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SYNTHESIS OF METHANOL

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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 tons⁷⁴. As a consequence of the development of the catalytic synthesis, production of methyl alcohol in the United States in 1953 exceeded 480,000 tons²⁷, 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 Fabrik⁶² 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 1923⁶³ 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 Cr₂O₃ 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 Ufers⁶⁷ who used a copper-base catalyst which also contained oxides of various metals

TABLE 1

	Synthesis of NH ₃	Synthesis of CH ₃ OH
ΔF° _{400°C} per mole of H ₂	+4,000 kcal	+7,400 kcal
ΔH° _{400°C} per mole of H ₂	-8,530 kcal	-12,325 kcal
ΔH° _{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 Corporation⁶², which had to overcome many difficulties. During World War II, the Lonza Company in Switzerland succeeded in the industrial realization of methanol synthesis from CO₂ and electrolytic hydrogen⁴⁷. Carbon dioxide was a by-product of the process for producing Ca(NO₃)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 H₂.

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 + H₂ 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.

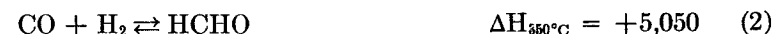
A thermodynamical approach to the equilibria related to all the possible reactions is quite useful in order to understand the reasons why the synthesis of methanol requires the use of highly selective catalysts and high pressures for its industrial realization.

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



$$\Delta F_{350^\circ\text{C}}^\circ = +12,100$$

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



$$\Delta F_{350^\circ\text{C}}^\circ = +16,100$$



$$\Delta F_{350^\circ\text{C}}^\circ = -4,000$$

The synthesis of methanol from carbon dioxide



$$\Delta F_{350^\circ\text{C}}^\circ = +15,800$$

may be considered as a composite equilibrium, whose individual reactions are the conversion of CO₂ into CO



$$\Delta F_{350^\circ\text{C}}^\circ = +3,700$$

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

* The thermodynamical data considered in this paragraph are those published by Parks and Huffman⁶⁴, by Rossini and co-workers⁶⁵, and by Smith⁷¹.



$$\Delta F^\circ_{350^\circ\text{C}} = -1,400$$



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:



$$\Delta F^\circ_{350^\circ\text{C}} = -15,826$$

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



$$\Delta F^\circ_{350^\circ\text{C}} = -19,526$$

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



$$\Delta F^\circ_{350^\circ\text{C}} = -16,730$$

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):



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 tem-

perature 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 $>180^\circ\text{C}$, 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

TABLE 2. FREE ENERGY OF REACTION, ΔF° (kcal/mole)

T ($^\circ\text{C}$)	27	127	227	327	427
$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$	-6.30	-0.80	+5.00	+10.80	+16.70
$2\text{CO} \rightarrow \text{CO}_2 + \text{C}$	-28.57	-24.31	-20.02	-15.73	-11.44
$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-33.87	-28.56	-23.01	-17.29	-11.44
$2\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{CO}_2$	-40.67	-34.36	-27.87	-21.22	-14.49
$n\text{CO} + 2n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O} (n = 2)$	-27.23	-19.34	-11.10	-2.67	+5.90
$n\text{CO} + (2n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} (n = 2)$	-51.32	-40.46	-29.18	-17.62	-5.87

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.

Experimental data, obtained (under conditions very close to the equilibrium) at 350 to 380 $^\circ\text{C}$ 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

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

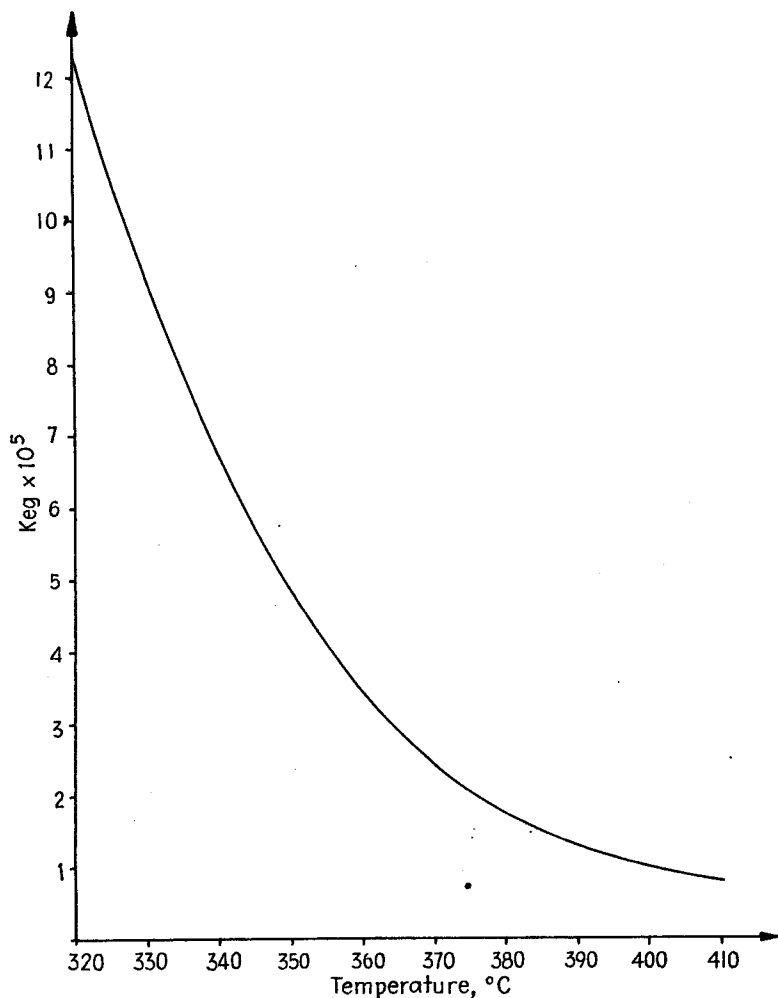


Figure 1. Equilibrium constant for the reaction $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$.

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 de-

composition 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

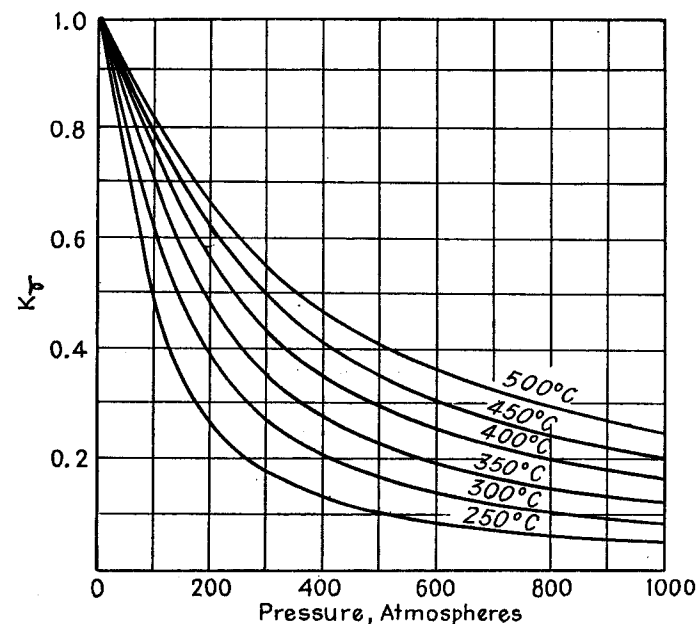


Figure 2. Values of K_γ for the reaction $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$. Ewell, R. H., *Ind Eng. Chem.*, **32**, 152 (1949).

a qualitative comparison among the catalysts prepared according to different methods.

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

* 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.

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-workers,²⁰ 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 Dodge³⁸ 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 investigators³⁹ found much lower conversions with a similar catalyst.

Hüttig and Goerk tested a number of different catalysts in the decomposition of methyl alcohol²². 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 Dolgov²⁸.

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. Natta⁴⁰ noticed a considerable decrease with time of the activity of a

* $Zn(OH)_2$ is isomorphous with $Ni(OH)_2$. Schwab and Block⁷⁰ 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.

Even more active and durable catalysts were obtained by the thermal

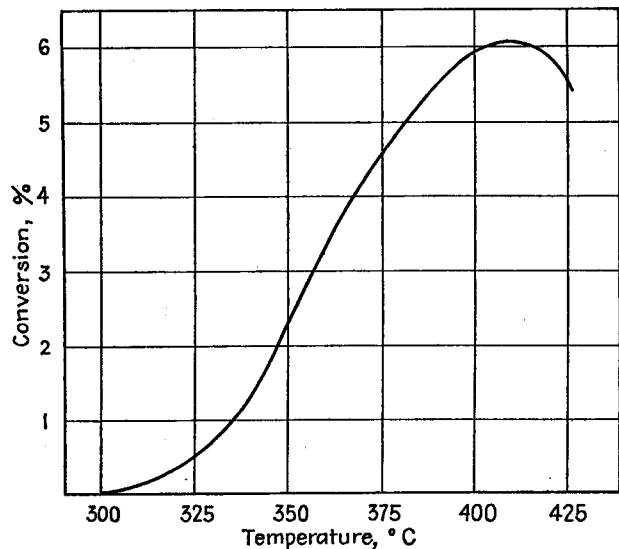


Figure 3. Synthesis of methanol from a 1:2 CO:H₂ mixture at a space velocity of 25,000 and a pressure of 178 atms³⁸.

decomposition of smithsonite (mineral ZnCO₃), 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 Hensinger³⁵. 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 Corradini⁴⁹

TABLE 3. EFFECT OF THE PRECIPITATING AGENT ON ACTIVITY OF ZnO CATALYSTS (Gas composition 1 CO:2 H₂; at 385°C and 178 atm.)

Catalyst Prepared from Zn(OH) ₂ Precipitated by	Inlet Space Velocity	Conversion (%)
NH ₄ OH	92,000	3.0
NH ₄ OH	95,700	2.6
Na ₂ CO ₃ excess	94,500	4.7
Na ₂ CO ₃ insuff.	95,000	8.5
Na ₂ CO ₃ excess	95,000	5.5

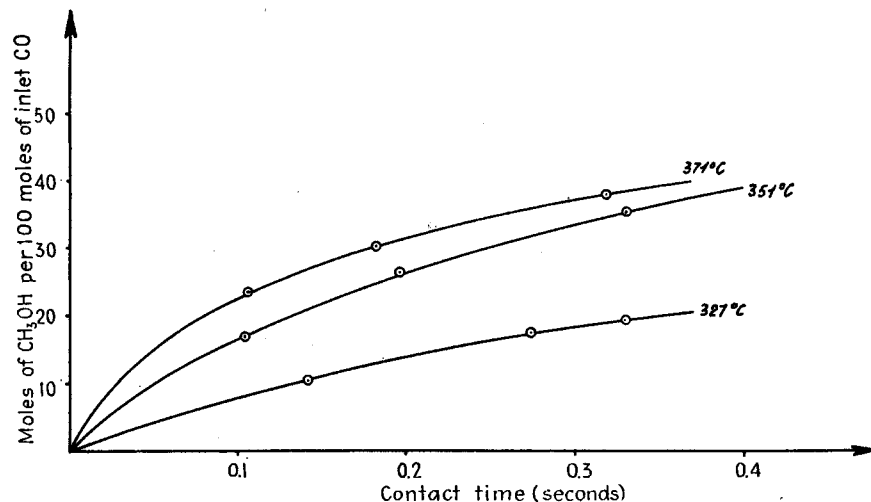


Figure 4. Moles of CH₃OH produced per 100 moles of inlet CO, as function of contact time at different temperatures with a ZnO catalyst from smithsonite. Pressure: 250 atm., inlet gas: CO:H₂ = 1:10. Contact time is defined as 3,600 times the ratio of the volume of the catalyst to the inlet volume of H₂-CO mixture per hour.

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).

The data of Natta and Corradini should not be directly related with

those of Molstad and Dodge³⁸, 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 CH₃OH 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 Na₂CO₃ 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,

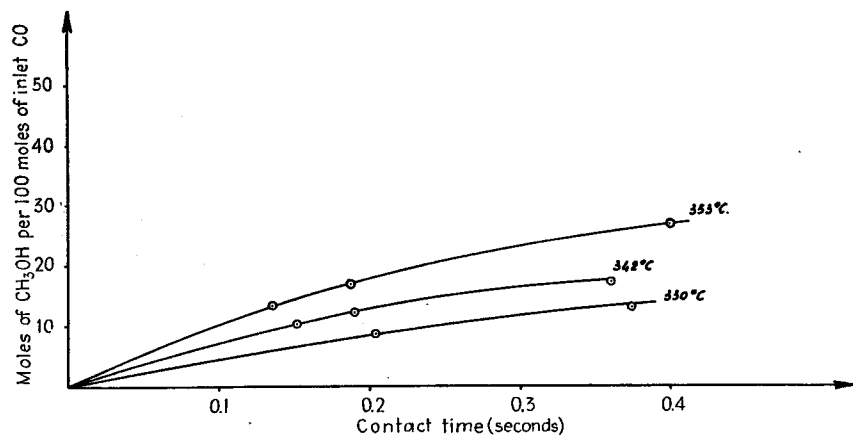


Figure 5. Moles of CH₃OH produced per 100 moles of inlet CO, as function of contact time at different temperatures, with a ZnO catalyst from zinc acetate. Pressure: 250 atm. Inlet gas: CO:H₂ = 1:10. Definition of contact time same as in legend of Figure 4.

drops much more rapidly with aging than that of ZnO from smithsonite or from zinc acetate.

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 Corradini⁴⁹ 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(NO₃)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 magnification of 20,000).

Luminescence of ZnO. Schleede, Richter and Schmidt⁶⁶ 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 investigators⁶⁹ have found no relationship between luminescence and catalytic activity of ZnO. Natta and Corradini⁴⁹ 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-Cr₂O₃ 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 Corradini⁴⁹ 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^{3,69}. According to the experiments of Veltistova, Dolgov and Karpov⁶⁸ 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 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 Cr₂O₃ prepared by the decomposition, in an atmosphere of CO and H₂, of Cr(OH)₃, which in turn is obtained from solutions of Cr(NO₃)₃

and ammonia. Molstad and Dodge³⁸ 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 oxalate³⁷. Figure 6, based on the experimental data of Molstad and Dodge, shows the dependence upon temperature of the conversion of CO, when pure Cr₂O₃ 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 Cr₂O₃ has an activation energy lower than that of ZnO.

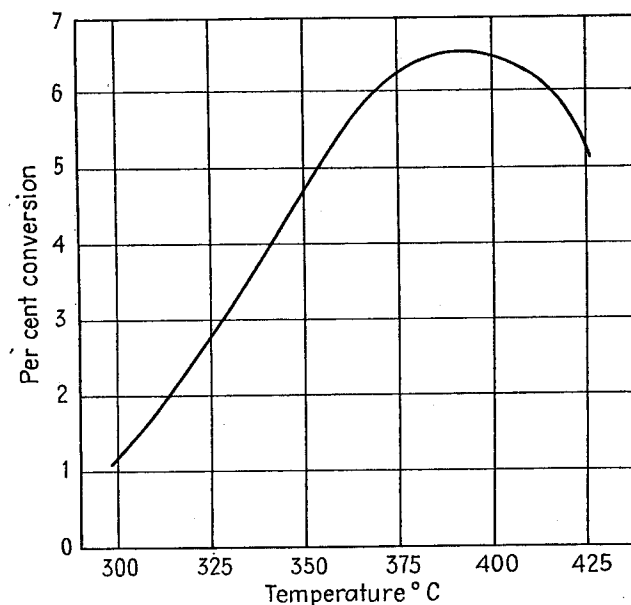


Figure 6. Percentage conversion of entering CO to methanol, under standard testing procedure at 178 atm., with a Cr₂O₃ catalyst³⁸.

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 Cr₂O₃ is much higher than that of ZnO from $Zn(OH)_2$ precipitated with ammonia. The purity of methanol prepared over Cr₂O₃ 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 Cr₂O₃ on its catalytic activity for the methanol synthesis has been emphasized also by Hüttig³⁴, who has found that only a very few varieties of Cr₂O₃ (for example, that from Cr(OH)₃ obtained by treating Cr(NO₃)₃ with ammonia) possess a relatively high catalytic activity.

G. Natta⁴⁰ tested a chromium oxide catalyst, and found it to have a very

poor activity. Lazier and Vaughen³⁷ found that their Cr_2O_3 catalysts showed a poor selectivity, but this may be due to the high working temperature ($>400^\circ\text{C}$).

In conclusion all the catalysts made with Cr_2O_3 , with the only exception of that prepared from $\text{Cr}(\text{NO}_3)_3$ 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 $\text{Cr}(\text{OH})_3$ (Molstad and Dodge) ³⁸	96	91
Zinc oxide from ammonia-precipitated $\text{Zn}(\text{OH})_2$ (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 ($^\circ\text{C}$)	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 $(\text{NH}_4)_2\text{CrO}_4$	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.

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. Natta⁴⁰ 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.

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-workers⁷⁵, however, claim that a mechanical mixture of ZnO and Cr₂O₃ is more active than other ZnO-Cr₂O₃ catalysts obtained by coprecipitation. Better results are obtained with the use of CrO₃, which appears to react more strongly with ZnO. The I. G. Farbenindustrie has used in its industrial operations²⁶ a catalyst prepared by mixing mechanically ZnO and Cr₂O₃. The grain density of such a catalyst has the value of 1.70–1.75.

(2) Adsorption of a solution of H₂CrO₄ by an active form of a pure ZnO catalyst leads to a surface corrosion of the crystals, with formation of ZnCrO₄ and of basic zinc chromate, which can be reduced to zinc chromite and to zinc oxide. Zinc chromite, ZnO·Cr₂O₃, 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 H₂CrO₄ 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 H₂CrO₄ leads to an appreciable lowering of the quality of the produced methanol⁷².

(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 Cr₂O₃) is completely amorphous to X-rays. Natta and Corradini⁴⁹ 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-Cr₂O₃ 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 Pschera¹⁸ the formation of spinel is related to the sublimation of the more volatile ZnO on the surface of Cr₂O₃. At high ratios of ZnO:Cr₂O₃, 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

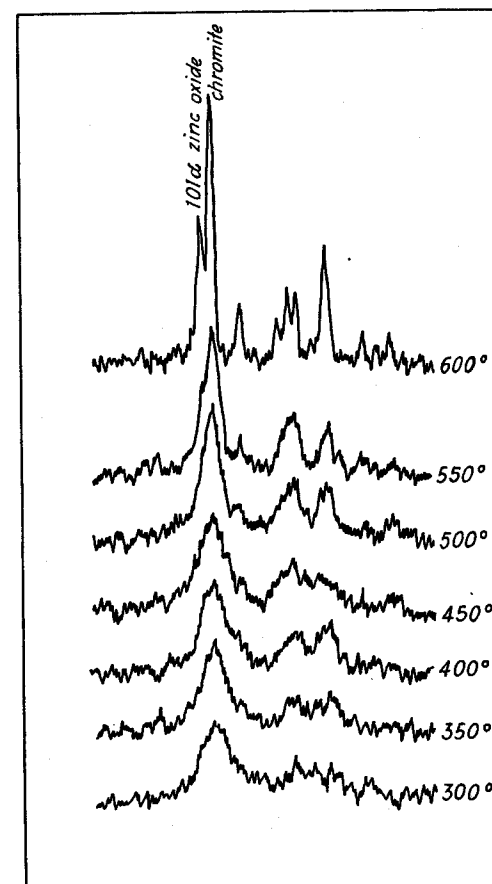


Figure 7. Development of pattern of ZnO and zinc chromite on heating a 1:1 ZnO:Cr₂O₃ catalyst⁴⁹.

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 Cr₂O₃ makes it possible to work in a temperature range, at which pure ZnO would lose its activity very easily³⁷. All the ZnO-Cr₂O₃ mixed catalysts present a high resistance to "aging."

Relationship between Cr₂O₃ Concentration and Activity of ZnO-

Cr₂O₃ 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 Cr₂O₃, while beyond a definite

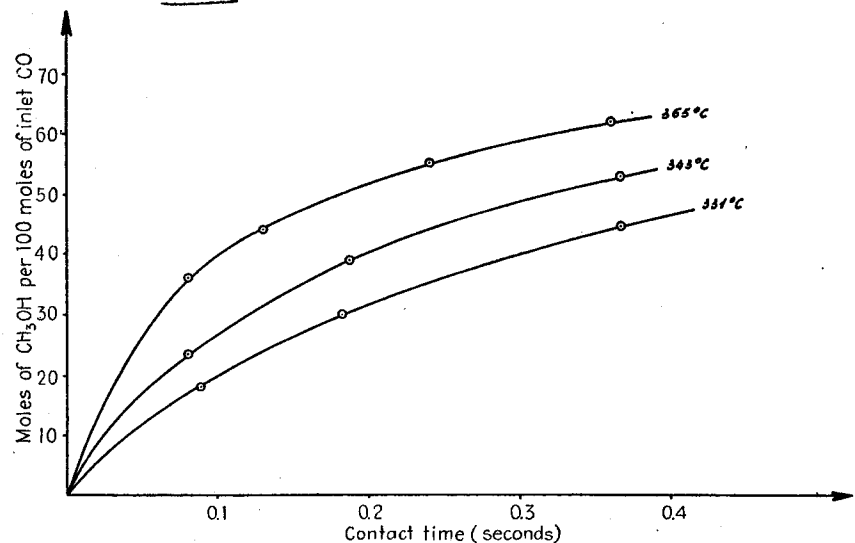


Figure 8. Moles of CH₃OH produced per 100 moles of inlet CO, as a function of contact time (see Figure 4 legend for definition of contact time) at different temperatures, with a ZnO:Cr₂O₃ catalyst prepared from a mixture of the acetates treated with chromic acid. Pressure: 250 atm. Inlet gas: CO:H₂ = 1:10.

Cr₂O₃ 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.

As far as activity is concerned, the optimum composition depends on the catalyst preparation method. The optimum percentage of Cr₂O₃ 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 percentages of chromium.

Extensive work on ZnO-Cr₂O₃ catalysts, obtained by precipitation of the

hydroxides with ammonia from the solutions of the nitrates has been carried on by Molstad and Dodge³⁸.

Figure 9 shows the variation of the CO conversion to methanol with the catalyst composition, according to the experimental data of Molstad and Dodge³⁸. 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 Cr₂O₃ lose their activity rapidly, while on the

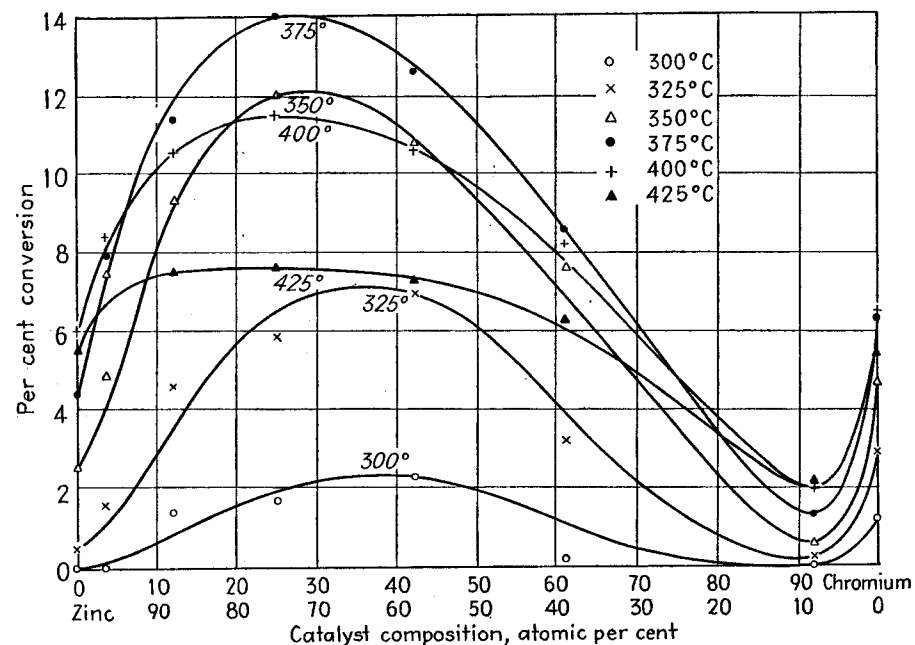


Figure 9. Percentage conversion of entering carbon monoxide to methanol during standard testing procedure at 178 atm³⁸.

contrary, the catalysts containing more than 25 per cent Cr₂O₃ seem to present an activity that increases as time goes on. The catalysts with high percentages of Cr₂O₃ show a shrinkage which varies directly with the percentages of chromium. One of the best catalysts, Zn₅₈Cr₄₂ 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.

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