CHAPTER 8

SYNTHESIS OF METHANOL

G. Natta

Institute of Industrial Chemistry, Polytechnic of Milan, Italy

INTRODUCTION

Among the main industrial organic reactions, the synthesis of methanol is an outstanding example of the practical importance of catalytic processes.

In 1924 methanol was produced almost exclusively by the destructive distillation of wood wastes. That year, the world production of CH_3OH was as low as 45,000 tons[74]. As a consequence of the development of the catalytic synthesis, production of methyl alcohol in the United States in 1953 exceeded 480,000 tons[27], matching that of ethyl alcohol.

While in the past the destructive distillation of 60 to 100 lbs of wood gave only about 1 lb of CH_3OH, with the synthetic process 1 lb of CH_3OH may be produced starting from CO and H_2, obtainable from the conversion of 315 grams of methane.

The large-scale synthesis of methanol was first carried out by Badische Anilin und Soda Fabrik (B.A.S.F.) which also developed the synthesis of ammonia on an industrial basis. The remarkable analogies between the synthesis of ammonia and that of methyl alcohol are shown in Table 1.

The experience in high-pressure operations, acquired previously in the synthesis of ammonia, has certainly contributed to the development of the methanol catalytic process. However, the synthesis of methyl alcohol had to overcome many more difficulties of a chemical nature.

In the synthesis of ammonia side reactions are not possible; molecular H_2 and N_2 can interact directly to give only ammonia. On the contrary, carbon monoxide reacts with hydrogen in many different ways; among the possible reactions, the synthesis of methyl alcohol is thermodynamically one of the least favorable. Methyl alcohol is formed only if certain selective catalysts are used, which are different from the typical hydrogenation catalysts. This synthesis is therefore representative of the importance of selective catalysts in directing a process in a definite way, and avoiding other reactions which would be preferred in the absence of highly selective catalysts.

This explains the fact that the methanol synthesis was developed in a relatively recent period, while other catalytic organic syntheses (i.e., that of methane) were found much earlier. From the historical point of view, however, the formation of methanol by high pressure synthesis was first reported by the Badische Anilin und Soda Fabrik② in its endeavors to produce liquid hydrocarbons from water gas, using as catalysts either mixtures of cobalt and osmium oxides with sodium hydroxide, or alkali treated iron oxide. Methyl alcohol was at that time present as a minor component among the products of the reaction, which were mainly hydrocarbons, alcohols, esthers, aldehydes, etc.

Only in 1923③ did B.A.S.F. find that methanol became the main product of the hydrogenation of carbon monoxide, when certain mixed catalysts containing ZnO and Cr_2O_3 were used, and when the reaction apparatus did not contain iron or iron alloys, which might react with CO to give iron pentacarbonyl. Similar results were reported by Schmidt and Ufer(67), who used a copper-base catalyst which also contained oxides of various metals

TABLE 1

	Synthesis of NH_3	Synthesis of CH_3OH
$\Delta F^\circ_{400°C}$ per mole of H_2	+4,000 kcal	+7,400 kcal
$\Delta H_{400°C}$ per mole of H_2	−8,530 kcal	−12,325 kcal
$\Delta H_{400°C}$ per mole of synthesis gas	−6,300 kcal	−8,200 kcal
Temperature of synthesis	400–500°C	300–450°C
Pressure range	100–1000 atm	100–500 atm
Number of gas moles reacting	4	3
Volume diminution (referred to 1 volume of reacted N_2 or CO)	2	2

In the years which followed a number of processes for the synthesis of methanol, based on the use of some particularly selective catalysts or on particular methods for the production of the water gas, have been developed in other European Countries (France, Italy, England) and in the United States.

The synthesis of methyl alcohol from carbon dioxide and hydrogen has also been successfully realized. This process was introduced in the United States by the Commercial Solvent Corporation[32], which had to overcome many difficulties. During World War II, the Lonza Company in Switzerland succeeded in the industrial realization of methanol synthesis from CO_2 and electrolytic hydrogen[47]. Carbon dioxide was a by-product of the process for producing $Ca(NO_3)_2$. Therefore, in order to be used in the synthesis of methyl alcohol, it had first to be purified from nitrous vapors and then partially reduced by coal to carbon monoxide. The same ZnO-base catalysts were used on this synthesis which had been developed in Italy by G. Natta for the synthesis of methanol from CO and H_2.

Nowadays, both in the United States and in Italy, the main starting material for the methanol synthesis is methane from natural gas, which is converted to $CO + H_2$ by partial combustion with oxygen or water.

THERMODYNAMIC CONSIDERATIONS*

As has already been pointed out, carbon monoxide and hydrogen may interact to give several different end products.

A thermodynamical approach to the equilibria related to all the possible reactions is quite useful in order to understand the reasons why the synthesis of methanol requires the use of highly selective catalysts and high pressures for its industrial realization.

The following reactions for the synthesis of methanol from carbon monoxide are of interest:

$$CO + 2H_2 \rightleftarrows CH_3OH \qquad \Delta H_{350°C} = -24{,}450 \quad \Delta F^\circ_{350°C} = +12{,}100 \tag{1}$$

Reaction (1) could be considered as divided into the two consecutive reactions:

$$CO + H_2 \rightleftarrows HCHO \qquad \Delta H_{350°C} = +5{,}050 \quad \Delta F^\circ_{350°C} = +16{,}100 \tag{2}$$

$$HCHO + H_2 \rightleftarrows CH_3OH \qquad \Delta H_{350°C} = -29{,}500 \quad \Delta F^\circ_{350°C} = -4{,}000 \tag{3}$$

The synthesis of methanol from carbon dioxide

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \qquad \Delta H_{350°C} = -15{,}335 \quad \Delta F^\circ_{350°C} = +15{,}800 \tag{4}$$

may be considered as a composite equilibrium, whose individual reactions are the conversion of CO_2 into CO

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad \Delta H_{350°C} = +9{,}115 \quad \Delta F^\circ_{350°C} = +3{,}700 \tag{5}$$

and the synthesis of methanol from carbon monoxide (Eq. 1). Reactions subsequent to that of Eq. (1) are:

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* The thermodynamical data considered in this paragraph are those published by Parks and Huffman[54], by Rossini and co-workers[63], and by Smith[71].

$$2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O \qquad \Delta H_{350°C} = -4{,}600 \qquad (6)$$

$$\Delta F°_{350°C} = -1{,}400$$

$$CH_3OH + nCO + 2nH_2 \rightleftarrows C_nH_{2n+1}CH_2OH + nH_2O \qquad (7)$$

$$CH_3OH + nCO + 2(n-1)H_2 \rightleftarrows C_nH_{2n+1}COOH + (n-1)H_2O \qquad (8)$$

These products may go through reactions of condensation, dehydration or ketonization, giving rise to the formation of olefins, esters, ketones, etc. The formation of these compounds may reach quite considerable values when alkali is contained in the methanol catalysts.

Reactions competitive to the synthesis of methanol are:

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \qquad \Delta H_{350°C} = -52{,}222 \qquad (9)$$

$$\Delta F°_{350°C} = -15{,}826$$

In practice the synthesis of methane, according to Eq. (9), is associated with the production of carbon dioxide, because the water vapor produced in reaction (9) participates in the water gas conversion reaction and converts a part of the carbon monoxide into dioxide. Accordingly, the reaction

$$2CO + 2H_2 \rightarrow CO_2 + CH_4 \qquad \Delta H_{350°C} = -61{,}337 \qquad (10)$$

$$\Delta F°_{350°C} = -19{,}526$$

which is reported in the old technical literature, must be regarded as derived from reactions (9) and (5).

Elementary carbon may also be formed, according to the reaction

$$2CO \rightarrow CO_2 + C \qquad \Delta H_{350°C} = -41{,}430 \qquad (11)$$

$$\Delta F°_{350°C} = -16{,}730$$

in the presence of metals of the eighth group.

The formation of hydrocarbons is also possible in the direct hydrogenation of carbon monoxide (Fischer-Tropsch synthesis):

$$nCO + 2nH_2 \rightarrow (CH_2)_n + nH_2O \qquad (12)$$

This reaction is not generally associated with the synthesis of methanol, because as a rule it takes place at considerably lower temperatures. However, substantial amounts of hydrocarbons are formed when thorium-containing catalysts are used in the temperature and pressure ranges of the synthesis of methanol.

Table 2 shows the dependence of the free energy of reaction on temperature for some typical reactions of hydrogenation of carbon monoxide. The ΔF° values for the synthesis of methanol are higher than those of the competitive reactions.

Although ΔF° of reaction (1), referred to standard conditions, is positive at temperatures >180°C, the synthesis of methyl alcohol is made possible by the use of high pressure, since this reaction is associated with a considerable volume contraction.

In the curve of Figure 1, the equilibrium constant K_{eq} of the methanol synthesis is plotted versus temperature. Whenever high pressures are used a correction has to be made for the non-ideal behavior of methyl alcohol. Figure 2 shows the values of the activity coefficient ratios, K_γ at different temperatures.

In practice the methanol synthesis is performed by operating at high space velocities and with low conversions at each cycle. This device helps to keep down the side reactions; on the other hand, CH_3OH concentrations are reached which are much lower than those corresponding to equilibrium.

Table 2. Free Energy of Reaction, ΔF° (kcal/mole)

T (°C)	27	127	227	327	427
$CO + 2H_2 \rightarrow CH_3OH$	−6.30	−0.80	+5.00	+10.80	+16.70
$2CO \rightarrow CO_2 + C$	−28.57	−24.31	−20.02	−15.73	−11.44
$CO + 3H_2 \rightarrow CH_4 + H_2O$	−33.87	−28.56	−23.01	−17.29	−11.44
$2CO + 2H_2 \rightarrow CH_4 + CO_2$	−40.67	−34.36	−27.87	−21.22	−14.49
$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O (n = 2)$	−27.23	−19.34	−11.10	−2.67	+5.90
$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O (n = 2)$	−51.32	−40.46	−29.18	−17.62	−5.87

Experimental data, obtained (under conditions very close to the equilibrium) at 350 to 380°C with gas mixtures containing an excess of hydrogen, show methanol concentration figures which are practically coincident with those predicted by thermodynamical calculations.

Catalysis in the Synthesis of Methanol

Classification of the Catalysts Used. The patent literature between 1920 and 1930 on catalysts for the production of methanol is somewhat chaotic. The catalysts listed in the patents of the B.A.S.F. cover complex mixtures of oxides or metals, including all the elements except those of the eighth group of the periodic system. Practically from the start all investigators discarded the iron group elements, which are active catalysts for the concurrent synthesis of methane.

In spite of the many papers describing the performance of the different

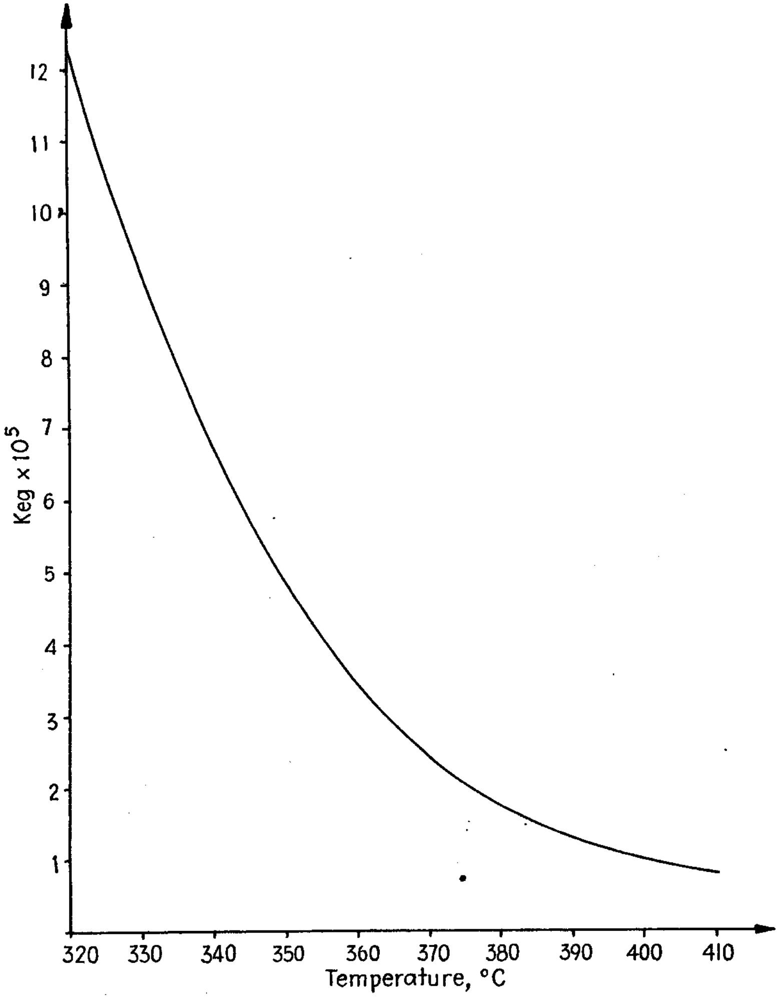

Figure 1. Equilibrium constant for the reaction $CO + 2H_2 \rightleftarrows CH_3OH$.

catalysts, it is practically impossible to relate the results of the different experimenters, because of the wide differences in the experimental methods which were followed; while some investigators studied the catalysis of the synthesis of methyl alcohol, most of the publications deal with studies of the catalysis of the decomposition of methanol. Now, particularly from the point of view of selectivity, there is lack of a satisfactory similarity between the catalytic activity in the reaction of synthesis and in that of decomposition of methyl alcohol. The activity of a catalyst in the decomposition of CH_3OH has often been measured from the total volume of gas produced, but some catalysts cause the formation of methyl formate, or formaldehyde, in addition to that of CO and H_2.

Catalysts made with the same precipitation method show activities which depend a great deal on the conditions of precipitation (i.e., excess or deficiency of the precipitating agent, temperature of calcination before use, and so forth). In spite of these circumstances, it is possible to make a qualitative comparison among the catalysts prepared according to different methods.

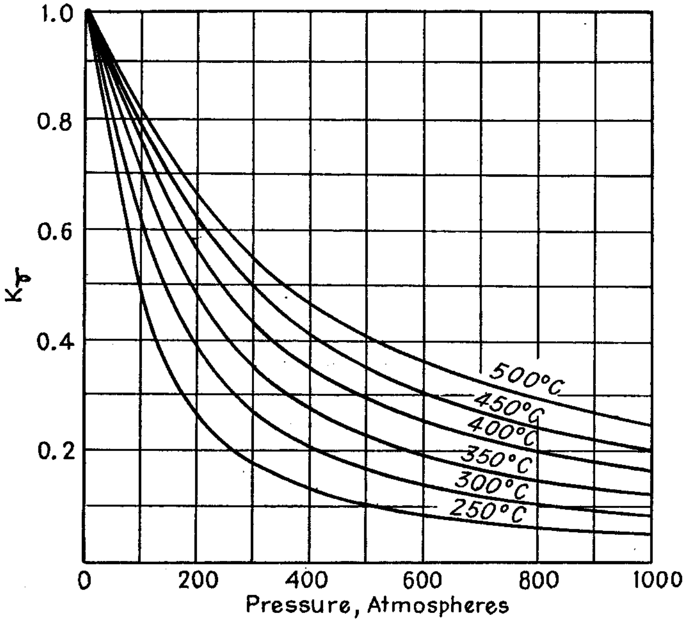

Figure 2. Values of $K\gamma$ for the reaction $CO + 2H_2 = CH_3OH$. Ewell, R. H., *Ind Eng. Chem.*, **32,** 152 (1949).

Among the various catalysts which have been proposed for the synthesis of methyl alcohol, only those containing ZnO or CuO have a real practical interest. The complexity in the composition of the majority of the catalysts listed in the various patents is somehow justified by the fact that the catalytic activity of pure ZnO or CuO is fairly low, while that of mixtures of these compounds with oxides of other metals is much higher and much more lasting.

In practice, the catalysts of industrial importance contain, beside ZnO, a promoter, in the form of a difficultly reducible oxide (i.e., Cr_2O_3). Several substances act as promoters, enhancing the catalytic activity of ZnO and

CuO. The German investigators who first studied this problem (Mittasch and co-workers) explained the high selectivity of mixed catalysts on a purely topochemical basis. As will be shown later, very active catalysts have been obtained with ZnO containing extremely small percentages of promoters of various kinds. These promoters have in common the property of being by themselves very poor hydrogenation catalysts, and of having high melting points; they also tend to prevent the aging (due to the growth of crystals) of the main catalytic agent.

In 1929–1930, G. Natta[40, 41] showed that very selective catalysts for the methanol synthesis may be obtained without the use of mixtures of metallic oxides. In fact, zinc carbonate (Smithsonite) heated at 350°C, gives a variety of zinc oxide, which is very active for the synthesis of methyl alcohol. The same investigator has obtained another very active variety of ZnO by the thermal decomposition of melted zinc acetate. The activity of such a catalyst is enhanced by the addition of a promoter. The next section is devoted to a detailed survey of the different types of catalysts which may be used for the synthesis of methanol.

Catalysts Containing Only One Metal Oxide

Preparation Methods and Activities of Zinc Oxide Catalysts.* Pure ZnO is not used at present for the industrial synthesis of methyl alcohol; however, this compound is considered as the most important component of the majority of the widely used mixed catalysts. Therefore the knowledge of the behavior of catalysts made with pure ZnO is of special interest for the interpretation of the mechanism of catalysis with mixed catalysts.

Zinc oxide is no doubt the most selective of all the catalysts for the synthesis of methyl alcohol. Certain forms of ZnO which are particularly active give pure methyl alcohol when used at temperatures lower than 380°C. Almost all these catalysts have the disadvantage of a rather short life.

In the technical literature several methods are given for the preparation of pure zinc oxide catalysts. Zinc oxide, when produced by the combustion of metallic zinc, is a very poor catalyst for the synthesis of methanol but is remarkably active in the decomposition reaction. Under the electron microscope, this catalyst appears to consist of trigonal star-like crystals.

The activity of ZnO catalyst obtained by calcination of precipitated zinc hydroxide seems to depend on the anion originally combined with

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* In this class those catalysts have been included, which consist of imperfectly crystallized zinc oxide. These catalysts are slightly reduced during their performance, and actually contain a deficiency of oxygen compared to the stoichiometric value for ZnO. Their very high catalytic activity is probably related to this imperfection of the crystalline lattice.

NO

the zinc. Starting from $ZnCl_2$ or $ZnSO_4$, one obtains catalysts that are considerably less active than those obtained from $Zn(NO_3)_2$. This, according to Hüttig and co-workers⑳ is due to the adsorption of traces of Cl^- or SO_4^{--} by the precipitate of $Zn(OH)_2$*.

TRIF.

Frolich and co-workers⑭ on the basis of their experience with copper catalysts advised precipitating all catalysts with NH_4OH rather than NaOH. They showed that the $Cu(OH)_2$ precipitated with NaOH is very active in the decomposition of methyl alcohol only if it is not previously washed free of its impurities. Purification of this precipitate by prolonged dialysis leads to a very poor catalyst. The catalyst prepared by precipitation with NH_4OH is not very active and its activity in the decomposition of methanol does not seem to be influenced by dialysis. The activity of catalysts containing traces of adsorbed NaOH decreases rapidly by heating them at temperatures above 300°C; this is probably related to the melting of the occluded sodium salts. The experiments dealing with the reaction of synthesis of methanol are not in agreement with those concerning its decomposition. In fact, the catalysts obtained by precipitation of $Cu(OH)_2$ with NaOH show lower activities and selectivities than those precipitated with NH_4OH.

Molstad and Dodge[38] operated with an ammonia-precipitated catalyst at a pressure of 178 atm. The conversions obtained by these authors with a gas ratio $CO:H_2 = 1:2$ and with space velocities of 25,000 are given in Figure 3. Similar results were obtained by several authors[5, 6, 15, 36], while other investigators[39] found much lower conversions with a similar catalyst.

Hüttig and Goerk tested a number of different catalysts in the decomposition of methyl alcohol[22]. They obtained the best results with catalysts prepared from the decomposition of complex zinc salts. Molstad and Dodge㊳ pointed out that the catalysts precipitated with Na_2CO_3 are more active than those precipitated with ammonia. This is in good agreement with the decomposition experiments performed by Ipatiev and Dolgov[28].

Table 3 shows some results obtained by Molstad and Dodge. It can be noticed that the best conversion is obtained by the use of a catalyst prepared with a slight deficiency of Na_2CO_3.

G. Natta[40] noticed a considerable decrease with time of the activity of a

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* $Zn(OH)_2$ is isomorphous with $Ni(OH)_2$. Schwab and Block[70] have recently observed that in the precipitation of $Ni(OH)_2$ from $NiCl_2$ solutions there are formed lamellar crystals grown regularly only in two directions (bidimensional crystals). The chloride ions are adsorbed on the surface of the planes composed of hydroxyl groups, thus hindering (because of their large size) the growth of the crystals along the z axis. It is possible that the chloride ions are adsorbed by the crystals through substitution of the hydroxyl ions located at the external lattice planes of the crystals. Possibly zinc hydroxide, whose crystals structure is similar to that of $Ni(OH)_2$, behaves in a similar manner.

catalyst prepared with precipitated basic zinc carbonate. The activity is reduced to one-third of the original value after only 10 hours of operation at 400°C. The same investigator has found that when ZnO is prepared by the thermal decomposition of melted zinc acetate (at 300 to 350°C) its activity is more prolonged. This thermal decomposition must be carried on in the absence of air. One then obtains a gray catalyst, the long life of which is probably due to the action of traces of elemental carbon, which prevents the recrystallization of ZnO.

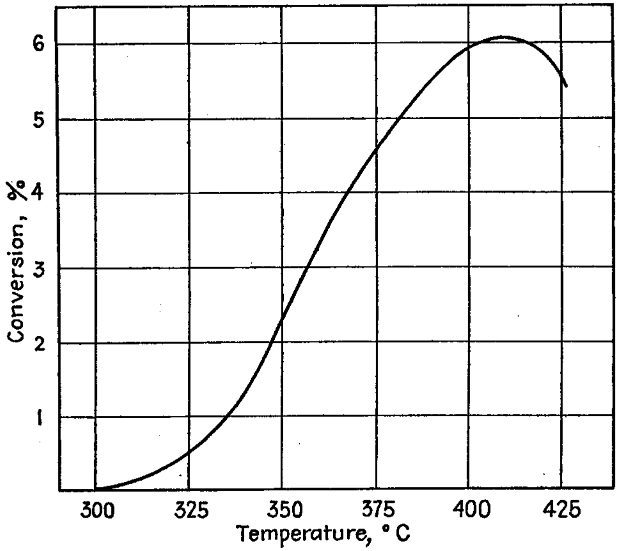

Figure 3. Synthesis of methanol from a 1:2 $CO:H_2$ mixture at a space velocity of 25,000 and a pressure of 178 atms[38].

Even more active and durable catalysts were obtained by the thermal decomposition of smithsonite (mineral $ZnCO_3$), whereas hydrozincite (basic zinc carbonate) gives a rather impermanent catalyst. The high activity of ZnO from smithsonite may be attributed to its high and uniform porosity, and its resistance to sintering. The higher activity of ZnO from smithsonite has been confirmed by the experiments of Kostelitz and Hensinger[35]. Zinc oxide obtained from smithsonite is not completely pure ZnO. It can generally be observed that the zinc minerals which give the most active catalysts contain, in the form of solid solution, small amounts of other divalent oxides (CdO, MgO, CuO) which are believed to behave as promoters. Whereas many varieties of ZnO go through a rapid aging, the zinc oxides obtained from acetate or from smithsonite are very durable, provided they are used below 390°C, and, more generally, at temperatures lower than that of their formation. Because of their stability, it was possible to study the action of these catalysts and to perform experiments at various temperatures, obtaining reproducible results. Thus Natta and Corradini[49] worked with two varieties of ZnO, one from a smithsonite of Val Brembana, Italy, and the other from zinc acetate. Figures 4 and 5 show the results of some of their experiments, in which the produced methanol had a high degree of purity (above 99 per cent). The two catalysts present similar values of the activation heat (27 kcal/mole for ZnO from smithsonite and 30 kcal/mole for ZnO from zinc acetate).

Table 3. Effect of the Precipitating Agent on Activity of ZnO Catalysts
(Gas composition 1 $CO:2\ H_2$; at 385°C and 178 atm.)

Catalyst Prepared from $Zn(OH)_2$ Precipitated by	Inlet Space Velocity	Conversion (%)
NH_4OH	92,000	3.0
NH_4OH	95,700	2.6
Na_2CO_3 excess	94,500	4.7
Na_2CO_3 insuff.	95,000	8.5
Na_2CO_3 excess	95,000	5.5

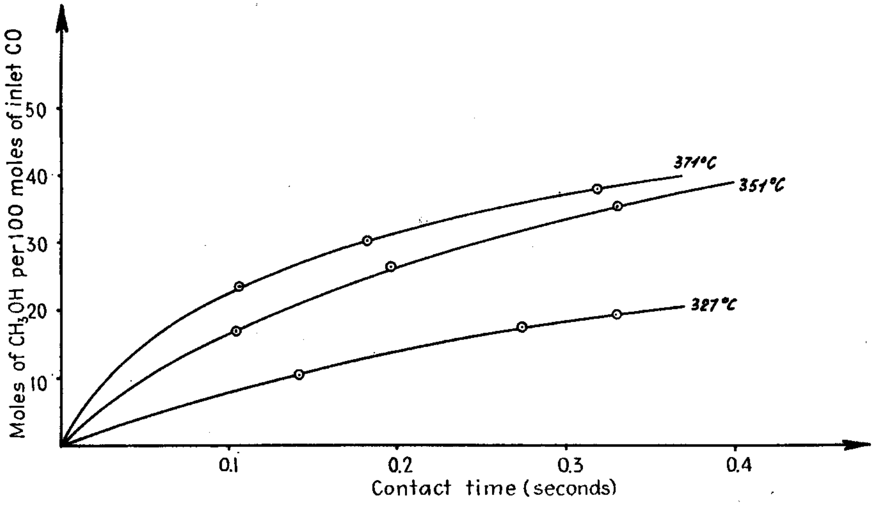

Figure 4. Moles of CH_3OH produced per 100 moles of inlet CO, as function of contact time at different temperatures with a ZnO catalyst from smithsonite. Pressure: 250 atm., inlet gas: $CO:H_2$ = 1:10. Contact time is defined as 3,600 times the ratio of the volume of the catalyst to the inlet volume of H_2—CO mixture per hour.

The data of Natta and Corradini should not be directly related with those of Molstad and Dodge[38], which are shown in Table 3. However, extrapolation of the data of Molstad and Dodge from 385 to 352°C, with the assumptions that the activation heat has a value of 30 kcal/mole and that for low conversions the amount of CH_3OH formed varies inversely with the space velocity, leads to the conclusion that among the different catalysts of Molstad and Dodge only the ZnO prepared from basic zinc carbonate, by precipitation with a slight deficiency of Na_2CO_3 yields initially an activity which is equal to that of ZnO from zinc acetate, if not to that of ZnO from smithsonite. The activity of the catalyst from basic carbonate, however, drops much more rapidly with aging than that of ZnO from smithsonite or from zinc acetate.

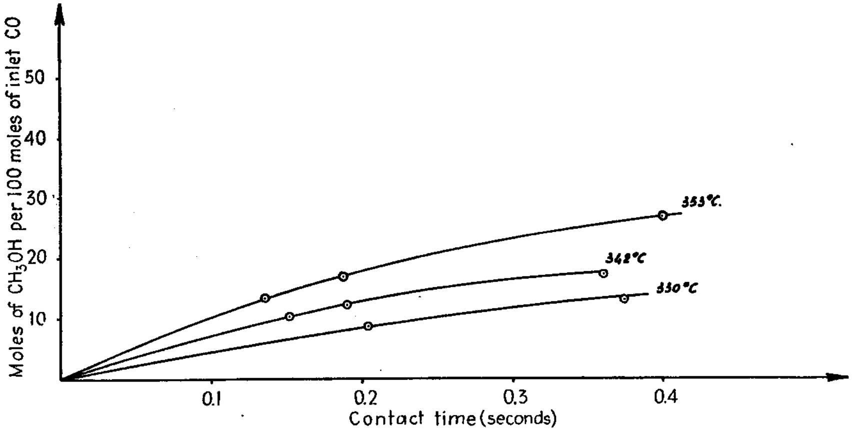

Figure 5. Moles of CH_3OH produced per 100 moles of inlet CO, as function of contact time at different temperatures, with a ZnO catalyst from zinc acetate. Pressure: 250 atm. Inlet gas: $CO:H_2 = 1:10$. Definition of contact time same as in legend of Figure 4.

Relationship between Activity and Crystal Size of Zinc Oxide. Several authors have established that the catalytic activity of ZnO obtained by the thermal decomposition of zinc compounds, is a function of the preparation temperature. The size of ZnO crystals increases with an increase in temperature, whereas the catalytic activity undergoes a corresponding decrease[29, 49]. It has to be pointed out that the catalytic activity is influenced much more by the crystalline size, than by the particle size (each particle being composed of a great number of individual crystals)[20].

Structural studies with X-rays and electron microscope observations by Natta and Corradini[49] have confirmed that the greater activity of some varieties of ZnO is due to the smaller crystalline size, and that the decrease of their activity is associated with an increase in the size of the individual crystals. As shown in Figures 10 and 11, the most durable catalysts show low variations in crystal size with time. Correspondingly, the activity of ZnO from zinc acetate is higher than ZnO from zinc nitrate, formate, or oxalate.

Table 4 shows some results of the X-ray examinations. A Geiger counter-recording type instrument was used, and the average crystalline size was calculated from the width of the diffraction bands.

The greater activity of ZnO from smithsonite appears to be associated with the smaller size of its crystals, the dimensions of which are not altered sensibly upon heating at 500°C. Similarly, the very low activity of ZnO from $Zn(NO_3)_2$ or from the combustion of metallic zinc should be considered as associated with the large crystal size.

TABLE 4

Method of Preparation of ZnO	Average Crystal Size (Å)
From zinc basic carbonate heated at 300°C	200
From zinc basic carbonate heated at 500°C	400
From zinc carbonate (smithsonite) heated at 350°C	100
From zinc carbonate (smithsonite) heated at 500°C	170
From zinc acetate, heated at 300°C	250
From zinc nitrate, heated at 500°C	>1000
From zinc formate, heated at 500°C	500
From zinc oxalate, heated at 500°C	500
From the combustion of metallic zinc	>1000

In the evaluation of the average crystal size of ZnO from zinc acetate there is an appreciable divergence between that obtained from electron microscopic examination and that calculated with the formula of Warren on the basis of X-ray diffraction measurements. The larger crystal size observed with the electron microscope may be justified by admitting that some of the biggest crystals observed should be regarded as aggregates rather than as individual crystals.

The gradual growth of the crystals of ZnO from zinc acetate, when heated with air at 500°C, can be followed by means of the electron microscope. Presumably the traces of elemental carbon present are eliminated by the calcination in air, and therefore crystallization can proceed much faster than in samples heated in the absence of air.

The variety of ZnO obtained from basic zinc carbonate (heated at 500°C) appears to consist of crystals which are very small and yet are in the visibility range of the electron microscope. The average crystal sizes of the zinc oxide from smithsonite and from basic carbonate (heated at 350°C) as calculated from X-ray measurements are in the range 100 to 200 Å; however, the individual crystals are not visible with the electron microscope (under a magnitude of 20,000).

Luminescence of ZnO. Schleede, Richter and Schmidt[66] have studied the luminescence of several varieties of ZnO, and have attempted to relate it to the catalytic activity of ZnO in the decomposition of methanol. ZnO obtained by the thermal decomposition of $Zn(NO_3)_2$ at 360°C presents an orange-red luminescence and does not act as a catalyst for the decomposition of CH_3OH at 360°C, while ZnO obtained by the decomposition of $Zn(OH)_2$ or $ZnCO_3$ is not luminescent and acts as a good catalyst.

Other investigators[69] have found no relationship between luminescence and catalytic activity of ZnO. Natta and Corradini[49] have pointed out that ZnO from basic zinc carbonate does not exhibit luminescence unless it was previously heated above 550°C. Whenever it is heated above 550°C, it exhibits a luminescence whose intensity grows with the heating temperature; meanwhile, its catalytic activity disappears. These investigators have also noticed that some other active forms of ZnO (for example, ZnO from basic zinc carbonate, or from smithsonite, or also from zinc oxalate) are not luminescent; this holds also for the most active mixed $ZnO\text{-}Cr_2O_3$ catalysts. On the contrary ZnO from nitrate, which is not very active, shows a fair luminescence. In other words, it seems that luminescence is characteristic of those varieties of ZnO which consist primarily of large crystals. With the exception of ZnO from acetate, which gives a greenish luminescence (and which consists of elongated, thin crystals), those varieties of ZnO which are good catalysts for the methanol synthesis are not luminescent.

Partially Reduced Copper Oxide. Although some mixed catalysts containing copper oxide are among the most active catalysts for the synthesis of methyl alcohol, pure copper oxide has a very weak catalytic activity. Copper oxide reduces itself rapidly to metallic copper, which then crystallizes readily. The crystals of metallic copper which are thus formed, according to the X-ray measurements performed by Natta and Corradini[49] appear to be of medium size (those which were brought to 350°C are as big as 500 Å). Reduced copper oxide gives a catalytic activity which depends very much upon the reduction temperature[3],(60). According to the experiments of Veltistova, Dolgov and Karpov(75) with a copper catalyst, methane, carbon, and about 10 to 15 per cent methanol are obtained.

Chromium Oxide. Almost all the different types of the more ~~of~~ or less hydrated chromium oxide are very poor catalysts for the synthesis of methyl alcohol. The highest activity in this group seems to be shown by the variety of Cr_2O_3 prepared by the decomposition, in an atmosphere of CO and H_2, of $Cr(OH)_3$, which in turn is obtained from solutions of $Cr(NO_3)_3$ and ammonia. Molstad and Dodge[38] have found that this catalyst has an activity which is considerably higher than that of the chromium oxide obtained by Lazier and Vaughen from chromium oxalate[37]. Figure 6, based on the experimental data of Molstad and Dodge, shows the dependence upon temperature of the conversion of CO, when pure Cr_2O_3 is used as a catalyst. A comparison of these conversion data with those obtained when ZnO is used as the catalyst, leads to the conclusion that Cr_2O_3 has an activation energy lower than that of ZnO.

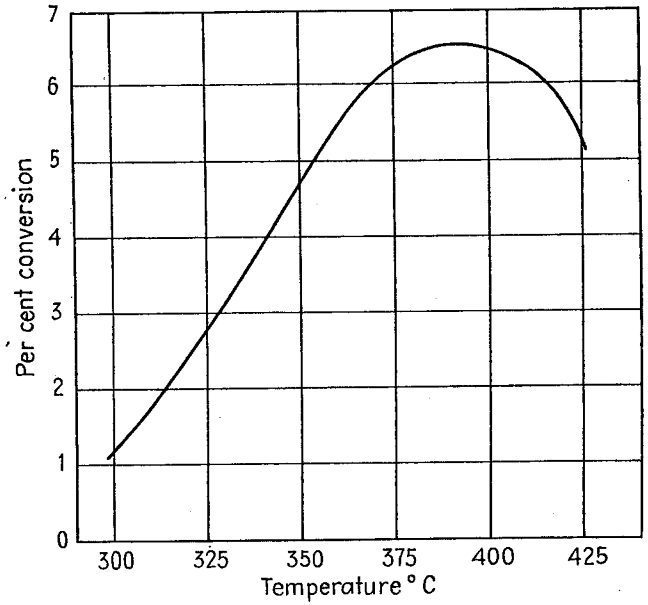

Figure 6. Percentage conversion of entering CO to methanol, under standard testing procedure at 178 atm., with a Cr_2O_3 catalyst[38].

The chromium oxide prepared by Molstad and Dodge has an activity, which is equivalent to that of the zinc oxide obtained from $Zn(NO_3)_2$ and ammonia. According to these investigators, the selectivity of their Cr_2O_3 is much higher than that of ZnO from $Zn(OH)_2$ precipitated with ammonia. The purity of methanol prepared over Cr_2O_3 is, however, not greater than that prepared over certain other ZnO catalysts (see, for example, Table 5).

The remarkable influence of the method of preparation of Cr_2O_3 on its catalytic activity for the methanol synthesis has been emphasized also by Hüttig(24), who has found that only a very few varieties of Cr_2O_3 (for example, that from $Cr(OH)_3$ obtained by treating $Cr(NO_3)_3$ with ammonia) possess a relatively high catalytic activity.

G. Natta[40] tested a chromium oxide catalyst, and found it to have a very poor activity. Lazier and Vaughen[37] found that their Cr_2O_3 catalysts showed a poor selectivity, but this may be due to the high working temperature (>400°C).

In conclusion all the catalysts made with Cr_2O_3, with the only exception of that prepared from $Cr(NO_3)_3$ and ammonia, show poor activities and low selectivities (see Table 6). Chromium oxide, however, has a considerable importance as a promoter of ZnO or CuO.

TABLE 5. PURITY OF SYNTHETIC METHANOL AS A FUNCTION OF THE TYPE CATALYST

Catalyst	% Methyl Alcohol in the Condensed Reaction Products	
	375°C	400°C
Chromium oxide from ammonia precipitated $Cr(OH)_3$ (Molstad and Dodge)[38]	96	91
Zinc oxide from ammonia-precipitated $Zn(OH)_2$ (Molstad and Dodge)	86	78
Zinc oxide from acetate (Natta)	99	97

TABLE 6. SYNTHESIS OF METHYL ALCOHOL WITH Cr_2O_3 AS CATALYST

Catalyst	Temperature (°C)	Pressure (Atm.)	Space Velocity	Yield in Raw Material cc. per hr. per 100 cc. Catalyst	Composition of raw product	
					Methanol %	Higher Alcohols (%)
Hydrated Cr_2O_3 gel	439	290	5,000	27.5	40	—
	440	290	10,000	36.0	60	—
	450	290	20,000	74.0	70	—
Cr_2O_3 from oxalate	375	280	10,000	43.0	41	—
	420	280	10,000	36.0	40	—
	450	280	10,000	39.0	34	23
Cr_2O_3 from $(NH_4)_3CrO_4$	425	280	10,000	14.0	48	7
	450	280	10,000	19.0	30	17
Chromium chromate	400	272	19,200	22.0	63	14
	448	272	19,000	26.0	49	22

Other metallic oxides, which have been proposed for the preparation of mixed catalysts (for example MnO, MgO, etc.) when used by themselves do not show any remarkable activity in the synthesis of methanol; therefore, they will not be considered in this section.

Mixed Catalysts

The catalysts of actual industrial importance for the synthesis of methyl alcohol are composed of mixtures of two or more oxides. In this treatment ZnO base and CuO base mixed catalysts are given separate attention.

ZnO Base Mixed Catalysts. All the varieties of pure ZnO (for example, that from smithsonite or that from zinc acetate), which were widely used in the past for their fairly good resistance to aging, have their activity increased upon addition of small amounts of promoters. The most widely used promoter is Cr_2O_3, which, as we have seen in the preceding paragraph, shows by itself a very limited catalytic activity and a low selectivity. Here promoters of ZnO will be considered as divided into two groups, namely intracrystalline and intercrystalline promoters, depending upon whether they are internal or external to the crystalline lattice of ZnO.

IMPORT.

Intracrystalline promoters include the oxides of those cations, whose ionic radius is in the range 0.6—0.9 Å, and hence very close to that of zinc oxide (0.75 Å); these oxides therefore may give rise to solid solutions with ZnO. Special care must be taken when a reducible oxide is used as a promoter. For example, G. Natta[40] has shown that solid solutions ZnO—FeO containing up to 12 to 13 per cent FeO are very active catalysts for the synthesis of methanol. These catalysts may be obtained by the thermal decomposition, in an atmosphere of hydrogen, of solid solutions of zinc and ferrous iron hydroxides or carbonates. This author points out that, if iron is initially present in the ferric form, or if the ferrous iron is not in solid solution with ZnO, it will go through reduction to metallic iron during the performance of the catalyst and it will thereafter catalyze the formation of methane.

Cadmium is often present as solid solute in smithsonite, and its presence was noticed in some particularly active catalysts obtained from smithsonite. During the performance of the catalyst, CdO is reduced to Cd, which has a relatively high vapor pressure, and may therefore be carried away by the reaction products. In the crystal lattice of ZnO a number of empty spaces are thus obtained, which appear to act favorably toward catalysis.

P. N 27

Also MgO, when present in solid solution is an efficient promoter of ZnO. Magnesium oxide has an extremely low solubility in the crystalline lattice of ZnO[40, 49]; on the contrary ZnO has a relatively high solid solubility (20 per cent by weight) in the lattice of MgO. The mixed catalysts ZnO—MgO are rather mixtures of ZnO with its saturated solid solution in MgO.

Intercrystalline promoters of ZnO include difficultly reducible, high melting oxides. These compounds, which by themselves show very low activities and selectivities for the synthesis of methanol, are widely used in industrial practice as promoters. The most important of them is chromium oxide, which deserves separate consideration.

Chromium oxide may be introduced in the catalyst in several different ways. The following are some of the simplest methods for obtaining good ZnO-Cr_2O_3 catalysts:

(1) The preparation of mechanical mixtures of zinc and chromium oxides does not lead to the production of very active catalysts if Cr_2O_3

is directly used. Veltistova and co-workers[75], however, claim that a mechanical mixture of ZnO and Cr_2O_3 is more active than other ZnO-Cr_2O_3 catalysts obtained by coprecipitation. Better results are obtained with the use of CrO_3, which appears to react more strongly with ZnO. The I. G. Farbenindustrie has used in its industrial operations[26] a catalyst prepared by mixing mechanically ZnO and Cr_2O_3. The grain density of such a catalyst has the value of 1.70–1.75.

(2) Adsorption of a solution of H_2CrO_4 by an active form of a pure ZnO catalyst leads to a surface corrosion of the crystals, with formation of $ZnCrO_4$ and of basic zinc chromate, which can be reduced to zinc chromite and to zinc oxide. Zinc chromite, $ZnO \cdot Cr_2O_3$, appears to act as an intercrystalline promoter: this may explain its property of preventing the recrystallization of ZnO in the temperature range of the industrial methanol synthesis. Very small quantities of H_2CrO_4 are often sufficient for improving at least the durability of ZnO. The treatment of ZnO with chromic acid has in general the effect of improving the catalytic activity of zinc oxide; however, care must be taken in adding the chromic acid, because an excess of H_2CrO_4 leads to an appreciable lowering of the quality of the produced methanol[72].

(3) Reduction, at low temperatures, of zinc chromate or zinc basic chromate, gives a mixture of zinc oxide and amorphous zinc chromite, which exhibits a high catalytic activity. Zinc chromite obtained by reducing zinc dichromate at low temperatures (<400°C) appears amorphous to X-rays, but has a low catalytic activity. This would indicate that zinc chromite is not a good catalyst for the synthesis of methanol, but rather a good promoter of ZnO.

(4) Calcination, at temperatures lower than 400°C, of coprecipitated zinc and chromium hydroxides or carbonates, leads to a mixture of zinc and chromium oxides, which contains some residual OH groups, and which (at the high percentages of Cr_2O_3) is completely amorphous to X-rays. Natta and Corradini[49] have noticed that a catalyst, composed of zinc and chromium oxides (Zn:Cr = 1:1) obtained by heating the corresponding carbonates at 300°C, gives only the diffraction lines of zinc chromite, with a line broadening effect due to the semi-amorphous condition of the catalyst. The diffraction lines of zinc chromite and zinc oxide appear in this catalyst, when the temperature is increased above 300°C (see Figure 7). Hüttig[21, 23, 25, 33], who studied the system ZnO-Cr_2O_3 by the determination of water adsorption, by magnetic susceptibility, by solubility, and through X-ray examinations, believes that there is a solid state reaction at 600°C with the formation of spinel. According to Kauffe and Pschera[18] the formation of spinel is related to the sublimation of the more volatile ZnO on the surface of Cr_2O_3. At high ratios of ZnO:Cr_2O_3, the diffraction lines of ZnO appear very clearly.

(5) Thermal decomposition of melted zinc acetate, containing small quantities of dissolved chromium acetate, according to Natta, gives a very good catalyst, which is more active than that obtained by the decomposition of pure zinc acetate. Similarly, the catalyst obtained by decomposition of a mixture of zinc and chromium acetates previously treated with chromic acid, is more active than the corresponding catalyst from pure zinc acetate treated with chromic acid. Figure 8 reports some reaction rate curves which were obtained with this type of catalyst. It has been pointed out that addition of Cr_2O_3 makes it possible to work in a temperature range, at which pure ZnO would lose its activity very easily[37]. All the ZnO-Cr_2O_3 mixed catalysts present a high resistance to "aging."

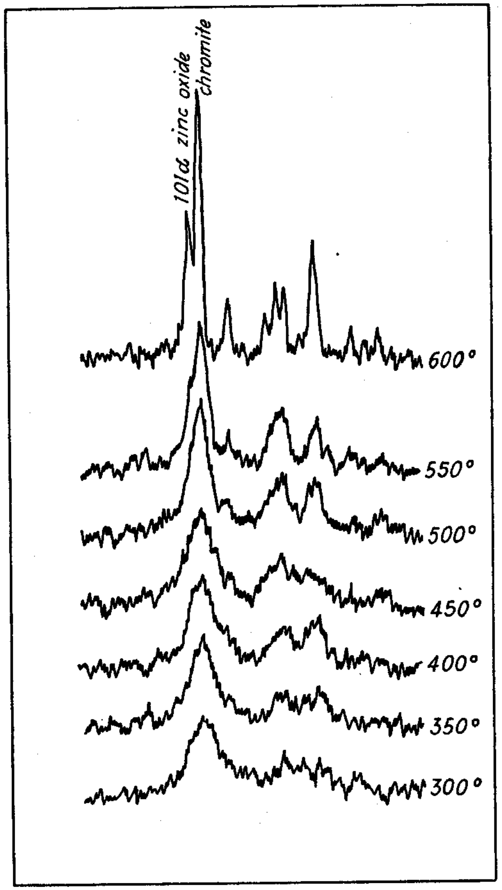

Figure 7. Development of pattern of ZnO and zinc chromite on heating a 1:1 ZnO:Cr_2O_3 catalyst[49].

Relationship between Cr_2O_3 Concentration and Activity of ZnO-

Cr_2O_3 Mixed Catalysts. There are several different opinions among the various investigators concerning the influence of chemical composition upon the catalytic activity of this class of catalysts. It has to be realized that, from a practical point of view, a catalyst should possess high activity, good resistance toward aging, and high selectivity. For evaluating the over-all influence of the promoter's concentration upon the catalyst's performance, it should be observed that the resistance of a ZnO catalyst toward aging varies directly with concentration of Cr_2O_3, while beyond a definite 2.) Cr_2O_3 concentration limit, the selectivity of a ZnO catalyst at a defined temperature appears to vary inversely with the concentration of the promoter. It is important to point out that some very active catalysts require considerably lower working temperatures, and thus generally work under conditions of relatively higher selectivity.

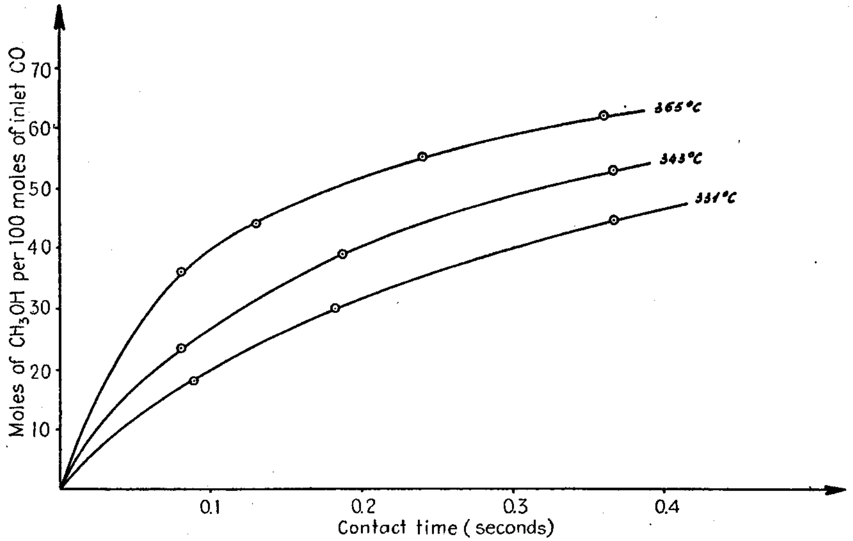

Figure 8. Moles of CH_3OH produced per 100 moles of inlet CO, as a function of contact time (see Figure 4 legend for definition of contact time) at different temperatures, with a $ZnO:Cr_2O_3$ catalyst prepared from a mixture of the acetates treated with chromic acid. Pressure: 250 atm. Inlet gas: $CO:H_2 = 1:10$.

As far as activity is concerned, the optimum composition depends on the catalyst preparation method. The optimum percentage of Cr_2O_3 is lower if this compound is used as promoter of some active ZnO catalysts, whose minute crystals are stabilized by a surface coating of chromium oxide or of zinc chromite. In the case of a real coprecipitation of zinc and chromium hydroxides or basic carbonates, the most active catalysts are those with higher perentages of chromium.

Extensive work on $ZnO\text{-}Cr_2O_3$ catalysts, obtained by precipitation of the hydroxides with ammonia from the solutions of the nitrates has been carried on by Molstad and Dodge[38].

Figure 9 shows the variation of the CO conversion to methanol with the catalyst composition, according to the experimental data of Molstad and Dodge[38]. It appears evident that the highest conversions are obtained with catalysts containing 20 to 30 per cent of chromium oxide. According to Molstad and Dodge, who studied also the effect of aging, the catalysts containing less than 25 per cent Cr_2O_3 lose their activity rapidly, while on the contrary, the catalysts containing more than 25 per cent Cr_2O_3 seem to present an activity that increases as time goes on. The catalysts with high percentages of Cr_2O_3 show a shrinkage which varies directly with the percentages of chromium. One of the best catalysts, $Zn_{58}Cr_{42}$ exhibits a shrinkage of 53 per cent after its regular performance. With the use of "preshrunk" catalysts, it has been noticed that the highest activity is given by catalysts with very high chromium contents.

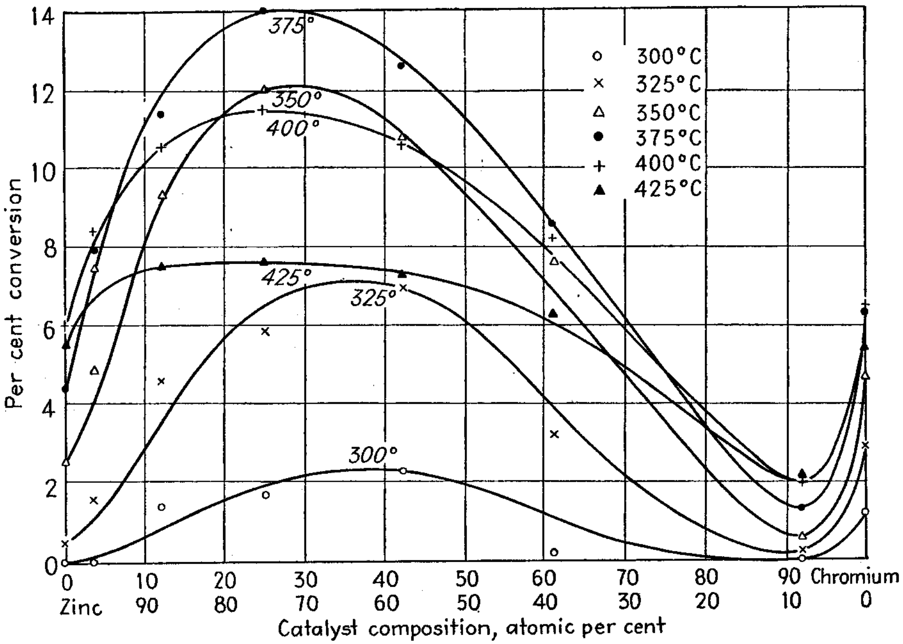

Figure 9. Percentage conversion of entering carbon monoxide to methanol during standard testing procedure at 178 atm[38].

Table 7 gives the conversion values for some catalysts with high chromium contents. The maximum conversions are obtained with catalysts whose Zn/Cr ratio is equal approximately to one.

The catalysts in which chromium was present in amounts insufficient for the formation of spinel are formed after a run, made up of crystals of ZnO, the sizes of which vary inversely with the percentage of chromium oxide present. Table 8 shows the result of crystal size determination of ZnO-Cr_2O_3 catalysts performed by Natta and Corradini by the X-ray diffraction method.

TABLE 7. VARIATION OF CONVERSION WITH CATALYST COMPOSITION FOR PRESHRUNK CATALYSTS* [38]

Composition	Temperature (°C) at which maximum Conversion Occurs	Inlet Space Velocity	Per cent Conversion
$Zn_{59}Cr_{41}$	320	25,000	24.4
$Zn_{58}Cr_{42}$	340	29,000	25.2
$Zn_{46}Cr_{54}$	340	30,000	26.4
$Zn_{45}Cr_{55}$	300	33,000	26.9
$Zn_{40}Cr_{60}$	300	25,000	21.8
$Zn_{35}Cr_{65}$	320	25,000	17.8
$Zn_{26}Cr_{74}$	340	25,000	7.4

* The temperature data reported in this table should be considered strictly on a comparative basis. The type of apparatus used, and the high conversion values, made it impossible to keep the temperature constant. The local temperature in certain zones of the catalyst's space reached values considereably higher than the indicated ones.

TABLE 8. PARTICLE SIZE OF PREHEATED CATALYSTS FROM PRECIPITATED BASIC ZINC AND CHROMIUM CARBONATES

Preheating temperature: 400°C

	Average Crystal Size in Å after a Heating Period of		
	2 hr	6 hr	15 hr
Pure ZnO	250 Å	300 Å	350 Å
Zn:Cr = 10:1	130	150	170
Zn:Cr = 5:1	110	150	170

The same authors have also studied the growth of the ZnO crystals, provoked by prolonged heating at definite temperatures. Figures 10 and 11 show clearly that ZnO from carbonate is less resistance to aging than ZnO from smithsonite, or than catalysts containing ZnO + Cr_2O_3.

In spite of the lack of data in the technical literature, the methanol industry is now successfully using some very active and resistant catalysts, which contain Cr_2O_3 in concentrations lower than those which were classified as "optimum." These catalysts present the advantage of being very selective: for example, a catalyst of Montecatini Chemical Co., containing 11 per cent by weight of chromium oxide, examined by Natta and coworkers[50] produced, at 375°C, a raw methyl alcohol of high purity (per cent methanol >99).

The activation energy of such a catalyst is about 30 kcal/mole, equal to that of pure ZnO. This seems to corroborate the hypothesis that the promoting action of Cr_2O_3 is mainly due to its hindering action upon the recrystallization of ZnO.

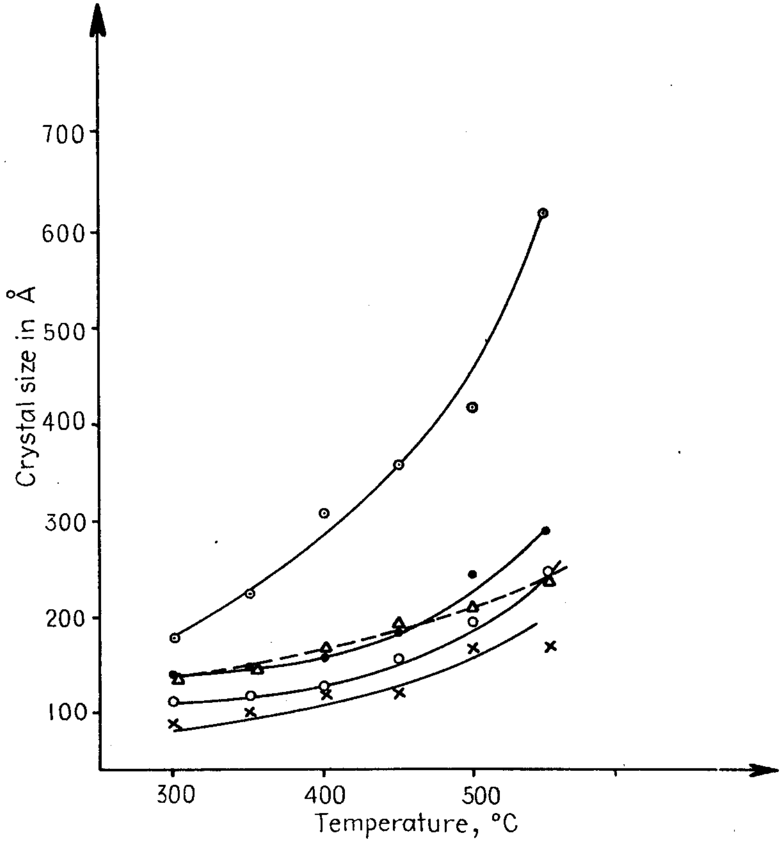

Figure 10. Growth of ZnO crystals in various catalyst preparations: ×, Smithsonite; ○, hydrozincite; △, basic zinc and chromium carbonates (Zn:Cr = 5:1); ●, basic zinc and chromium carbonates (Zn:Cr = 10:1); and ⊙, basic zinc carbonate[49].

Other Promoters of ZnO

In spite of the abundance of patents which claim the use of many promoters of ZnO besides Cr_2O_3, the available experimental data are extremely scarce. Aluminum oxide has an action, which is somewhat similar to that of a) Cr_2O_3. Al_2O_3 may combine with ZnO to give a spinel, $ZnO\cdot Al_2O_3$[8], which may be also obtained by calcination of the coprecipitated basic carbonates. However, Al_2O_3 seems to be far less efficient as a promoter than Cr_2O_3.

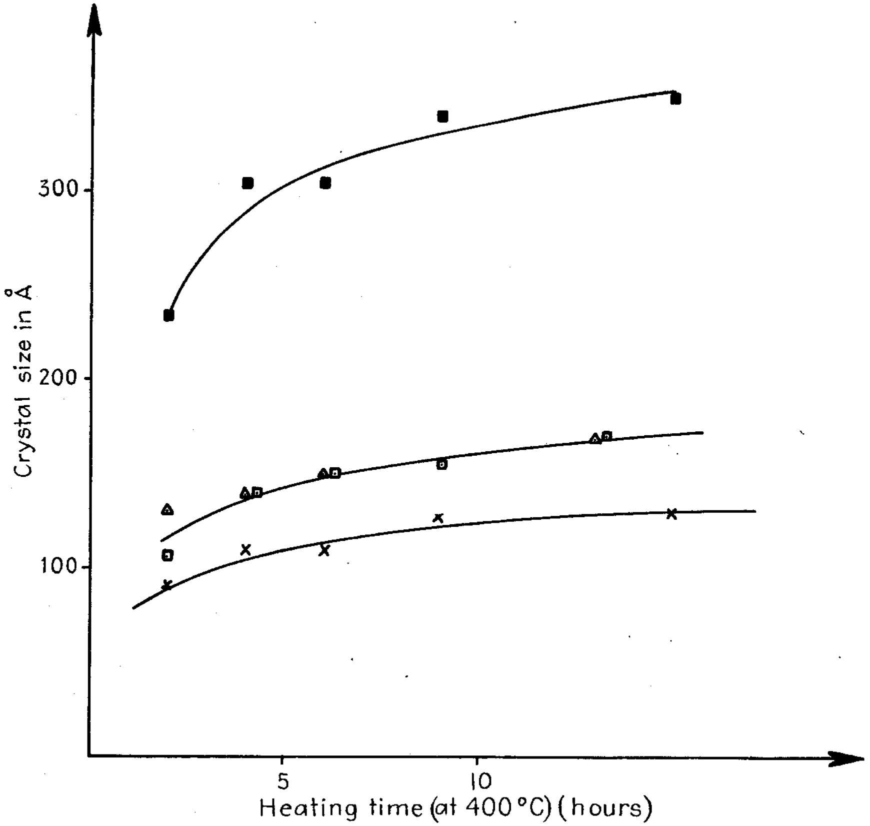

Figure 11. Growth of ZnO crystals as a function of heating time at 400°C: ×, Smithsonite; △, basic zinc and chromium carbonates (Zn:Cr = 5:1); ⊡, basic zinc and chromium carbonates (Zn:Cr = 10:1); and ■, basic zinc carbonate[49].

It has also been observed that Al_2O_3 favors the dehydration reaction of CH_3OH to give $(CH_3)_2O$; therefore $ZnO\text{-}Al_2O_3$ catalysts have had no practical interest.

b) Weltistowa and co-workers[75] claimed that ThO_2, when added in amounts of the order of 1 per cent to $Al_2O_3\text{-}Cr_2O_3$ catalysts, causes a yield increase of 50 per cent, provided pure gases are used; with technical gases, the authors reported no apparent improvement of yield. The results of Weltistowa were corroborated by Dolgov and Karpinski[9] who used successc) fully small quantities of ThO_2, ZrO_2 and TaO_2 as promoters of a $ZnO\text{-}Cr_2O_3$ catalyst. According to Veltistova[75], vanadium oxide (V_2O_5) acts as an activating agent, by increasing considerably the yield of methyl alcohol when used in concentrations of the order of 1 per cent. Several other non-reducible oxides have been proposed, but comparative data concerning their behavior as promoters are missing.

Copper-containing Catalysts

While in the old scientific literature certain catalysts containing ZnO, CuO, Cr_2O_3 are considered very active for the synthesis of methyl alcohol, these catalysts have had only slight practical interest owing to their poor resistance to aging, and to their high sensitivity to poisons. These copper-containing catalysts were not considered in the discussion concerning $ZnO\text{-}Cr_2O_3$ catalysts, because copper oxide behaves in a manner which is different from that of Cr_2O_3, which acts mainly by hindering the recrystallization of ZnO, and which does not bring about any variation of the activation heats of the catalysts. The catalysts composed of CuO and ZnO have activation energies lower than those of the corresponding ZnO catalysts, even in the presence of chromium oxide. The catalysts containing ZnO and CuO are examples of mutual promoting action (Wechselverstärker). Kostelitz and Hüttig[34] have observed that in the decomposition reaction of methanol all the mixed catalysts CuO-ZnO exhibit activities higher than those of each of the two oxides, separately. Also certain mixed catalysts containing CuO, but without ZnO (for example, $Cr_2O_3\text{-}CuO$ catalysts) have a good activity for the synthesis of methanol; their activity increases considerably when ZnO is present.

Pure cupric oxide is practically inactive for the synthesis of methyl alcohol, but small amounts of promoters are sufficient for raising its activity to relatively high values. Tagashi Eguchi[10] has activated CuO by the addition of traces of alkali. (See p. 357.) This investigator obtained conversions of the order of 20 to 30 per cent operating at 230° and 80 to 100 atmospheres, with an inlet space velocity of 10,000. Methanol production was in the range 1.3 to 2.8 pounds per hour per liter of catalyst. With different CuO-base catalysts the same author has obtained conversions as high as 70 per cent. Patart[16] had shown in a previous work that very good conversions in the synthesis (or in the decomposition) of methanol were obtained using a CuO catalyst containing 10 per cent ZnO. While the experiments of Fleury[12] confirmed Patart's conclusions on the behavior of the mixed copper-zinc catalysts, Frolich and co-workers[15, 16, 17] found that the most efficient catalysts contain 30–40 per cent CuO. Nussbaum and Frolich[53] worked with a catalyst of the composition 58.3 per cent ZnO, 41.7 per cent

CuO. The catalytic activity in the decomposition of methanol seems to vary directly with temperature of reduction up to a certain temperature limit, after which it drops rapidly. The concentration of carbon monoxide in the decomposition products follows exactly the catalytic activity, while the concentration of formaldehyde in the same decomposition products varies inversely with the activity of the catalyst. The catalyst's activity decreases when the reduction time is prolonged.

Cupric oxide is progressively reduced to Cu, and in the meantime a small amount of ZnO is also reduced to metallic zinc, which forms a solid solution with Cu. X-ray analysis gave for the side of the elementary cell the value of 3.624 Å (correspondent to a brass containing 13 per cent Zn). Zolotov and Shapiro[76] noticed that complete reduction of CuO and partial reduction of ZnO occurred only at temperatures higher than 220°C.

Ternary Catalysts Cu-ZnO-Cr_2O_3. According to Fenske and Frolich⑪ the catalyst $Cu_{49}Zn_{43}Cr_8$ is more active than all the binary catalysts ZnO-Cr_2O_3 or ZnO-CuO. At 220°C, this catalyst decomposes methyl alcohol to the extent of 90 per cent. In the synthesis, at 322°C and 200 atm., equilibrium is easily reached even with much higher space velocities. The catalysts ZnO-CuO-Al_2O_3 have a lower activity and are not as resistant as ZnO-CuO-Cr_2O_3 catalysts.

Frolich and Lewis[13] have worked with a catalyst of the composition:

$$(ZnO)_{36}(CuO)_{44}(Al_2O_3)_{20},$$

precipitated from a mixture of the acetates with ammonia, using a copper support. This catalyst, at 300 to 350°C and 204 atm. gives pure methyl alcohol, with negligible side reactions. It should be noticed that Al_2O_3, which does not act as a good promoter of ZnO, has a very good promoting effect upon copper. One should be careful, with Al_2O_3-containing catalysts, not to work at too high temperatures, because of the dehydrating action of Al_2O_3 on methanol.

According to Ivanov[30, 31] and to Plotnikov[57-59] the activity of copper oxide-base catalysts is affected only to a limited extent by the addition of ZnO, while it increases considerably upon addition of Cr_2O_3. The best catalysts used in experiments by these authors have the composition

$$Cu_{82}(ZnO)_{16}(Cr_2O_3)_2 \quad \text{and} \quad Cu_{60}(ZnO)_{35.6}(Cr_2O_3)_{4.4}$$

Similarly, Dolgov[8] gives the following compositions for the best of his catalysts:

$$Cu_{49}Zn_{43}Cr_8 \quad \text{and} \quad Cu_{50}Zn_{40}Bi_{10}$$

This investigator had obtained with the above catalysts yields of 86 to 87 per cent and 75 per cent at 360 to 400°C and 100 to 150 atm.

Ivanov[30, 31] prepared his catalysts by precipitation, and reduction of the dry precipitates in an atmosphere of hydrogen at 200 to 220°C. X-ray examination indicates that the primary function of Cr_2O_3 is to prevent the reduction of a small portion of the CuO; the existing active centers are thus attributed to Cu-CuO interfaces. During the catalyst's performance Zn and Cu form the α phase of brass, with an increase of the lattice constant of Cu, and with a consequent decrease in the catalytic activity.

Pospekhov(61) has observed a high initial activity, even at temperatures as low as 190 to 230°C and at pressures of the order of 100 atm., in a catalyst of the composition: $Cu_{60}(ZnO)_{35.6}(Cr_2O_3)_{4.4}$. This catalyst is reduced at a space velocity of 80,000 and at an initial temperature of about 200°C; it becomes very active, giving rise to a complex mixture of CH_3OH, water, and oxygenated compounds. The activity of this catalyst decreases with time, and at low space velocities (13,000 to 20,000) there is formation of CO_2 and CH_4. It is practically impossible to relate all the data of the technical literature on this matter, because of the wide differences in the operating conditions of the various investigators. The temperature data in particular are not very reliable, because of the carelessness in avoiding local overheating due to the reaction heat.

Natta and his co-workers(51) have recently studied the behavior of several catalysts containing Cu-Cr_2O_3 and Cu-ZnO-Cr_2O_3, obtained by the thermal decomposition of the acetates. Their apparatus was especially designed to give over the entire length of the catalyst a temperature that was constant to 1°C; therefore, it was not too difficult to obtain good comparable results. The catalysts examined by these investigators showed a good initial activity, which then decreased with time. For example, the catalyst Zn:Cu:Cr = 6:3:1 showed at 320°C a very high activity; after 72 hours of performance its activity was reduced by 40 per cent. A copper chromite catalyst, obtained by the thermal decomposition of copper and ammonium chromate (precipitated from a copper nitrate solution) has an activity which is lower than that of other catalysts containing ZnO and Cr_2O_3. The high resistance to the aging of this catalyst has to be attributed to the high concentration of Cr_2O_3. In Figure 12 the aging curves of three different catalysts listed by Natta and co-workers are shown.

Under X-ray examination, the reduced catalyst shows the lines of copper, and their intensity increases with time. With such low working temperatures the authors did not notice the formation of brass which had been noticed by other investigators[17], who probably have worked at higher local temperatures. The average crystal size of the copper crystals is 400 to 500 Å after about 100 hours of performance. The average size of the crystals of ZnO increases also, from 300 Å to about 350 Å.

If the catalysts are submitted to "aging" by prolonged heating at 330°C in an atmosphere of CO and H_2, they are sufficiently stabilized to make kinetic measurements possible at temperatures lower than 330°C.

In Figures 13 and 14 the results of such kinetic determinations are given for the copper chromite catalyst and for the catalyst Cu:Cr:Zn = 1:1:8. Such catalysts showed the following values for the apparent activation energy: Copper chromite, activation energy at 292 to 326°C of 14 kcal per mol; Copper-chromium-zinc catalyst (1:1:8) activation energy at 307 to 325°C) of 17 kcal per mol.

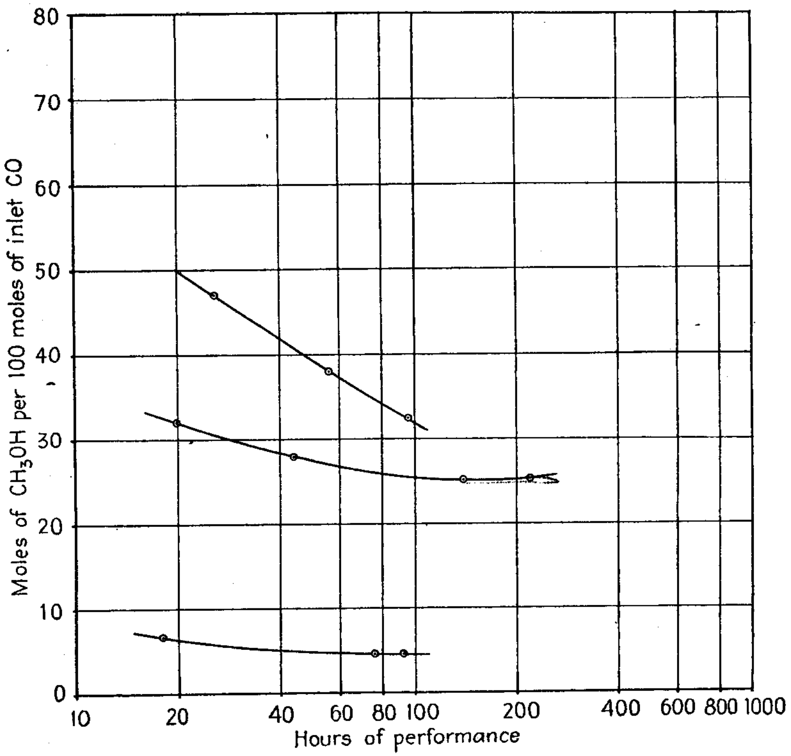

Figure 12. Aging runs on Zn–Cu–Cr methanol synthesis catalysts. Time of contact 0.1 sec for each run. Top curve is for a catalyst of the composition Zn:Cu:Cr = 6:3:1 and an operating temperature of 321°C; middle curve, Zn:Cu:Cr = 8:1:1 and temperature, 325°C; bottom curve, copper chromite and temperature, 292.5°C.

From the reaction isotherms of Figure 15, obtained with the catalyst Zn:Cu:Cr = 6:3:1, which had previously worked for 70 hours at higher temperatures (320 to 350°C), a value of 18 kcal per mol has been calculated for the activation energy in the temperature range 276 to 321°C.

From a practical point of view, the use of copper-containing catalysts which show high activities at temperatures lower than 300°C (at which the ZnO-Cr_2O_3 catalysts do not give any appreciable activity), is advisable only when any overheating (due to the reaction heat) which would rapidly reduce the activity of the catalyst, is avoided.

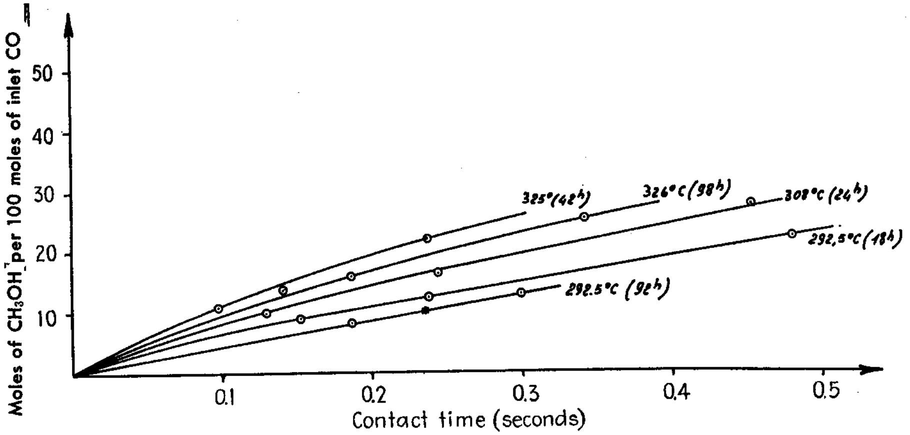

Figure 13. Moles of methanol produced per 100 moles of inlet CO, as function of contact time at different temperatures, with a copper chromite catalyst. Pressure: 250 atm. Inlet gas: CO:H_2 = 1:10. See legend of Figure 4 for definition of time of contact.

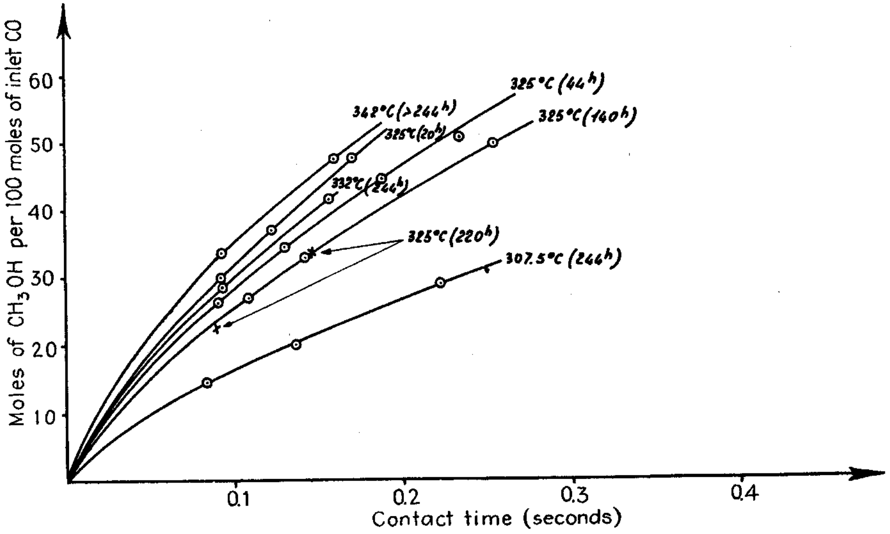

Figure 14. Moles of methanol produced per 100 moles of inlet CO as a function of contact time at different temperatures with a catalyst ZnO:CuO:Cr_2O_3 = 8:1:1. Pressure = 250 atm. Inlet Gas: CO:H_2 = 1:10. See Legend of Figure 4 for definition of time of contact.

ANTISELECTIVITY AGENTS AND POISONS

Antiselectivity Agents

The synthesis of methanol is greatly influenced by the presence of certain substances, even at low concentrations. For example, the presence of metallic iron or nickel in the catalyst leads to the formation of methane while the presence of strongly alkaline substances inhibits the formation of methane and synthesizes the higher alcohols. For this specific action on the selectivity of the catalysts, it would be erroneous to consider these compounds as real poisons, because a poison is a substance which, when adsorbed at the active surface of a catalyst, inhibits the activity of the catalyst itself. Iron and nickel when present in very low concentrations do not inhibit the activity of zinc oxide, but behave rather as independent catalysts for a concomitant reaction, the synthesis of methane, which is thermodynamically more favorable and kinetically faster than the synthesis of methyl alcohol. Therefore these metals should be named "antiselectivity agents," rather than "poisons." Traces of finely divided Fe or Ni in the catalyst are sufficient to cause the formation of a large quantity of methane. The synthesis of CH_4 is strongly exothermal and, when performed in the presence of Ni or Fe, proceeds very rapidly; therefore, local temperatures, high enough (600 to 700°C) to prevent the formation of methanol are easily reached. A considerable diminution of the yield of methyl alcohol is due also to the lowering of the partial vapor pressure of CO and H_2, caused by the formation of CH_4, H_2O, and CO_2. The formation of water causes the lower concentration of the methanol obtained. When the reaction is performed with gases rich in CO and poor in H_2 (for example, with water gas) a small part of the carbon monoxide is disproportioned to give elemental carbon and carbon dioxide.

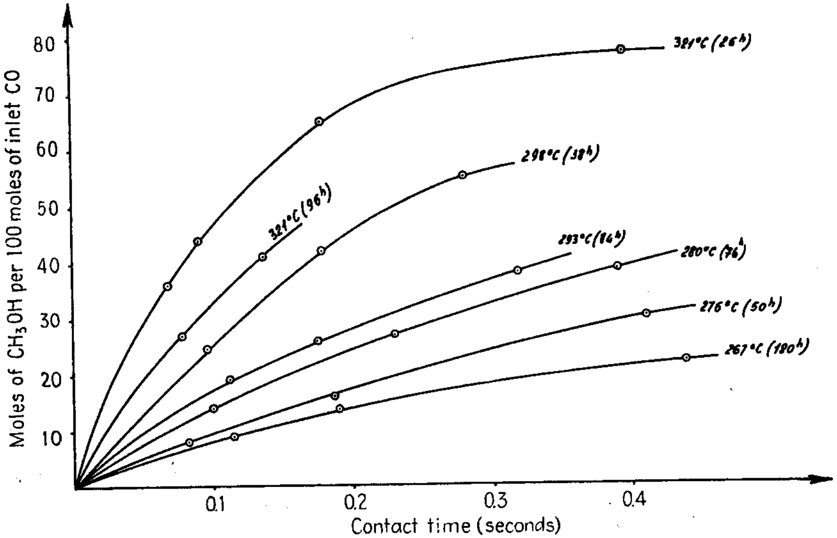

Figure 15. Moles of CH_3OH produced per 100 moles of inlet CO as a function of contact time at different temperatures. Pressure 250 atm. Inlet Gas: $CO:H_2 = 1:10$. The experiments were performed with a catalyst $ZnO:CuO:Cr_2O_3 = 6:3:1$. Time of contact is as defined in Figure 4.

The rate of the synthesis of methane is very high only at temperatures higher than 400°C; therefore when the reaction is carried out at lower temperatures (350 to 370°C) small amounts of iron in the catalyst may be allowed, particularly when iron is present as ferrous oxide (which may be dissolved in ZnO) or as ferric oxide (combined with ZnO as spinel $ZnO—Fe_2O_3$).

The most active forms of metallic iron or nickel in the catalysis of the synthesis of methane are those obtained by the thermal decomposition of iron or nickel carbonyls,[62] $Fe(CO)_5$, $Ni(CO)_4$, etc., which may be accidentally present in the reacting gases. For this reason the early patents of the Badische Anilin und Soda Fabrik claim that for the synthesis of methyl alcohol gases should be used free from carbonyl iron, and catalysts free from metals belonging to the iron group. In order to avoid the formation of iron or nickel carbonyls no iron or nickel-base apparatus which might react with CO is being used for the synthesis of methanol.

Natta[40] showed that when FeO is present in relatively high amounts, as solid solution in ZnO, it behaves as a promoter for the synthesis of methanol, without causing the formation of appreciable amounts of methane, which would take place if iron were present as free iron oxide or in the metallic state. Such solid solutions are greenish and ferrous iron is not reduced to the metallic state, if the working temperatures are not too high.

Natta observed that catalysts containing traces of iron (which may be present as impurity in the mineral smithsonite) transfer it to the circulating gases (as carbonyl iron) during the synthesis, provided these gases are initially free of carbonyl iron. After a period of performance at temperatures lower than 400°C, the iron originally present in the catalysts is almost entirely gone, so that eventually the produced methanol has a higher degree of purity and it contains less water than the methyl alcohol produced with fresh catalyst.

The reaction of formation of carbonyl iron is an equilibrium process:

$$Fe + 5CO \rightleftarrows Fe(CO)_5$$

Therefore the percentages of iron which may be present in the gases without damaging the synthesis of methanol depend on the partial pressure of CO, on total pressure, and (even more strongly) on temperature.

The data of Table 9 were calculated[46] with the assumption that the activity is equal to the partial pressure of each reacting gas; this assumption, however, does not hold for iron carbonyl, the critical temperature of which is relatively high; therefore, the above data should be considered as approximate, and probably lower than the real ones.

A catalyst, whose selectivity has been reduced as a consequence of the deposition at its surface of iron (or nickel) carbonyl coming from the reacting gases, may recover its original selectivity, provided it is used at lower temperatures with gases free from $Fe(CO)_5$ or $Ni(CO)_4$.

Some strongly alkaline substances ($NaOH$, Na_2CO_3, $Ca(OH)_2$, etc.), behave as antiselectivity agents, provoking the formation of higher alcohols. These substances are often present in methanol catalysts prepared by precipitation from zinc salts, and not previously washed carefully. When these compounds are present in the catalyst there is a decrease of activity with time, because of the formation of high molecular weight organic compounds which remain adsorbed in the catalysts.

TABLE 9. EQUILIBRIUM OF THE REACTION $Fe + 5CO = Fe(CO)_5$

Temp. (°C)	$\log K_p = \log \frac{(CO)^5}{Fe(CO)_5}$	Equilibrium Concentration of $Fe(CO)_5$ (g $Fe(CO)_5$ per Cubic Meter of Total gas at a CO Pressure of 100 Atm.)*
250	10.67	18.7
300	12.37	3.7
350	13.81	.01
400	15.12	.007

* These figures are the grams of $Fe(CO)_5$ per cubic meter of gas at 0°C and one atmosphere pressure.

Alkalies act also as inhibitors of the synthesis of methane when iron group metals are present.

Poisons

The catalysts composed of ZnO together with difficultly reducible oxides (Cr_2O_3, MgO, Al_2O_3, etc.) as promoters are not very sensitive to the common poisons of hydrogenation catalysts (H_2S, PH_3 etc.). For this reason, and for their good resistance toward aging, zinc-base catalysts are generally preferred to the copper-base catalysts, though the latter may show higher initial activities. The copper-base catalysts are rapidly and completely poisoned by sulfur compounds. Not only H_2S, but also COS and CS_2 behave as poisons for copper-base catalysts, even when their concentration in the gas is of the order of a few milligrams per cubic meter.

The different behavior of ZnO and CuO is due to the different values of the equilibrium constants for the reactions:

$$(a)\ ZnO + H_2S \rightleftarrows ZnS + H_2O$$

$$(b)\ Cu + H_2S \rightleftarrows CuS + H_2$$

While reaction (a) is reversible at temperatures of the order of 300 to 400°C, reaction (b) is shifted completely to the right. The reversibility of reaction (a) was shown in the case of a zinc-chromium catalyst containing 4.8 per cent of sulfur combined as sulfide. Sulfur had totally disappeared from the surface of the catalyst after 18 hours of performance[75].

The small amounts of water which are always present in the synthesis gases* are sufficient to regenerate zinc oxide from ZnS, or, in other words, to prevent the formation of zinc sulfide. Catalysts containing ZnS have been proposed by some authors[4, 7, 36]. It should be pointed out that sulfur originally present in the catalysts may be elminated also combined in organic compounds as, for example, according to one of the following equilibria which lead to methyl mercaptan:

$$ZnS + CH_3OH \rightleftarrows ZnO + CH_3SH$$

$$H_2S + CH_3OH \rightleftarrows CH_3SH + H_2O$$

It is therefore advisable to work with gases and catalysts free from sulfur if methyl alcohol without a bad odor is desired.

If the catalysts are obtained by precipitation from solutions of the sulfates, they may contain basic sulfates; these slowly eliminate their sulfur as H_2S or CH_3SH.

The presence of NO in the gases has to be avoided because it may cause the formation of amines. On the other hand the use of nitrogen-containing gases does not lead to the formation of ammonia; this agrees with the fact that CO acts as a poison for catalysts for the synthesis of ammonia from N_2 and H_2.

Copper-base catalysts are poisoned by compounds containing chlorine or sulfur. Therefore, good copper-base catalysts may not be obtained by precipitation from solutions of copper sulfate or chloride, whereas they are easily made by precipitation from solutions of copper acetate or nitrate.

According to Tagashi Eguchi[10] acetylene and (to a smaller extent) ethylene behave as poisons for the methanol synthesis. However, olefines are always present during the synthesis of higher alcohols with alkaline catalysts, and their addition to the synthesis gases causes an increase in the production of higher alcohols. Therefore, it is unlikely that small quantities of olefins act as poisons for the ZnO-base catalysts.

Occasionally small amounts of lubricating oils are carried by the reacting

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* Water is also formed in the reaction $2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O$.

gases, and then are strongly adsorbed by the catalysts. These substances are not real poisons, but they have, naturally, a tendency to lower the activity of the catalysts. Similarly, the easily reducible oxides (PbO, SnO) whose corresponding metals have low melting points act as depressants. Cadmium, which may be formed by the reduction of CdO contained in ZnO as a solid solute, does not behave as a poison, because of its high vapor pressure; it is slowly carried away by the circulating hot gases. In other cases the catalytic activity of ZnO may be reduced by some low-melting compounds that facilitate the recrystallization of ZnO.

Rate of Reaction

The first attempts at a thorough kinetic study of the synthesis of methanol gave results which can be considered only as approximate, and valuable only within narrow intervals of composition and pressure. It is the opinion of the author that the oldest kinetic data for the synthesis of methanol should not be considered valid as a basis for a rigorous kinetic interpretation of this reaction, owing to the experimental difficulty of maintaining the entire mass of the catalyst at a strictly constant temperature. In order to avoid secondary reactions, one must use very short contact times. This can be done only by operating the reaction continuously. The constancy of temperature indicated in the reports of the old experiments should be interpreted as referring to only a small part of the bulk of the catalyst. The rate of the reaction is very high when active catalysts are used. Therefore in a typical continuous operation of synthesis of methyl alcohol performed at 250 atm. and 380 to 400°C, methanol is actually produced in amounts corresponding to 80 to 110 pounds per hour per cubic foot of catalyst, with a corresponding reaction heat as high as 25,000 to 45,000 kcal per hour. The synthesis, even if performed with high space velocities, may cause an adiabatic temperature rise of the order of 100°C in the reacting gases.

The experimental data which may be obtained by systematic experiments performed in large industrial apparatus should not be used for kinetic interpretations because of the considerable temperature rise along the reactor despite the efficient systems employed for cooling the catalyst. As far as laboratory-scale experiments are concerned, the data of the different authors are not mutually comparable because of the wide differences in the reaction apparatus, and of the uncertainty in the value of the temperature rise through the catalyst. The systematic experiments performed by Molstad and Dodge[38] with stoichiometric mixtures of CO and H_2, and with a specially designed apparatus, had pointed out the existence of a considerable rise in the temperature of the catalyst (about 25°C), with conditions under which the adiabatic temperature rise due to the reaction then taking place would have been about 125°C.

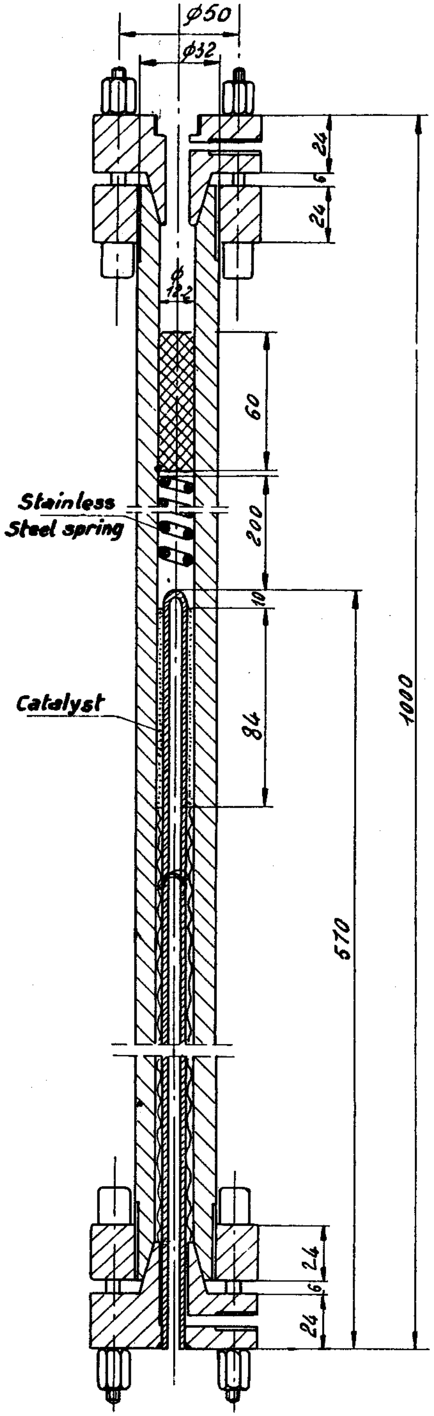

Figure 16. Reactor belonging to the laboratory apparatus used by Natta and his co-workers for the kinetic measurements on the synthesis of methanol.

Only very recently, Natta and his co-workers[50, 51] have performed systematic experiments with a laboratory apparatus particularly designed for kinetic measurements. These investigators used a reaction in which the catalytic space had an annular shape (see Figure 16). The relatively great thickness of the well of the reactor, and the close contact between the catalyst and the reactor's well, have made possible the performance of kinetic experiments in which the temperature measured along the catalyst maintained a constant value (within ±1°C) for over 90 per cent of the length of the catalyst. The temperature of the catalyst could also be kept constant (within ±1°C) for the entire time of each experiment. The apparatus used by these investigators is shown in Figure 17. The experiments were performed with a catalyst whose composition is ZnO, 89 per cent; Cr_2O_3, 11 per cent; and with another catalyst of the composion ZnO, 60.9 per cent; Cu, 29.8 per cent; Cr_2O_3, 9.3 per cent. The first of these has shown a very high resistance toward aging; the stability of the second was obtained, as it was already pointed out, by a prolonged (350 hours) treatment at 335°C in the presence of CO and H_2. The very high degree of purity of the methyl alcohol obtained under such conditions showed that secondary reactions were practically eliminated, and that the catalysts were very selective.

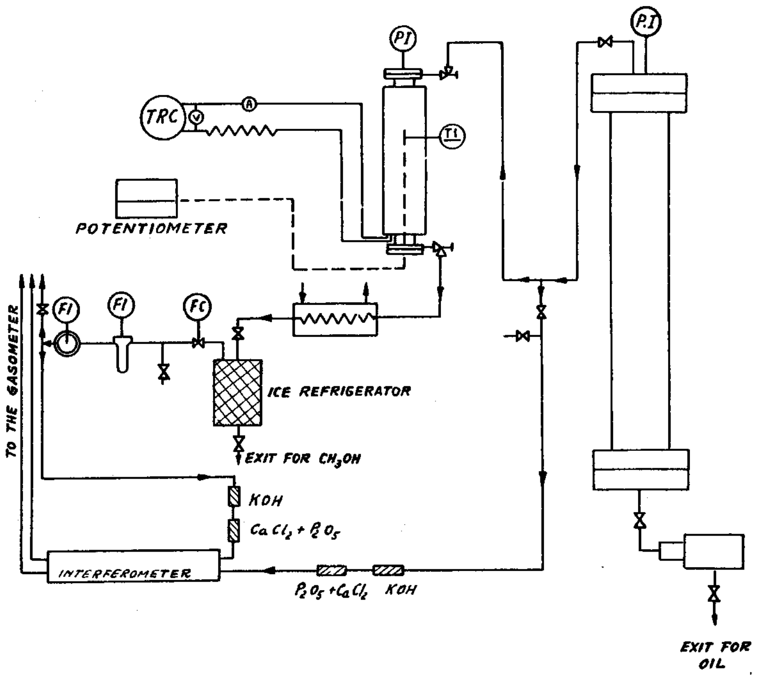

Figure 17. Apparatus used by Natta and his co-workers for the kinetic study of the synthesis of CH_3OH.

Figures 18 and 19 give some of the isotherms obtained with constant pressure experiments. In the plots the moles of CH_3OH per 100 moles of inlet gas (referred to one mole of total input gases) are plotted against a time-depending factor, grams of catalyst per mole of inlet gas per hour. All the isotherms reproduced deal with gaseous mixtures containing an excess of hydrogen over the stoichiometric composition, because with such mixtures it is easier to transfer away by conduction the heat evolved in the reaction, and to calculate the quantity of converted carbon monoxide from the variation of the H_2:CO ratio. From such isotherms it may be concluded that practically complete equilibrium is reached with space velocities lower than 15,000, with gases having $\frac{H_2}{CO} > 10$, at temperatures of at

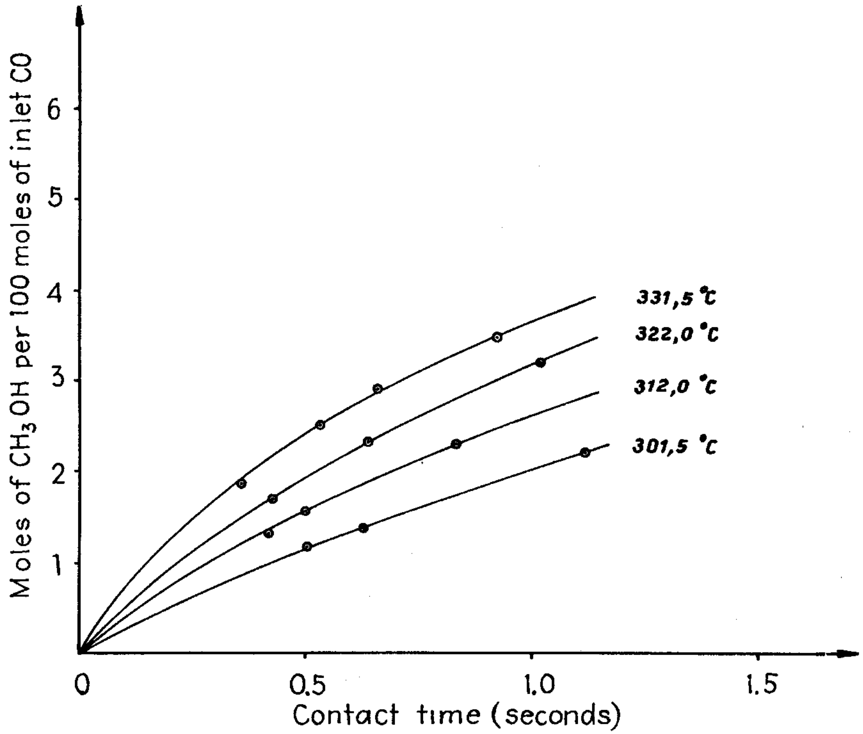

Figure 18. Rate of CH_3OH synthesis at constant temperatures as a function of the time of contact expressed as 3600 times the grams of catalyst per mole of inlet gas per hour. Catalyst composition: ZnO:CuO:Cr_2O_3 = 2:1:1. Inlet Gas: CO:H_2 = 9.3:90.7. Pressure: 200 atm.

least 390°C. From calculations of mass transfer and of thermal conductivity of the gas, it may be concluded that, even in the least favorable experimental conditions considered, the catalyst temperature is higher than the gas temperature by approximately 1°C, and that the gas temperature is about 1°C above the temperature of the external wall of the reaction vessel. The temperature values indicated in the plots of Figures 18 and 19 refer to the thermocouple located in the well inside the reactor; therefore, they may be considered equal to the temperatures of the gas.

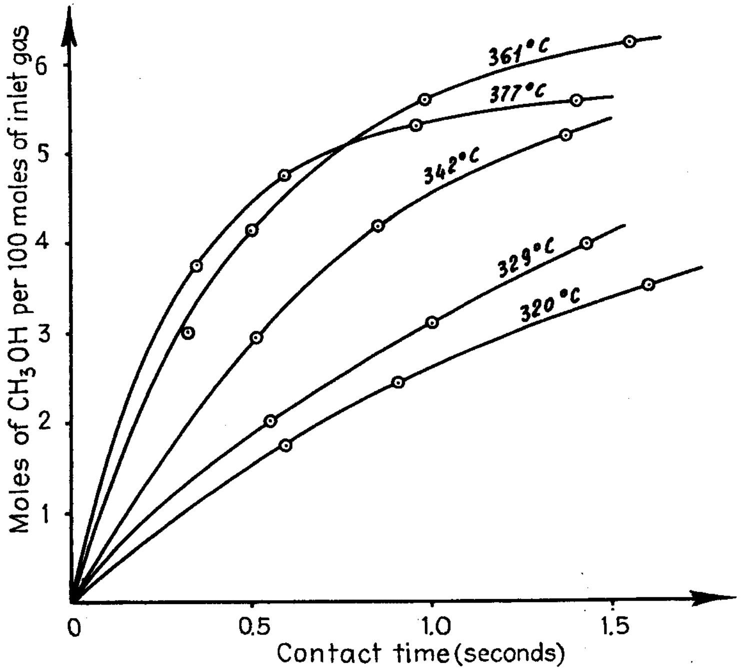

Figure 19. Rate of CH_3OH synthesis as a function of time of contact expressed as 3600 times the grams of catalyst per mole of inlet gas per hour. $CO:H_2 = 9.1:90.9$. Prsesure: 300 atm[32].

Interpretation of Kinetic Data

Older Experiments. The first attempts[43] to interpret the quantity of methanol produced as a function of temperature and contact time, with the assumption that the rate of reaction varied directly with the partial pressure of the reacting gases, led to results which were valuable only in a limited field of application, and with gases of a limited range of composition. In fact, the kinetic study of a catalytic reaction, taken as a homogeneous reaction* leads to valuable conclusions only whenever the concentrations of all the reacting gases in the adsorbed phase are proportional to their respective gas phase activities. The old adsorption measurements had given, for long adsorption periods, molar concentrations of adsorbed CO approximately equal to those of adsorbed H_2 ; this seemed sufficient to justify the kinetic classification of the synthesis of methanol as that of a homogeneous reaction, at least at the beginning of the reaction, when the amounts of CH_3OH formed are not too high.

Natta and Pastonesi[45] found a fair agreement between experimental data, and theoretical rate equations for the yield as a function of space velocity, assuming that the synthesis of methanol was a second-order reaction (i.e., proportional to the first power of CO concentration, and to the first power of H_2 concentration) and that the decomposition of methanol was a first-order reaction (i.e., proportional to the first power of the CH_3OH concentration). These two investigators worked with gaseous mixtures of constant composition ($H_2/CO = 2:1$) and made a few measurements, all at constant pressure but at different temperatures. They used an apparatus which was not strictly isothermal, and in which the temperature was measured in the central part of the catalyst. The authors assumed that the synthesis of methanol was divided into two consecutive reactions: (1) synthesis of formaldehyde (slow); (2) hydrogenation of formaldehyde to methanol (fast). The slower reaction of synthesis of formaldehyde would then be determinant for the apparent order of the over-all reaction. This hypothesis was corroborated by the fact that the formaldehyde concentration in the reacted gases was approximately equal to the equilibrium concentration for the hydrogenation of HCHO to CH_3OH under the conditions of the experiments.

The incorrectness of this kinetic interpretation was not noticed till recently because of the lack of experimental measurements with different $CO:H_2$ ratios. However, the forms of the isothermal rate curves calculated with this hypothesis are not very different from those calculated on the basis of a different kinetic interpretation, provided that mixtures having equal initial values of the $CO:H_2$ ratio are considered.

Recent Studies. When experimental data, conducted with different $CO:H_2$ ratios under the best conditions of temperature constancy, were available, it was possible to undertake a more rigorous kinetic study of the

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* *Editor's note:* Since a catalyst was needed, the reaction of carbon monoxide and hydrogen could never be considered as occurring as a homogeneous reaction in the gas phase. By the words "taken as a homogeneous reaction" the author means that the kinetics were interpreted in terms of the concentrations as partial pressures of the gaseous components and not in terms of the function of the surface covered by the reactants and products.

synthesis of methyl alcohol. The treatment of this reaction, interpreted as a heterogeneous catalytic process, was based on the method described by Hougen and Watson[19]. For this purpose Natta and his co-workers[50] have used the data of isothermal rate curves which were obtained with the apparatus described above. This approach is probably the first thorough study of a heterogeneous catalytic reaction operated at high pressures; therefore, a detailed discussion of the method of treatment follows.

The following parts of the complex process have been considered separately:

(1) Diffusion of the gases from the bulk of the gaseous phases to the gas-catalyst interface.

(2) Chemisorption of each component gas at the active surface of the catalyst.

(3) Reactions among the chemisorbed gases, according to different kinetic hypotheses.

(4) Desorption of the reaction products.

(5) Diffusion of the reaction products from the gas-catalyst interface to the bulk of the gaseous phase.

Assumption was made, that the gaseous phase behaves as an ideal mixture of real gases, in which the following equality is valid:

$$a_i = x_i P \gamma_i$$

where

a_i = activity of the ith component in the gaseous phase.
P = total pressure of the system.
x_i = molar fraction of the ith component.
γ_i = fugacity coefficient of the ith component, calculated for the pressure P and for the temperature of the experiment.

The processes (1) and (5) were so fast with the experimental values of space velocities and reactor shape, that their effect upon the kinetics of the reaction could be neglected. Therefore, with the assumption that the activity of each component at the interface catalyst-gas is equal to that of the component in the flowing gas phase, the adsorption rates of CO(A) and H_2(B) are:

$$r_A = k'_A a_A C_L - k''_A C_A$$

$$r_B = k'_B a_B C_L - k''_B C_B$$

where $r = \dfrac{dx}{dt}\,\dfrac{1}{W}$ is the resulting adsorption rate (the difference between adsorption and desorption rates expressed as the number of moles adsorbed by 1 gram of catalyst in unit time).

k' = adsorption rate constant
k'' = desorption rate constant
a = activity of the considered component at the interface catalyst-gas
C_L = molar concentration of the free active sites referred to the unit mass of the catalyst
C_A , C_B = concentrations of A and B, expressed in moles of A or B adsorbed by the unit mass of catalyst
W = weight of the catalyst in grams.

The following mechanism was assumed for adsorption on the active sites:

$$A + L \rightleftarrows A^*$$

$$B + L \rightleftarrows B^*$$

where L represents an active site. With the assumption that the reaction proceeds in the adsorbed phase, the following distinct schemes were considered:

(1) Bimolecular reaction

$$H_2^* + CO^* \rightleftarrows H_2CO^* + L$$

$$r_{s_1} = \frac{s}{C_{L_0}}\, k'_{s_1} C_A C_B - \frac{s}{C_{L_0}}\, k''_{s_1} C_F C_L$$

$$H_2CO^* + H_2^* \leftrightarrows CH_3OH^* + L$$

$$r_{s_2} = \frac{s}{C_{L_0}}\, k'_{s_2} C_F C_B - \frac{s}{C_{L_0}}\, k''_{s_2} C_R C_L$$

where s is the number of active sites located next to a given active site, and C_{L_0} is the molar concentration of active sites per unit of mass of the catalyst, and C_F and C_R the molar concentrations of formaldehyde and methanol, respectively, adsorbed by unit mass of catalyst.

(2) Trimolecular reaction

$$CO^* + 2H_2^* \rightleftarrows CH_3OH^* + 2L$$

$$r_s = \frac{s^2}{2C_{L_0}^2}\, k'_s C_A C_B^2 - \frac{s^2}{2C_{L_0}^2}\, k''_s C_R C_L^2$$

where k'_s and k''_s are the rate constants for the direct and reverse reactions in the adsorbed phase.

For the desorption of methyl alcohol (R) the following mechanism, similar to the last one, was chosen:

$$R^* \rightleftarrows R + L$$

$$r_R = k_R C_R - k'_R a_R C_L$$

From the experimental work of Natta and his co-workers[50] it has been concluded that the processes of adsorption and desorption proceed at much higher rates than the reaction at the surface, and that the process which determines the rate of the reaction is that of reaction among the adsorbed molecules. On that basis, it was possible to admit the existance of equilibrium between the activity of each component in the gas phase and its concentration in the adsorbed phase. It follows then:

$$C_A = K_A a_A C_L$$

$$C_B = K_B a_B C_L$$

$$C_R = K_R a_R C_L$$

where the constants K_A, K_B, K_R are the equilibrium constants for the adsorption of the components A, B, R.

The concentration of free active sites is given by the difference between the molar concentration of all the sites C_{L_0}, and that of the filled sites:

$$C_L = C_{L_0} - (C_A + C_B + C_R + C_I)$$

where C_I represents the concentration of the sites filled with other components which may be present (for example, inert substances). Operating in the absence of inert gases, it follows that

$$C_L = \frac{C_{L_0}}{1 + K_A a_A + K_B a_B + K_R a_R}$$

Substitution of the above value of C_L in the expressions which give the rate of reaction in the adsorbed phase, leads to expressions which give the reaction rate as a function of the rate constants of the direct and inverse reactions, of the constants of adsorption, and of the concentrations of active sites C_{L_0}.

These constants may be calculated on the basis of the kinetic data, whenever a sufficient number of accurate experimental data are available.

It has been shown[50, 51] that the kinetic equations, based on the hypothesis that the surface reaction is bimolecular, do not fit the isothermal rate curves.

Only with the hypothesis of a trimolecular reaction was it possible to solve this problem. The rate of a surface reaction for a trimolecular reaction results:

$$r = \frac{s^2 k_s' C_{L_0} K_A a_A K_B^2 a_B^2 - s^2 k_s'' C_{L_0} K_R a_R}{2(1 + K_A a_A + K_B a_B + K_R a_R)^3}.$$

Considering that the ratio $\frac{k_s'}{k_s''}$ is equal to K*, i.e., to the equilibrium constant of the reaction in the adsorbed phase, and that the thermodynamical equilibrium constant K_{eq} is related to the constants of equilibrium for the surface reaction by the relationship

$$\frac{K^* K_A K_B^2}{K_R} = K_{eq}$$

the following equation is easily obtained:

$$r = \frac{a_A a_B^2 - a_R/K_{eq}}{(A + B a_A + C a_B + D a_R)^3}$$

The four constants A, B, C, D represented in this equation are all positive and all of them are functions of the temperature only, if the assumption is made that the number of active sites C_{L_0} is independent of temperature. Substitution of the activities with the products of partial pressures and fugacity coefficients:

$$a_A = \gamma_A p_A; \qquad a_B = \gamma_B p_B \cdots$$

gives:

$$r = \frac{\gamma_{CO} p_{CO} \gamma_{H_2}^2 p_{H_2}^2 - \dfrac{\gamma_{CH_3OH} p_{CH_3OH}}{K_{eq}}}{(A + B\gamma_{CO} p_{CO} + C\gamma_{H_2} p_{H_2} + D\gamma_{CH_3OH} p_{CH_3OH})^3} \qquad (1)$$

Equation (1) interprets the surface reaction according to the following scheme:

$$CO^* + 2H_2^* \rightleftharpoons CH_3OH^* + 2L$$

For a very short contact time, starting with methanol-free gases, the concentration of methyl alcohol is nearly zero, and therefore Eq. (1) is thus simplified:

$$A + B\gamma_{CO} p_{CO} + C\gamma_{H_2} p_{H_2} = \sqrt[3]{\frac{\gamma_{CO} p_{CO} \gamma_{H_2}^2 p_{H_2}^2}{r_0}} \qquad (2)$$

In Eq. (2) r_0 is the initial reaction rate, or, in other words, the tangent of the reaction isotherm at the origin.

Equation (2) contains three unknowns, whose correspondent constants may be determined by measuring the initial rates of reaction in three experiments performed at the same temperature, but at different pressures and composition. This was done at several different temperatures, and the values of A, B, C were determined as functions of temperature. To establish the values of the constant D, the values of A, B, C, as previously determined, were substituted in Eq. (1) which was solved by introducing the experimental r values resulting from different values of time factor and with the experimental values of the partial pressures of CO, H_2, CH_3OH. Figures 20 and 21 give the values of A, B, C, D at several different temperatures for the catalysts $ZnO\text{-}Cr_2O_3$ and $Zn_{50}Cu_{25}Cr_{25}$. It results that the ratio $\frac{B}{C} = \frac{K_{CO}}{K_{H_2}}$ varies between 5 (at 330°C) and 8 (at 390°C).

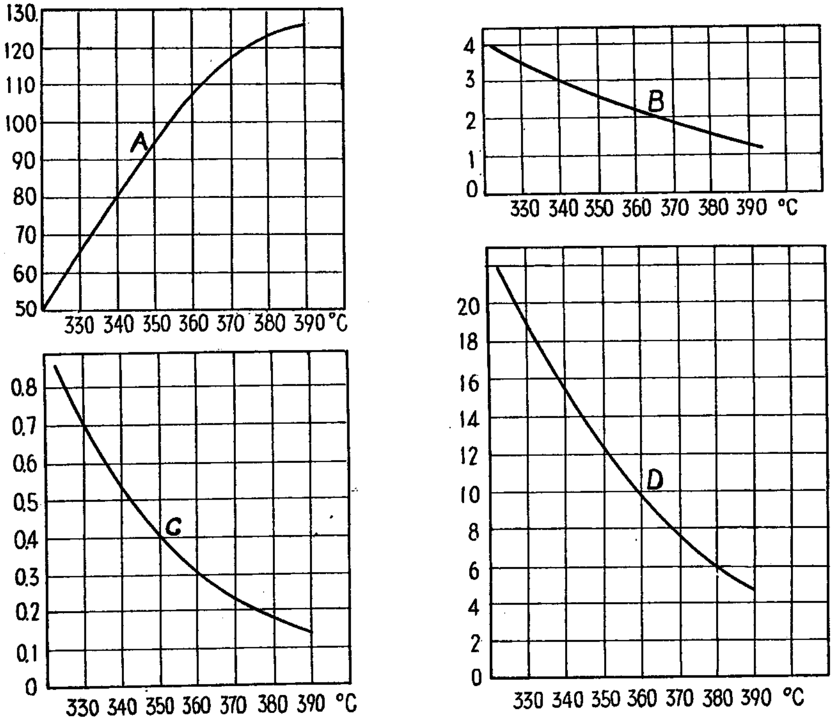

Figure 20. Dependence on temperature of the constants A, B, C, D ($ZnO\text{-}Cr_2O_3$ catalyst) (See Eqs. (1) and (2)).

The ratio $\frac{D}{C} = \frac{K_{CH_3OH}}{K_{H_2}}$ varies between 26 (at 330°C) and 37 (at 390°C). In the Zn-Cu-Cr catalyst the ratio $\frac{B}{C}$ has the constant value of 5 between 300 and 330°C while the ratio $\frac{D}{C}$ varies between 35 (at 300°C) and 29 (at 330°C). Such constants vary continuously with temperature. It is worthwhile to notice that the two above ratios have approximately equal values for the two catalysts. The adsorption heats vary in the sense $CH_3OH >$ CO $> H_2$. Such values of the ratios of the adsorption constants explain the facts that the reaction rate is higher when $\frac{H_2}{CO} > 2$, and that the produced methanol acts as a depressant of the reaction rate, because of its strong adsorption energy, which reduces the number of active sites available for the adsorption of CO and H_2.

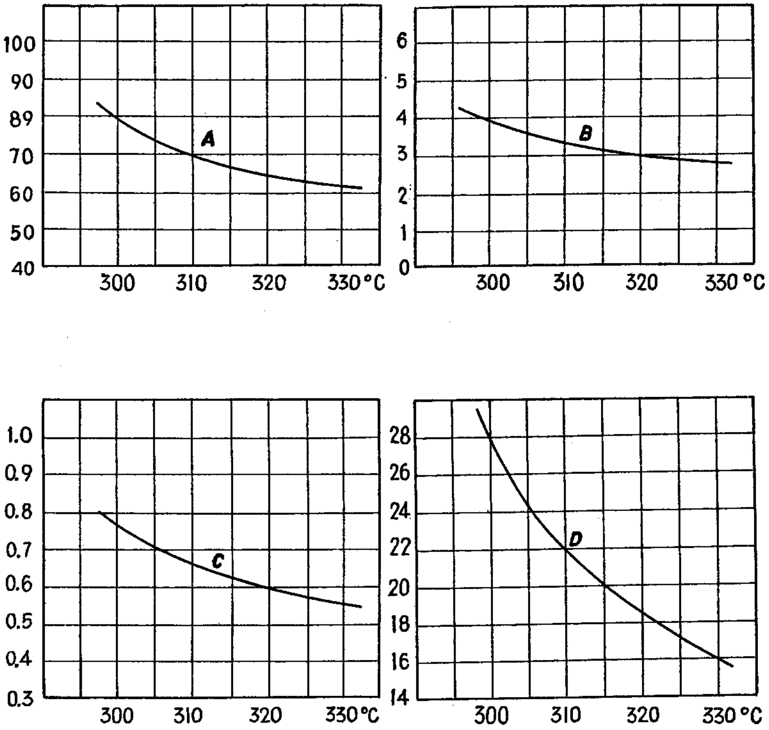

Figure 21. Dependence on temperature of the constants A, B, C, D. Catalyst composition = Zn:Cu:Cr = 2:1:1 (See Eqs. (1) and (2)).

Verification of the Kinetic Equations

Once the values of the constants A, B, C, D in the kinetic equation of the surface reaction (which is assumed to be the rate-controlling reaction) have been established, it is possible to predict the reaction rate for any values of temperature, gas composition, and pressure, within the field of applicability of the kinetic equation considered.

For a verification of such possibility, Natta and his co-workers[50] have integrated the differential equation:

$$r\,dW = F\,dx \qquad (3)$$

where F is the input rate (or the moles of gas introduced in the reactor in unit time, W is the weight of the catalyst, x the moles of produced methanol per input gas mole, and r is the rate of the reaction, expressed as moles of methyl alcohol produced in the unit time with the unitary weight of catalyst. Integration of (3) gives:

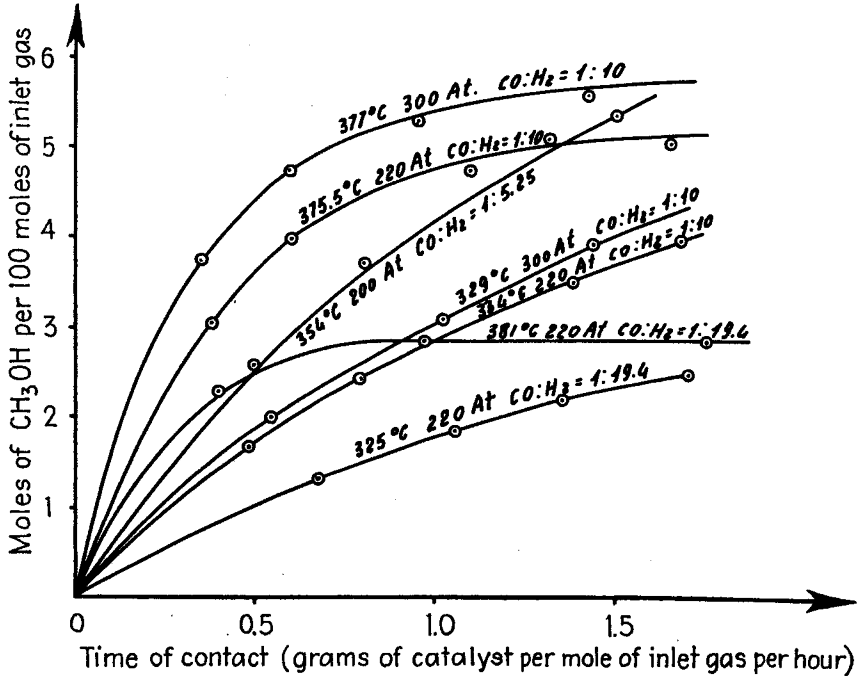

Figure 22. Verification of the kinetic equation proposed by Natta and his coworkers for a $ZnO\text{-}Cr_2O_3$ catalyst. Time of contact (3600 times the grams of catalyst per mole of inlet gas per hour). ⊙ Represents experimental points.

$$\frac{W}{F} = \int_0^x \frac{dx}{r}$$

or:

$$\frac{W}{F} = \int_0^x \frac{(A + B\gamma_{CO}\rho_{CO} + C\gamma_{H_2}\rho_{H_2} + D\gamma_{CH_3OH}\rho_{CH_3OH})^3}{\gamma_{CO}\rho_{CO}\gamma^2_{H_2}\rho^2_{H_2} - \dfrac{\gamma_{CH_3OH}\rho_{CH_3OH}}{K_{eq}}}\,dx \qquad (4)$$

If one determines on the basis of just a few isotherms the values of A, B, C, D, and then introduces these values into Eq. (4), one can compare the moles of experimentally produced methanol with those calculated from Eq. (4) for different values of temperature, pressure, and gas composition. Figure 22 shows the theoretical curves and the experimental data for the $ZnO\text{-}Cr_2O_3$ catalyst.

It appears clear that the experimental data agree exactly with the calculated ones, whenever the temperature and the concentration of CH_3OH are sufficiently low (in other words, whenever the production of methanol, and therefore the heat evolved in the reaction, are sufficiently low). Small divergencies of experimental from theoretical data (lower than 3 per cent referred to the moles of produced methanol) have been measured at higher temperatures with gases richer in CO, for long contact times. These divergencies are probably due to the greater difficulty of maintaining the temperature rigorously constant.

The good agreement between experimental and theoretical results is an evidence of the hypothesis that the rate-controlling process of the synthesis to methanol is the trimolecular reaction in the adsorbed phase.

A mechanism based on the hypothesis that the surface reaction is the resultant of two equally slow consecutive stages was not considered; the reason for this is that such a mechanism would require a more difficult mathematical treatment. The good agreement between experimental and calculated data in the case of the trimolecular reaction may be considered sufficient to establish the reliability of such an hypothesis. It should be pointed out that when dealing with surface phenomena, one finds reactions of the third or fourth order rather frequently, whereas, on the contrary, one usually finds complex homogeneous reactions to be divisible into simpler mono- or bimolecular stages.

Effect of Total Pressure

Since the synthesis of methanol is a reaction which proceeds with a considerable volume contraction, pressure has a very marked effect on the composition at equilibrium. When catalysts of normal activity are used, which react at temperatures higher than 350°C, it is necessary to operate at very high pressures to obtain good conversions.

Whenever in the synthesis of methanol gas mixtures containing N_2 or other inert gases are used, it is necessary to operate with pressures higher than the normal, the rate of reaction being a function of the activities of CO, H_2, and CH_3OH, which in turn are functions of the corresponding partial pressures of such gases.

This is the main reason why in industrial practice very often the synthesis of methanol is carried out at rather high pressures (200 to 250 atm.); equivalent conversions could be obtained at much lower pressures if pure gases were used. With very active copper-base catalysts, which may be used at temperatures close to 300°C, high conversion values may be obained even with pressures of 100 to 120 atm., but such catalysts as a rule ave the drawback of aging too rapidly.

Effect of Gas Composition

The first investigators of the synthesis of methanol observed that when the reaction was performed with a gas containing CO in excess of the stoichiometrical value, a greater decrease in the yield was noticed, than could be predicted on the basis of the law of mass action; some authors noticed also a kind of poisoning of the catalysts under such conditions. On the contrary, with H_2 greatly in excess of the stoichiometric composition, the yield of conversion decreases less than would be predicted theoretically. This effect was at that time attributed to the activating action of water vapor upon the catalysts.*

However, such an hypothesis is not sufficient to explain satisfactorily his remarkable effect, which is also noticed at lower temperatures (300 to 50°C) and with highly selective catalysts under such conditions as to make practically impossible the formation of water vapor. With highly selective atalysts the maximum rate of reaction occurs with $\boxed{\frac{C_{H_2}}{C_{CO}} \gg 2.}$

Natta and Casazza(42) attributed the favorable effect of a relative excess f H_2 upon the methanol yield in the experiments performed with very high pace velocities, to the fact that the rate of adsorption of CO is higher than hat of H_2. At that time, however, experimental data of adsorption at high ressures were missing. The data referring to adsorption experiments conucted at considerably lower pressures show that the volumes of CO and H_2 which are adsorbed under the same conditions are approximately equal, rovided the gas quantities adsorbed over relatively long periods are considered. If, however, very short adsorption periods are considered, the dsorption rate of CO appears to be higher, although the rate of diffusion f H_2 is much higher than that of CO.

The apparently greater slowness of the adsorption of hydrogen is probbly due to its diffusion into the inner part of the crystals; the part of hyrogen which is adsorbed slowly, therefore, is not concerned with the atalytical process, which takes place on the surface of the catalyst.

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* When the reaction is performed with an excess of carbon monoxide, the water apor (which is always present at least in small amounts among the reacting gases) isappears in the well known conversion reaction of carbon monoxide:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

nd therefore it may no more exert its activating action. The presence of traces of ater vapor is probably due to the formation of dimethyl ether:

$$2CH_3OH \rightarrow (CH_3)_2O + H_2O.$$

The results of the kinetic experiments performed by Natta and his coworkers[60] are able to explain the fact of a higher initial rate of reaction, as it is measured with ratios $\frac{C_{H_2}}{C_{CO}}$ higher than two. The values of the adsorption constants, as deduced from the results of the kinetic measurements, on the over-all reaction, which was interpreted as a surface reaction, show that hydrogen is adsorbed to a smaller extent than carbon monoxide. (1) Accordingly, in order to obtain a stoichiometrical $2H_2{:}1CO$ composition in the adsorbed phase, it is necessary to operate with concentration ratios in the gaseous phase of the order at least of $10H_2{:}1CO$. (2) Methyl alcohol itself is strongly adsorbed, thereby acting as an inhibitor of the synthesis reaction.

(3) The presence of small quantities of CO_2 in the gas has a favorable effect on the conversion to methanol, when the reaction is performed at high space velocities. Such favorable effect of CO_2 is probably due to the combination of the following factors:

(1) It causes a decrease in the formation of dimethyl ether.

(2) It prevents the conversion of CO into CO_2, which would take place in the presence of water vapor.

(3) It allows a better temperature regulation, because the heat evolved in the reaction:

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O$$

is about 10 kcal per mole lower than that which is evolved in the reaction:

$$CO + 2H_2 \rightleftarrows CH_3OH$$

Therefore, for a given amount of produced methanol, a smaller temperature increase along the reactor is noticed in the presence of CO_2. Furthermore, Natta and Rigamonti(44) noticed that the reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O$$

which proceeds toward the right at the higher temperatures, is catalyzed by zinc oxide: this endothermic reaction acts in the sense of regulating the temperature of the system, thus preventing any overheating of the catalyst.

The only apparent negative effect of the presence of carbon dioxide is that the amount of hydrogen consumed for a given quantity of methanol produced is higher. However, in the presence of small quantities of CO_2, the total amount of CO + H_2 consumed in the industrial practice is found to be slightly lower than in the absence of CO_2. It should be pointed out (4) that when the synthesis is performed with recycle of the reacting gases, it is not convenient to work with gaseous mixtures containing high percentages of carbon dioxide, because in such cases a relatively large amount of carbon dioxide is dissolved in the produced methanol during the separation of the latter (through condensation) from the circulating gases.

Effect of Inert Gases

Some of the oldest patents dealing with the synthesis of methanol (Badische Anilin und Soda Fabrick, Terni Co., etc.) mentioned the fact that the presence of an inert gas (N_2, CH_4, etc.) may exert a favorable action upon the synthesis by preventing competitive reactions. However, the lessening of the amount of methane produced should not be attributed to a mass action effect of the methane already present upon the reaction:

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O.$$

In fact, such reaction is at the high pressures almost completely shifted toward the right, and the effect of the presence of a small amount of methane would be negligible. Such effect would become important only with very high concentrations of methane (80 to 90 per cent) in the reaction gases. A high concentration of methane in the circulating gases would be harmful when operating at low pressures, because it provokes a diminution of the conversion at each passage of the gases through the catalyst. If, nevertheless, the synthesis of methanol is conducted at high pressures, a fairly high concentration of methane in the gas appears to be advantageous for the purity of the produced methanol. This may be connected with an effective reduction of the temperature rise of the reacting gases (due to the heat evolved in the reaction), as a consequence of: (1) the diminution of the production of methanol, on account of the lower partial pressures of CO and H_2; (2) the increased thermal capacity of the gas, because the specific heat of methane is higher than that of CO and that of H_2.

Pressures greater than 300 atm. may be conveniently used in the synthesis of methanol, if inlet gases containing 4 to 5 per cent of inert components are used, and if the reaction is operated with high inert gases concentrations (40 to 50 per cent) in the circulating gases.

Kinetic experiments in the presence of inert gases were performed by Natta and co-workers[50] with a $ZnO\text{-}Cr_2O_3$ catalyst. The molar concentrations of the produced methanol correspond exactly to those which may be predicted theoretically with Eq. (4), by simply admitting that the activities of CO and H_2 are proportional to the respective partial pressures, and to the fugacity coefficient related to the total pressure (see Table 10). It turns out, therefore, that neither methane nor nitrogen is sensibly chemisorbed by the catalyst, and that the only influence of these gases is their lowering of the partial pressures of CO and H_2 in the reaction gases, thus behaving effectively as inert gases.

Effect of Temperature and Space Velocity

The old data which appeared in the technical litera optimum temperature range for the synthesis of methanol, tradictory. Furthermore, the data of the various authors are not comparable, because their experiments were not performed under str isothermal conditions. The experiments by Molstad and Dodge appear to be the most reliable of the earliest published work. The experiments of these authors were performed under well defined physical conditions, and the temperature rise due to the heat evolved in the exothermic reaction was pointed out. According to these authors, the optimum temperature for a space velocity of 25,000 and for catalysts containing 10 to 50 per cent Cr_2O_3, and not submitted to preshrinkage, is 375°C. With preshrunk catalysts the optimum temperature appears to be lower (see Table 8). If one considers carefully the type of apparatus used by Molstad and Dodge, the conclusion may be drawn that the reaction temperatures may be considerably lower than the actual catalyst temperatures; the temperature difference may be as high as 10 to 20°C. The optimum temperature for the reaction varies with the type and activity of the catalyst employed, and it also depends on space velocity.

TABLE 10. Comparison of Experimental and Calculated Rates of Methanol Synthesis*

Pressure Atm.	Temp. (°C)	Time factor	Moles of produced methanol per mole of inlet gas	
			Experimental	Theoretical
295	363	0.40	2.70×10^{-2}	2.60×10^{-2}
295	363	0.84	3.65×10^{-2}	3.55×10^{-2}
295	363	1.40	4.00×10^{-2}	3.95×10^{-2}
265	353	0.48	2.20×10^{-2}	2.20×10^{-2}
265	353	0.70	2.85×10^{-2}	2.80×10^{-2}
265	353	1.13	3.75×10^{-2}	3.75×10^{-2}
250	340	0.53	2.15×10^{-2}	2.10×10^{-2}
250	340	0.75	2.70×10^{-2}	2.65×10^{-2}
250	340	1.15	3.55×10^{-2}	3.50×10^{-2}

* For the runs at 250 atm. the inlet gas contained 7.8% CO, 73.5% H_2 and 18.7% CH_4; for the other runs shown, it contained 6.6% CO, 70.1% H_2 and 23.3% N_2.

As far as the optimum temperature is concerned, two cases should be considered separately: (1) the optimum temperature for the maximum production in unit time for unit of catalyst volume; (2) the optimum temperature for maximum production, in unit time, obtained with unit volume of circulating gases.

In (1) it is concluded that the production of methanol at a definite temperature varies directly with space velocity, while in (2) it varies inversely with space velocity, provided that the reaction is performed at such a temperature as to insure a good selectivity of the catalyst. For example, with a ZnO-Cr_2O_3 catalyst it is possible to obtain raw methanol of high purity (98 per cent CH_3OH) only by operating at temperatures lower than 390°C. If the synthesis of methanol is performed at temperatures higher than about 400°C, some secondary concurrent reactions take place, the extent of these side reactions increasing with an increase in temperature. Only with extremely high velocities of gas circulation is the occurrence of these secondary reactions kept negligibly small.

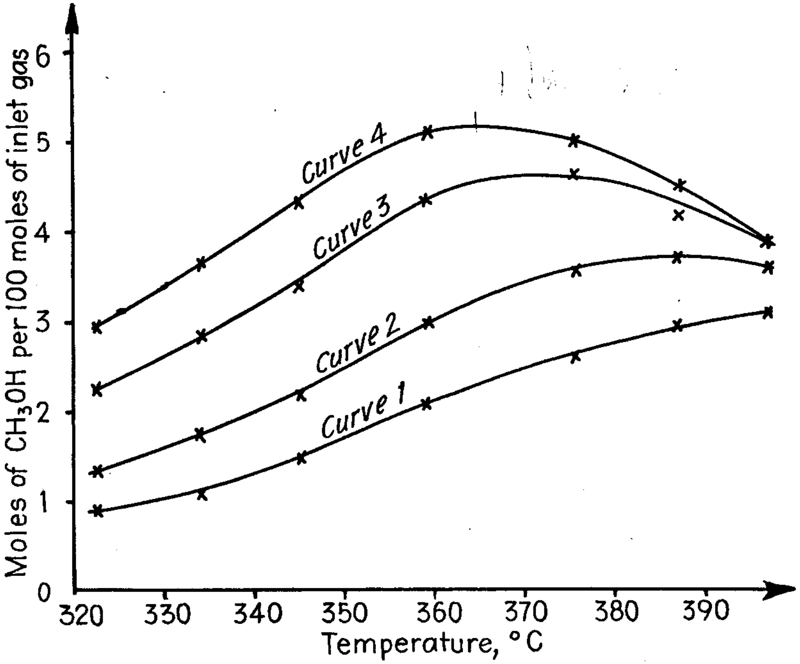

Figure 23. The conversion of a 1:10 $CO:H_2$ mixture to methanol as a function of temperature at 22.0 atm. pressure over a 89:11 $ZnO:Cr_2O_3$ catalyst at times of contact (as used in Figure 22) of 0.3, 0.5, 1.0, and 1.5 seconds, respectively for Curves 1, 2, 3, and 4.

Figures 23 and 24 show the conversion values obtained as a function of temperature, for different time factors, for a catalyst containing 89 per cent ZnO and 11 per cent Cr_2O_3 and for one in which $ZnO:CuO:Cr_2O_3 = 4:2:1$.

Activation Heat

The oldest data concerning this subject, which appeared in the technical literature may not be considered in our treatment, because the kinetic

mechanism of the synthesis of methanol and that of the reverse reaction (dissociation of methanol) were almost completely unknown till recently.

Although the older literature contains abundant experimental data on the decomposition of methanol, it is practically impossible to consider them as starting points for the prediction of the catalyst's behavior in the synthesis of methyl alcohol, because the experiments on the decomposition of methanol were performed at low pressures, while the synthesis reaction was generally conducted at much higher pressures; furthermore, the types of side reactions which may take place are different in the two cases. Only when pure zinc oxide is used as the catalyst are the undesired side reactions really negligible. In this case a direct comparison between the synthesis and the decomposition data may be of some interest. For this reason the kinetic data obtained by Shekhter and Moshkovskii[68, 69] are reported in Table 11. These investigators worked with ZnO catalysts, one of which was prepared by the decomposition (at 350°C) of zinc carbonate, the other by the direct combustion of zinc in an electric arc in a current of air.

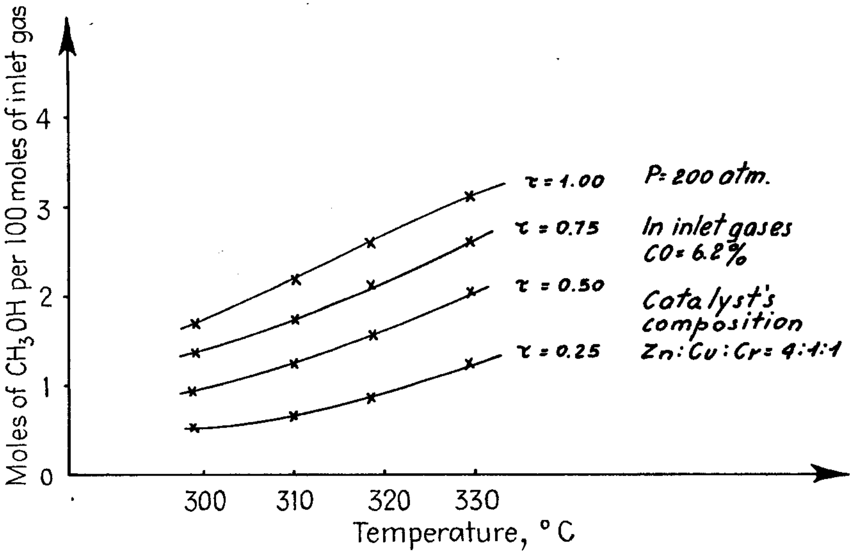

Figure 24. The conversion of a CO-H_2 (1:10) mixture to methanol as a function of temperature over a Zn-Cu-Cr (4:1:1). τ is the time of contact as defined in legend of Figure 22.

For the synthesis of methanol, Natta and his co-workers[49, 50, 51] have recently obtained the apparent values of the activation energy reported in Table 12. It should be noticed that the activation heats for the ZnO-Cr_2O_3 mixed catalysts are approximately equal to those for pure ZnO catalysts. This is in good agreement with the hypothesis that Cr_2O_3 behaves as promoter mainly through its action of preventing the decrease of the surface area of ZnO. The copper-containing catalysts have lower activation energies, and may be used also at relatively low temperatures. It may be noticed that the lowest activation heat is that for the $CuO\text{-}Cr_2O_3$ catalyst.

Mechanism of the Synthesis of Methanol

It has been pointed out that zinc oxide is the most important component of the catalysts for the synthesis of methyl alcohol. ZnO, when conveniently prepared, shows by itself a fairly good catalytic activity. Its durability may be increased by the addition of a promoter, which is generally a difficulty reducible oxide, whose hydrogenating properties are extremely poor. Chromium oxide (Cr_2O_3) is one of the most used promoters of ZnO, even when it is combined to it as zinc-chromite, $ZnO—Cr_2O_3$.

TABLE 11. KINETIC DATA OBTAINED IN THE DECOMPOSITION OF METHANOL (Reaction of Zero Order in the Range 0.04–0.09 ml CH_3OH/min.)

k = cc of gas evolved per minute per gram of catalyst

Catalyst I: ZnO prepared by the thermal decomposition of $ZnCO_3$; (Specific surface area of 80 m²/g).

Catalyst II: ZnO prepared by combustion of Zn at 1,000°C; (Specific surface area of 12 m²/g).

Catalyst I	Temp. (°C)	322	300	290	
	k	153	61	41	
	E_{act} =	28 kcal per mole			
Catalyst II	Temp. (°C)	339	328	319	300
	k	152	101	36	10.5
	E_{act} =	51 kcal per mole			

TABLE 12. ENERGY OF ACTIVATION FOR METHANOL SYNTHESIS

	Temp. Range (°C)	E (cal/mole)
Pure ZnO catalysts		
ZnO from smithsonite	325–370	27,000
ZnO from zinc acetate	330–353	30,000
Mixed catalysts		
CuO 34.6%-Cr_2O_3 65.4%	292–326	14,000
ZnO 90%; Cr_2O_3 5%; imbibed Cr_2O_3 5%	331–365	28,000
ZnO 89%; Cr_2O_3 11%	325–380	30,000
ZnO 80.8%; CuO 9.9%; Cr_2O_3 9.3%	307–325	17,000
ZnO 60.9%; CuO 29.8%; Cr_2O_3 9.3%	280–320	18,000
ZnO 51.3%; CuO 25.1%; Cr_2O_3 23.6%	300–330	18,000

Most of the promoters have the main function of inhibiting the sintering of ZnO, and, therefore, stabilizing the lattice vacant sites, and the anionic deficiencies, which are present to a greater or lesser degree in zinc oxide, according to its method of preparation. It should be here pointed out that a

slight excess of zinc over the stoichiometrical value (10^{17} atoms per ml) is present even in the zinc oxide obtained by combustion of metallic zinc; there is evidence of a real homogeneous phase $ZnO_{(1-x)}$. The ZnO prepared from the combustion of metallic zinc is a rather poor catalyst while on the contrary ZnO obtained from zinc salts whose anion has a reducing action (for example, ZnO from $Zn(CH_3COO)_2$) is catalytically much more active. This appears to be connected with the greater number of anionic deficiencies in the lattice of ZnO, due to the presence of metallic zinc.

The introduction into the lattice of ZnO of oxides of trivalent cations in solid solution leads to the formation of cationic vacant sites, which may be filled by the excess of zinc present in ZnO. These trivalent ions have the function of stabilizing the excess of zinc atoms in the lattice, and therefore they increase the number of available electrons in the catalyst. This is in agreement with the higher conductivity measured in those zinc oxides which contain trivalent cations. The high catalytic activity of certain types of zinc oxide appears to be connected with the presence in the ZnO lattice of these available electrons due to elemental zinc.*

Taylor and Kistiakowsky noticed[73] that CO, H_2 and CO_2 are strongly adsorbed by ZnO, and that the mixed catalysts $ZnO\text{-}Cr_2O_3$ adsorb such gases to an even greater extent. The same authors pointed out that the adsorption heats are higher than the liquefaction heats. Several investigators in later works have shown that the mechanism of the synthesis of methanol with ZnO-base catalysts has to be correlated to the activated adsorption of CO and H_2 on the surface of zinc oxide. The temperature range at which the activated adsorption is possible (200 to 450°C) includes the temperatures at which ZnO acts as a catalyst for methanol synthesis.

Some active hydrogenating metals (Fe, Co, Ni) chemisorb carbon monoxide; however, the chemical reaction involved in the adsorption of CO by ZnO is quite different from that involved in the adsorption of CO by the above metals. If a finely divided or partially amorphous zinc oxide is heated in atmosphere of CO or H_2, traces of CO_2 or H_2O are found in the desorption of the adsorbed gases, as a consequence of the partial reduction of ZnO to Zn. For example, Natta and Agliardi[48] noticed that the number of Zn gram-atoms per mole of ZnO, which are formed in a single adsorption-desorption operation is of the order of 1×10^{-4}.

Fe, Co, and Ni chemisorb carbon monoxide because of their tendency to

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* The catalytic experiments with such semiconductive ZnO catalysts[55, 70] have been performed generally with catalysts obtained at very high temperatures (for example, $ZnO—Al_2O_3$), and having low catalytic activity for the synthesis of methanol. Al_2O_3 is not a good promoter of the ZnO and CuO-base catalysts, in which it is present as a solid solute. In the case of Cr_2O_3, however, one may conclude that Cr_2O_3, which is in contact with the surface of zinc oxide or of copper oxide, has a stabilizing action upon the surface cationic deficiencies.

combine with this gas to give carbonyl compounds. These metals, however, in the absence of hydrogen may provoke the disproportionation of CO to $C + CO_2$, and also may cause the formation of metallic carbides. It is reasonable to believe that the synthesis of hydrocarbons, catalyzed by these metals, proceeds through the transformation of CO into chemisorbed elementary C, which in turn is hydrogenated by the chemisorbed hydrogen.

Chemisorption of carbon monoxide on the surface of a metal belonging to the iron group is not entirely reversible. In fact, it is impossible to recover through desorption all the carbon monoxide chemisorbed on these metals, because a part of it is reduced to elementary carbon or to metallic carbide.

Chemisorption of carbon monoxide (or H_2) on zinc oxide is also not completely reversible, but in this case a part of the chemisorbed CO (or H_2) is desorbed as CO_2 (or H_2O), while ZnO is reduced to Zn. This reduction of ZnO to Zn proceeds sensibly only if the crystals of ZnO are defective; those promoters which hinder the complete crystallization of ZnO also make easier its partial reduction, stabilizing, therefore, the ZnO lattices containing an excess of electrons.

In the chemisorption of CO on the iron group metals there is a tendency toward the reduction of the carbon atoms, through removal of the oxygen previously linked to it; on the contrary in the chemisorption of CO on ZnO the divalent carbon is saturated, and there is no removal of the oxygen atoms combined with it. For this reason, when CO and H_2 are simultaneously present, iron group metals cause the formation of methane and higher hydrocarbons, while ZnO catalyzes the formation of methanol.

A complete reduction of ZnO to Zn, under the conditions of the synthesis of methanol, is impossible because small traces of CO_2 and H_2O are sufficient(65) to prevent the reaction of reduction. In fact, the equilibrium constant of the reaction

$$ZnO + CO \rightleftarrows Zn + CO_2$$

has extremely low values in the temperature range of the synthesis of methanol. The partial oxidations of CO to CO_2 and of H_2 to H_2O, which take place during the desorption of the chemisorbed CO and H_2 from active ZnO, have to be attributed to the presence of amorphous or imperfectly crystallized ZnO, for which the free energy of the reduction reaction assumes more favorable values, because of the absence of the contribution of the free energy of crystallization to the free energy of formation of ZnO.

The unusual behavior of ZnO, which is the most selective catalyst for the synthesis of methyl alcohol, may be thought of as being correlated with its crystal structure. Zinc oxide is, together with copper oxide, the only divalent metallic oxide having an ionic radius in the range 0.5 to 1.1 Å, which does not crystallize in the cubic system. ZnO crystallizes in the hexagonal system. Therefore, some planes of its lattice are composed entirely of oxygen atoms; others, entirely of zinc atoms. Eucken[10a] (private communication) attributed to the crystalline structure of zinc oxide its unusual catalytic behavior, which is shown, for example, in the decomposition of ethyl alcohol. In fact, while metals dehydrogenate ethyl alcohol to acetaldehyde, and, on the other hand, the nonreducible oxides (Al_2O_3, Cr_2O_3) dehydrate ethyl alcohol to ethylene, zinc oxide behaves intermediately, giving rise simultaneously to both ethylene and acetaldehyde.

The catalysts containing copper oxide behave substantially like the ZnO-base catalysts, the main difference being due to the higher reducibility of CuO. The short durability of copper-base catalysts, obtained through reduction of CuO in the presence of promoters, has to be attributed to the fact that the true catalyst of the methanol synthesis is not the metallic copper phase (cubic), but the copper oxide which is present in the incompletely reduced catalysts (for example, as copper chromite in the CuO-Cr_2O_3 catalysts). During a synthesis run there is a gradual reduction of CuO to Cu, and the separation of crystals of pure cubic metallic copper provokes the lowering of the catalyst's activity. The copper-containing catalysts are very active at the low temperatures, at which the reduction of CuO (specially when combined with Cr_2O_3) is fairly slow, but they lose their activity rapidly if the temperature is raised.

The behavior of copper-base catalysts in the synthesis of methanol is in many respects similar to that of the copper-base catalysts used in the hydrogenation of fatty acids to alcohols. These catalysts (for example, copper chromite) have a very short life when used at temperatures higher than 300°C, and lose their activity entirely when the copper oxide is completely reduced to copper.

The hypothesis that copper oxide, and not metallic copper, is the real catalyst for the synthesis of methanol, is substantiated by considering the behavior of silver-base catalysts, whose properties are in many cases similar to those of copper-base ones. In some instances (for example, in the oxidation of methanol to formaldehyde) silver is an even more active catalyst than copper. In the synthesis of methanol, however, silver is a bad catalyst: this is probably connected with the higher reducibility of silver oxide with respect to copper oxide.

The combination ZnO and CuO gives catalysts which are extremely active in the synthesis of methanol. This has been attributed to an improvement in the hydrogen adsorption capacity of the catalyst. However, this idea has not been corroborated by kinetic experiments on mixed Cu-Zn-Cr catalysts[51].

It has been mentioned that the activity of copper-base catalysts is connected with the presence of nonreduced copper oxide. This is shown also by the activating action of oxygen in the dehydrogenation of methanol to formaldehyde. The copper catalysts, which were widely used in the industrial production of formaldehyde from methanol, have a durable activity only when the reaction is performed in the presence of air or oxygen.

Activated adsorption of CO and H_2 on various oxides takes place generally starting from temperatures much lower than those corresponding to the complete reduction of the oxides. From this point of view, it is interesting to correlate the reducibility of some metallic oxides to their free energies of formation at the temperature of the methanol synthesis.

Oxide	$\Delta F^\circ_{400^\circ C}$
MnO	−89.9
$\frac{1}{3}Cr_2O_3$	−75.2
ZnO	−67.0
CdO	−54.7
$\frac{1}{2}WO_2$	−51.9
FeO	−51.5
NiO	−43.3
CoO	−43.2
CuO	−32.0

Of the above oxides, Cr_2O_3 and MnO were used as promoters. CdO also is a very active promoter (as it is shown by the high activity of certain ZnO catalysts from smithsonites containing cadmium as impurity) but it is easily reducible. FeO, CoO, NiO are also easily reducible, but they act as catalysts for the competitive synthesis of methane. The hydrogenating (and dehydrogenating) properties of Cr_2O_3 are generally observed at higher temperatures, and they are utilized in the industrial dehydrogenation of some hydrocarbons.

The free energies of the reactions of formation of spinels from the corresponding oxides have values of a few kcal per mole. Therefore, spinels are not reduced as easily as the corresponding free oxides; accordingly, zinc chromite is less active than the mixtures ZnO-Cr_2O_3 richer in ZnO. The reducibility of copper chromite is intermediate between that of CuO and that of ZnO; therefore copper chromite gives catalysts which last longer than those made with ZnO-CuO mixtures containing an equal amount of CuO.

The equilibrium constants for the adsorption of CO, H_2, CH_3OH on the active sites which are of interest in the catalysis have been deduced from the kinetic interpretation of the experimental data, as reported by Natta and his co-workers[50] for a catalyst, the composition of which is 89 per cent ZnO and 11 per cent Cr_2O_3. The values of such constants were obtained by calculating the ratios B/A, C/A, and D/A for the four constants in Eq. (1) for different temperatures (page 391). Natta and co-workers[51] have calculated the analogous constants for a catalyst containing 50 per cent ZnO, 25 per cent CuO and 25 per cent Cr_2O_3. In Figure 25 the logarithms of the values of such equilibrium constants are plotted versus $\frac{1}{T}$. The higher reactivity of CO in the surface reaction is probably connected with the higher absolute value of the free energy of the reduction of ZnO with CO, with respect to that of ZnO with H_2. As was pointed out in one of the preceding paragraphs, the fact that the values of the equilibrium constants for the

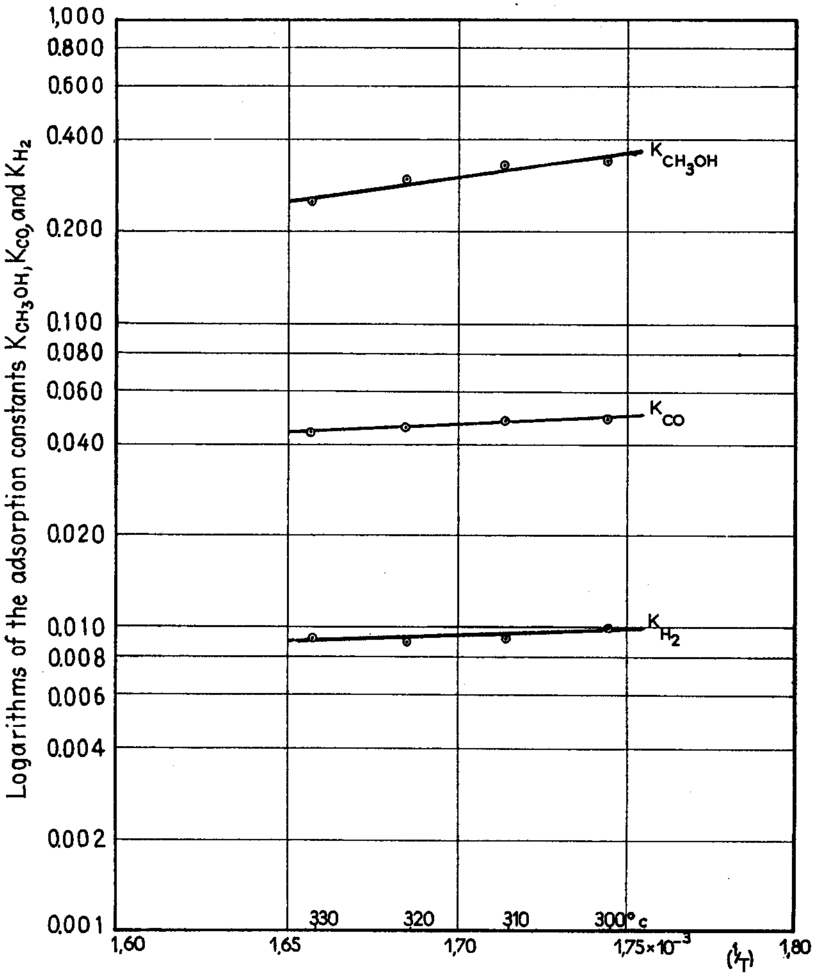

Figure 25. Logarithmic plots of K_{CH_3OH}, K_{CO}, and K_{H_2} as a function of temperature.

adsorption of CO are higher than those corresponding to the adsorption of H_2, explains the apparent abnormality of having the maximum reaction rate at each temperature with ratios H_2:CO much higher than the stoichiometrical ratio for the synthesis of methanol. These results corroborate the hypothesis that the heterogeneous catalysis occurs with CO and H_2 in the adsorbed phase, and that the rate of such reaction is a function of the concentrations of CO and H_2 in the adsorbed phase. However, if a comparison is made between the kinetically deduced chemisorption data and the experimental data concerning low pressure adsorption of CO and H_2 at the surface of ZnO, an apparent disagreement is found. In fact, for long adsorption periods at low pressures CO and H_2 are adsorbed in about equal molar concentrations. If one considers the experimental data of Sartori[64], related to the adsorption of CO and H_2, it is clear that, for very short adsorption periods, carbon monoxide is adsorbed much more readily than H_2. This is in good agreement with the results obtained from the kinetic interpretation of methanol synthesis.

TABLE 13. COMPARISON OF ADSORPTION CONSTANTS FOR CO, H_2, AND CH_3OH AT 325°C AS CALCULATED FROM KINETIC DATA FOR METHANOL SYNTHESIS CATALYSTS*

Catalyst	A	B	C	D	K_{CO}	K_{H_2}	K_{CH_3OH}	Ratios K_I/K_{II}		
								K_{CO}	K_{H_2}	K_{CH_3OH}
I	50.0	3.80	0.82	21.2	6.6×10^{-2}	14×10^{-3}	3.9×10^{-1}	1.44	1.52	1.44
II	62.5	2.85	0.57	17.1	4.6×10^{-2}	9.2×10^{-3}	2.7×10^{-1}			

* Catalyst I) ZnO:Cr_2O_3 = 89:11
Catalyst II) ZnO:CuO:Cr_2O_3 = 50:25:25
(For the meaning of the constants A, B, C, D see page 391.)

It appears therefore evident that not all the molecules of adsorbed CO and H_2 are actually related to catalysis, but, only those which are rapidly adsorbed on the most easily available active sites. The slow adsorption in the inner part of the crystals (or else on sites of lower activity) most probably are not involved in the catalytic processes which occur at very high space velocities.

The fairly high value of the adsorption constant for CH_3OH explains the fact that the presence of CH_3OH in the reacting gases inhibits the synthesis, and that therefore when high values for the concentrations of methanol are reached, a further conversion of CO and H_2 is slower than would be predicted by virtue of the reversibility of the reaction. Similar results were obtained with copper-base catalysts, whose adsorption constants are quite different from those pertaining to ZnO-base catalysts. However, the ratios $\frac{K_{CO}}{K_{H_2}}$ and $\frac{K_{CH_3OH}}{K_{CO}}$ are almost equal in the two cases (Table 13)[51, 52].

We may conclude this chapter by pointing out that the accurate kinetic study of the reaction of synthesis of methanol has given a remarkable contribution to the understanding of the mechanism of this reaction. Such a kinetic approach has also contributed to a better knowledge of the phenomena connected with activated adsorption.

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