 2H_2 \rightarrow 2KOH + CH_3CH_2OH$$

$$2CH_3COOK \rightarrow K_2CO_3 + CH_3COCH_3$$

$$2CH_3COOK + H_2 \rightarrow K_2CO_3 + CH_3CHOHCH_3$$

(4) Higher alcohol catalysts tested by Natta and co-workers were found to give optimum yields at about 400°C. This temperature value is higher than the corresponding optimum temperature in the synthesis of methanol. It is interesting to note that the temperature of 400°C corresponds to effective equilibrium conditions between the formation and decomposition of fatty acid salts on the catalyst surface.

(5) Alkali carbonates adsorbed by ZnO or ZnCO₃ are partly reduced by high pressure hydrogen, to alkali formates[32].

(6) Alkali hydroxides react with carbon monoxide to give formates. These alkali formates are easily reduced by high pressure hydrogen to give methylates and methanol. The alcoholates react readily with carbon monoxide, thus forming the salts of higher fatty acids. In the specific case of methanol, its reaction with CO to give acetic acid in the presence of certain oxides or carbonates has been reported by several authors[61].

(7) The decomposition of alkali salts of fatty acids explains the forma-

tion of ketones and the production of secondary alcohols, such as, for example, isopropyl and isobutyl alcohol.

The following reactions, which are assumed to take place with the participation of alkali formate, explain the formation of aldehydes and of primary alcohols:

$$HCOOK + CH_3COOK \rightarrow K_2CO_3 + CH_3CHO$$

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH$$
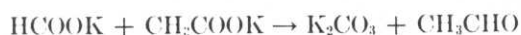
It has been reported that the production of aldehydes and ketones is particularly high when the reaction is operated with a low concentration of hydrogen.

(8) Zinc oxide appears to be a very good catalyst for the following reactions:

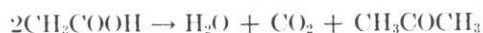$$2CH_3COOH \rightarrow H_2O + CO_2 + CH_3COCH_3$$

$$CH_3COOH + HCOOH \rightarrow CH_3CHO + H_2O + CO_2$$

(9) In the reaction products, practically all the acids corresponding to the alcohols formed in the synthesis[53, 54] are present.
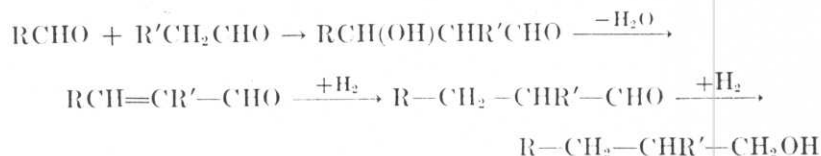
The hypothesis of the formation of higher alcohols through the direct reduction of fatty acids is apparently unable to explain the fact that in the higher alcohols synthesis only low amounts of ethanol are produced. This could be explained by claiming that acetic acid, rather than reacting with hydrogen to give ethanol, tends to react with other acids to give ketones or acetaldehyde. Experimental evidence for this behavior of acetic acid is lacking.

A satisfactory hypothesis concerning the mechanism of the higher alcohol synthesis should explain the fact that the main reaction products, other than methanol, are isobutyl alcohol and n-propyl alcohol. If, according to the above mentioned hypothesis, one assumes that these alcohols are formed through the corresponding acids, one should conclude that secondary alcohols are adsorbed by the catalyst more readily than primary alcohols or branched alcohols. Also, one should assume that isopropyl alcohol (formed in the reduction of acetone) reacts promptly with carbon monoxide to give isobutyric acid, which in turn undergoes reaction with alkali formate and hydrogen to yield isobutyl alcohol.

It may be convenient at this point to note that also in "isosynthesis," which is operated with thorium-base catalysts (not necessarily alkali-activated) there is a similar reaction product distribution, with low concentration of ethanol and relatively high concentration of isobutanol. The possible absence of alkali in the isosynthesis catalysts is in apparent contrast with
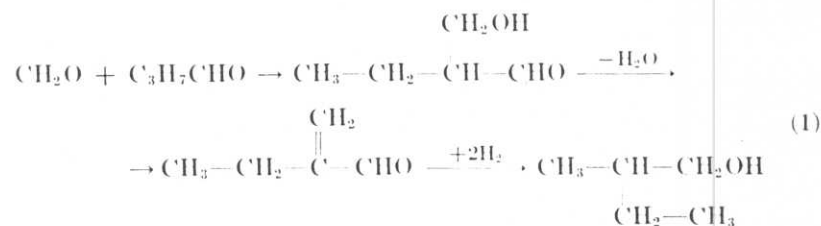
the hypothesis that assumes a direct participation of alkali salts in the reaction mechanism. However, the structural differences between the $ThO_2$ catalysts for "isosynthesis" and the alkali-activated ZnO catalysts make a direct comparison of these catalysts rather unreliable. It is, however, interesting to refer to the hypotheses which have been proposed for the mechanism of isosynthesis discussed in Chapter 5, Volume IV of the present series of books on "Catalysis."

An interesting hypothesis concerning the mechanism of the higher alcohols synthesis was proposed by Morgan, Hardy and Procter[28]. These investigators suppose that the formation of higher alcohols takes place through an aldolic condensation of formaldehyde, according to the following scheme:

$$RCHO + R'CH_2CHO \rightarrow RCH(OH)CHR'CHO \xrightarrow{-H_2O}$$

$$RCH{=}CR'{-}CHO \xrightarrow{+H_2} R{-}CH_2{-}CHR'{-}CHO \xrightarrow{+H_2}$$

$$R{-}CH_2{-}CHR'{-}CH_2OH$$

These authors base their hypothesis upon the fact that, among the condensation products obtained from CO and $H_2$ in the higher alcohols synthesis, they have identified a number of aldehydes, including unsaturated and hydroxyaldehydes*. The scheme proposed by Morgan and coworkers is able to explain the formation of those primary alcohols, which have actually been found among the products of the synthesis. In fact, it is possible to determine theoretically, from the above scheme, which of the alcohols with 5, 6, 7, 8 or 9 carbon atoms may actually be formed in the reaction.

For example, the following reactions explain the formation of the two alcohols with 5 carbon atoms which have actually been observed among the products of the synthesis:

$$CH_2O + C_3H_7CHO \rightarrow CH_3{-}CH_2{-}\overset{\displaystyle CH_2OH}{\underset{}{CH}}{-}CHO \xrightarrow{-H_2O}$$

$$\rightarrow CH_3{-}CH_2{-}\overset{\displaystyle CH_2}{\underset{}{\overset{\|}{C}}}{-}CHO \xrightarrow{+2H_2} \cdot CH_3{-}\overset{\displaystyle }{\underset{\displaystyle CH_2{-}CH_3}{CH}}{-}CH_2OH \qquad (1)$$

---

* Such hydroxy-aldehydes are probably not of the linear aliphatic type, but rather of the type $R{-}C_6H_3(OH)CHO$. However, the product obtained by Morgan had properties different from those of hydroxybenzaldehyde.

$$CH_3CHO + C_2H_5CHO \rightarrow CH_3-\underset{\underset{CH(OH)CH_3}{|}}{CH}-CHO \xrightarrow{-H_2O}$$

$$\rightarrow CH_3-\underset{\underset{CH-CH_3}{\|}}{C}-CHO \xrightarrow{+2H_2} CH_3-\underset{\underset{CH_2-CH_3}{|}}{CH}-CH_2OH \tag{2}$$

$$CH_3CHO + C_2H_5CHO \rightarrow C_2H_5CH(OH)CH_2CHO \xrightarrow{-H_2O}$$

$$\rightarrow C_2H_5CH=CHCHO \xrightarrow{+2H_2} C_2H_5CH_2CH_2-CH_2OH \tag{3}$$
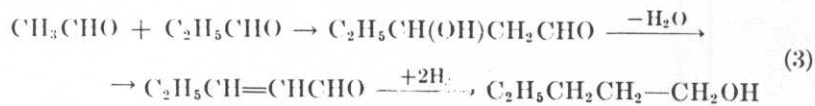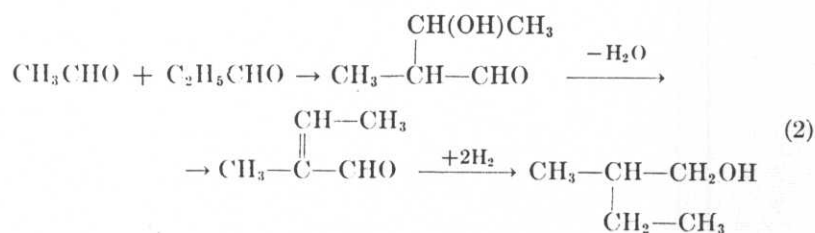
Similarly, 2-methylpentanol and 2,4-dimethylpentanol may be produced in the reactions:

$$CH_3-CH_2CHO + CH_3-CH_2-CHO \rightarrow$$

$$CH_3CH_2-CH(OH)-\underset{\underset{CH_3}{|}}{CH}-CHO \xrightarrow{-H_2O}$$

$$\rightarrow CH_3-CH_2-CH=\underset{\underset{CH_3}{|}}{C}-CHO \xrightarrow{+2H_2} \tag{4}$$

$$CH_3-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$$

$$CH_3-CH-CHO + CH_3-CH_2-CHO \rightarrow$$
$$\underset{CH_3}{|}$$

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH(OH)-\underset{\underset{CH_3}{|}}{CH}-CHO \xrightarrow{-H_2O}$$

$$\rightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-CH=\underset{\underset{CH_3}{|}}{C}-CHO \xrightarrow{+2H_2} \tag{5}$$

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$$
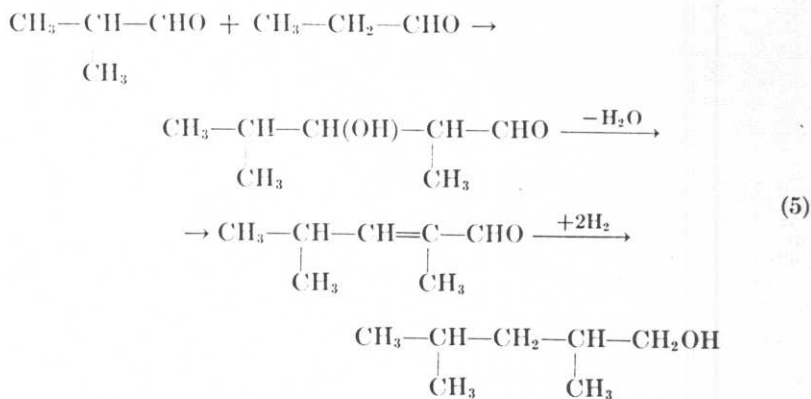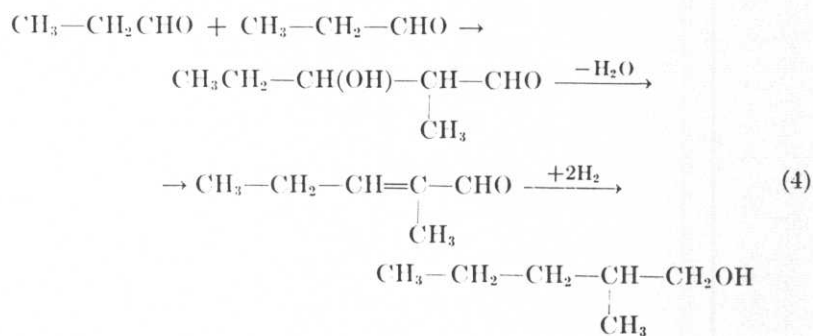
This mechanism is able to explain the formation of compounds with 3 or more carbon atoms. However, this picture fails to explain the mechanism

of the initial chain growth, starting from methanol. In fact, while it is known that the reaction:

$$CH_2O + CH_2O \rightarrow CH_2OH-CHO$$

takes place in appropriate conditions, it seems very unlikely that this reaction may occur under the conditions of the higher alcohol synthesis (high temperature and very low partial pressure of $CH_2O$). Moreover, this mechanism does not consider the formation of isopropyl alcohol and of secondary butyl alcohol, which are always present in the reaction products. In order to take into account the presence of such secondary alcohols, this mechanism would have to assume the isomerization of normal alcohols.

The $CO:H_2$ ratio in the input gas has an influence upon the synthesis of higher alcohols. Such influence is not fully understood if only the equilibrium:

$$alcohol \rightleftarrows aldehyde + hydrogen$$
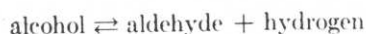
is considered. In this case a slight increase in the temperature would be sufficient to compensate for a diminution of the $CO:H_2$ ratio and thus give an equivalent equilibrium composition for the system aldehyde-alcohol. While this mechanism is not satisfactory for the formation of higher alcohols, it seems likely that the formation of certain aldehydes takes place through an aldolic condensation. An example of this is given by crotonic aldehyde, whose methylacetal was identified by Natta* in the top fraction of the methanol rectification. Such aldehyde should be considered as formed by the aldolic condensation of acetaldehyde.

An interesting hypothesis for explaining the mechanism of higher alcohols formation is that of the condensation of lower alcohols. An hypothesis of this type was first advanced by Guerbert[22] who advanced it to explain the condensation of alcohols to give higher alcohols in the presence of alkali metals, in liquid phase.

The presence, in the products of higher alcohols synthesis, of certain primary and secondary alcohols, and the exclusion of others which instead may be formed in this type of condensation, was explained by Graves[21] who assumed that:
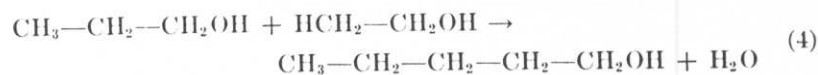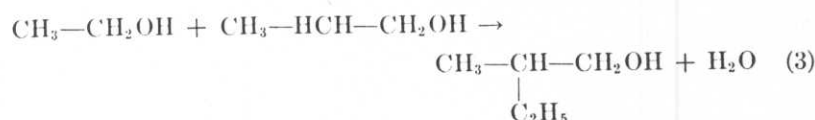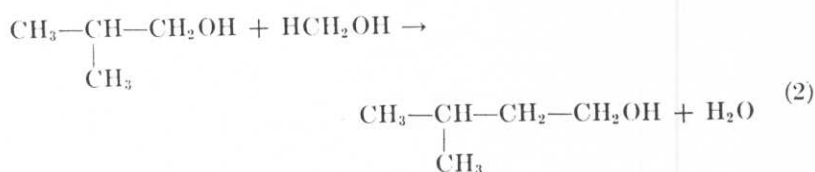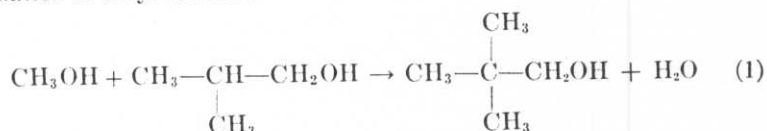
(1) Higher alcohols may be formed in the intermolecular dehydration between pairs of lower alcohol molecules.

(2) Such dehydration may involve even a hydrogen atom bonded to the carbon atom of methanol. However, the rate of this dehydration is lower than the dehydration rate involving a hydrogen atom bonded to a secondary carbon.

* Unpublished results.

(3) The condensation takes place with difficulty on methyl groups and does not take place in CH groups. The majority of alcohols result from a condensation on methylenic groups.

More recently, Nagishi[29], after a thorough evaluation of the several hypotheses advanced for explaining the mechanism of formation of higher alcohols, considers the direct condensation hypothesis as the most reliable, with the assumption that the methylic hydrogen reacts more readily when the $CH_3$ group is in $\alpha$-position. Another assumption of this author concerns the possibility of an aldolic condensation between aldehydes and ketones which are formed in the higher alcohol synthesis through secondary reactions.

The first assumption made by Nagishi may be justified if the possible reactions of condensation between two alcohols (chosen among methanol, ethanol, $n$-propanol, isobutanol) are considered, which give rise to the formation of amyl alcohols:

$$CH_3OH + CH_3-CH-CH_2OH \rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2OH + H_2O \quad (1)$$
$$\underset{CH_3}{|}$$

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH + HCH_2OH \rightarrow$$

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2OH + H_2O \quad (2)$$

$$CH_3-CH_2OH + CH_3-HCH-CH_2OH \rightarrow$$

$$CH_3-\underset{\underset{C_2H_5}{|}}{CH}-CH_2OH + H_2O \quad (3)$$

$$CH_3-CH_2-CH_2OH + HCH_2-CH_2OH \rightarrow$$

$$CH_3-CH_2-CH_2-CH_2-CH_2OH + H_2O \quad (4)$$

If the amyl alcohols which are actually produced in the synthesis of higher alcohols are considered, the prevalence of 2-methyl-1-butanol (reaction 3) is noticed, as well as the almost complete absence of $n$-amyl alcohol (reaction 4), *tert*-butylcarbinol (reaction 1) and isoamyl alcohol (reaction 2). It may therefore be concluded in agreement with the condensation hypothesis, that the H atoms of $CH_3$ and $CH$ radicals react with more difficulty than those of $CH_2$ radicals. With this assumption Graves is able to explain the prevalent formation of those primary alcohols identified among the products of higher alcohols synthesis, up to octyl alcohols.
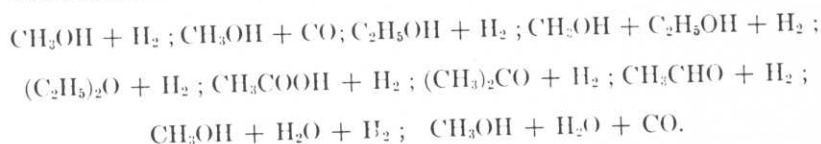
In a similar way the formation of the observed secondary higher alcohol may be explained by the assumption that the condensation takes place with the preferential loss of a hydrogen atom bonded to an $\alpha$ carbon; when this condensation occurs with the participation of secondary higher alcohols, they lose their hydroxyl rather than their hydrogen.

This hypothesis is, however, in disagreement with the fact that higher alcohols have never been obtained through the condensation of methanol. The first step of the condensation hypothesis is thus missing:

$$CH_3OH + CH_3OH \rightarrow C_2H_5OH + H_2O$$

The presence, among the synthesis products, of a low concentration of ethanol does not appear to be a sufficient proof for the hypothesis of condensation of methyl alcohol.

The views of Graves are in substantial agreement with the earlier results of Frolich and Cryder[19], who studied the behavior of the following gas mixtures under the conditions of higher alcohol synthesis:

$$CH_3OH + H_2 \; ; CH_3OH + CO; C_2H_5OH + H_2 \; ; CH_3OH + C_2H_5OH + H_2 \; ;$$

$$(C_2H_5)_2O + H_2 \; ; CH_3COOH + H_2 \; ; (CH_3)_2CO + H_2 \; ; CH_3CHO + H_2 \; ;$$

$$CH_3OH + H_2O + H_2 \; ; \quad CH_3OH + H_2O + CO.$$

These authors have obtained the following important results:

(1) The mixtures $CH_3OH + CO$ and $H_2 + CO$ have equivalent behaviors;

(2) When the reaction is operated with methanol-hydrogen mixtures less satisfactory results are obtained, because of the formation of large amounts of water;

(3) The amounts of acid formed do not depend upon the presence of CO in the initial mixture;

(4) Water acts as an inhibitor toward the synthesis of higher alcohols;

(5) The mixture ethanol-hydrogen gives rise to butanol + water, with partial dehydration of ethanol to ethylene;

(6) When the reaction is performed with methanol-ethanol mixtures, higher alcohols are obtained with a predominance of propanol;

(7) Dimethylether may not be formed starting from methanol alone;

(8) The mixture diethylether + hydrogen gives rise to the formation of higher alcohols, with a predominance of ethanol and butanol.

From these data Frolich and Cryder have reached the following conclusions:

(1) Methanol is an intermediate product in the synthesis of higher alcohols.

(2) The formation of higher alcohols takes place predominantly through the condensation of lower alcohols, with the following rate controlling reaction:

$$2CH_3OH \rightarrow C_2H_5OH + H_2O.$$

(3) Ethers do not appear to be intermediate products.

(4) The formation of esters takes place presumably through the condensation of aldehydes.

(5) Acids may be involved in the mechanism of the synthesis.

(6) The type of mechanism may be affected by the nature of catalyst, and by other experimental conditions, such as $CO:H_2$ ratio, pressure, etc.

However, bearing in mind the conditions of the experiments carried out by Frolich and Cryder, one is not able to exclude the possibility that the decomposition of the reacting gases under the synthesis conditions leads to results which are not essential in the mechanism of this synthesis.

Several other hypotheses have been formulated by various investigators, but none of them appears to be entirely satisfactory. For example, Fischer and Tropsch have supposed in one interesting paper[13] that the formation of "Synthol" compounds is due to hydrogenation of formaldehyde condensation products. These authors presume that formaldehyde is the first compound formed in the reaction of hydrogen with carbon monoxide when metals are present as hydrogenation catalysts. This assumption is corroborated by the actual presence of such compounds in the reaction products when the synthesis is accomplished with iron-containing catalysts at relatively low pressures. However, this hypothesis does not seem to be valid in the case of catalysts not containing iron or other elementary metals. A mechanism has been proposed, according to which free methylene radicals are formed, in the hydrogenation of carbon monoxide. These radicals would easily condense to form olefins. The formation of higher alcohols would take place through the hydration of these olefins. As pointed out by Fischer and Tropsch, such an hypothesis appears to be very involved, considering also the nature of alcohols which would be formed in this case. The hypothesis of higher alcohol formation through the homologation of methanol should be seriously considered after the interesting experimental work of Wender, Levine and Orchin[62], who synthesized ethyl alcohol from methanol, hydrogen and carbon monoxide:

$$CH_3OH + CO + 2H_2 \rightarrow C_2H_5OH + H_2O$$

This hypothesis is limited by the following experimental data:

(1) The homologation reaction has been accomplished only with cobalt-base catalysts (carbonyl-cobalt).

(2) The fact that methyl alcohol has a greater tendency than ethanol

towards homologation should agree with a relatively high concentration of ethanol in the reaction products, but this is in contrast with experimental evidence. Among the several other hypotheses which have been proposed for this synthesis, attention should be given to the mechanism of higher alcohol formation with a reaction analogous to that of oxosynthesis. This hypothesis was originated by the actual presence of traces of olefins in the products of higher alcohol synthesis.

Natta and Ercoli[37] have shown that methyl alcohol may participate in oxosynthesis reactions. In fact, these authors have produced acetaldehyde from methanol, carbon monoxide and hydrogen, operating the reaction in a temperature range (120°C) lower than that of the experiments of Wender, Levure and Orchin[62]. It should be noticed that this synthesis could be considered as belonging to the oxosynthesis type, if the formation of free methylene radical through dehydration of methanol is assumed.

This hypothesis is limited by the two considerations which were listed above for the homologation of methanol. In fact, oxosynthesis reactions require the presence of cobalt-containing catalysts. Moreover ethyl alcohol is practically absent from the reaction products of higher alcohol synthesis. This latter circumstance might be explained by postulating a rapid dehydration of ethanol in the physicochemical conditions of the synthesis and the consecutive formation of higher molecular weight products from ethylene. There is still another evidence against this hypothesis. In the oxosynthesis of propylene, over a relatively large temperature range, n-butyric aldehyde is formed as the principal product rather than isobutyric aldehyde, whereas isobutyl alcohol is one of the main products of higher alcohol synthesis.

## CONCLUSION

From this review of the results achieved by the various investigators in the direct synthesis of higher alcohols from hydrogen and carbon monoxide, the following considerations can be made:

(1) The synthesis of higher alcohols is always to be related to the presence of strongly basic substances.

(2) When the reaction is operated at temperatures above 400°C with ZnO-base catalysts, higher alcohols may be produced together with methanol. Among the higher alcohols, isobutanol and n-propanol are formed in relatively high proportions.

(3) When the synthesis is performed with catalysts containing certain transition metals (in particular, metals of the iron group) the formation of higher alcohols takes place at temperatures considerably below 400°C. With catalysts containing Fe, Co, or Cu, the formation of higher alcohols with an unusually high content of ethanol has been noticed.

(4) When the reaction is performed with catalysts containing metals of

the iron group (or with ThO₂) hydrocarbons are formed together with higher alcohols. When, on the contrary, ZnO-base catalysts are employed, in the absence of iron group metals and of a dehydrating catalyst (like $Al_2O_3$), the formation of hydrocarbons is almost totally prevented.

From the above statements it may be concluded that different reaction mechanisms are to be considered for various possible cases:

(a) When iron group metals (or ThO₂) catalysts are employed, the presumable reaction mechanism is strictly connected with the Fischer-Tropsch synthesis*, and the reaction goes probably from the formation of methylene groups to that of olefins and to aldehydes through oxo reactions on these olefins. Alcohols could then be formed through the reduction of aldehydes.

(b) When ZnO-base catalysts are employed the production of alcohols is not connected with the formation of hydrocarbons. In these circumstances, the necessity of using strongly alkaline promoters is a decisive factor in favor of the reaction mechanisms by which the catalytic action of alkali plays a decisive role. The reactions of aldolic condensation, and perhaps the condensation of alcohols with aldehydes are also possible for the conditions under which the synthesis is usually performed. However, the presence of salts of fatty acids in catalysts preemployed in the synthesis of higher alcohols and the results obtained in the hydrogenation of such fatty acid salts with alkalized ZnO catalysts are in favor of the reaction mechanism proposed by Natta.

It should be noted that the temperature range of the higher alcohols synthesis with ZnO-base catalysts (400 to 450°C) represents the limit for the stability of the majority of oxygenated organic compounds. This affects undoubtedly the equilibrium of many of the reactions involved in the mechanism and probably favors some isomerization reactions. Under these conditions, the thermodynamic factors probably play a more important role than at lower temperatures, and therefore they may exert a considerable influence on the composition of the end product.

The possibility should be considered, that the presence of relatively high amounts of branched compounds, which is noticed in the synthesis of higher alcohols, as well as in the isosynthesis process for the production of hydrocarbons, is partly due to the fact that many isomerization equilibria are shifted at higher temperatures towards the formation of branched molecules.

While in the industrial synthesis of methanol it is possible, with the use of highly selective catalysts, to obtain a pure compound as end-product with very high yields, this is not feasible in the direct synthesis of higher alcohols from CO and $H_2$. The formation of alcohols is due to a chain of reactions which cannot practically be arrested at a definite step. There is

* For a thorough treatment of this subject, see Chapter 3, Vol. IV of this treatise, written by Dr. R. B. Anderson.

therefore the formation of a complex mixture of reaction products, among which primary alcohols are predominant but not the only ones present. This is the main reason for the gradual decrease of interest in the industrial synthesis of higher alcohols from CO and $H_2$ compared to other processes such as, for example, those derived from oxosynthesis or from the aldolic condensations followed by hydrogenations.

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