parts of the apparatus is taken into account, with the possibility of methane being formed from the decomposition of ethane or acetylene formed from carbon and hydrogen in the hotter part of the furnace, or the lack of attainment of equilibrium due to too great a rate of flow through the reaction chamber, we feel that all variations are properly explained.

The writers' average value of I is -51.591. The curve of Figure 3 has been drawn to represent Equation 7 with this average value of I. This curve is in agreement, within the experimental error of all the points. The shaded points represent equilibrium starting in the reverse direction.

We can thus write

We can thus .....  $C(\text{graph}) + 2H_2(g) = CH_4(g)$   $\Delta F^{\circ}_{238\cdot1} = -11,573 \text{ cal.}$   $\Delta H^{\circ}_{238\cdot1} = -16,963 \text{ cal.}$   $\Delta F^{\circ} = -14,343 + 11.1 T \ln T - 0.0081T^2 + 0.000006T^3 - 51.591T \quad (8)$ 

This result is in complete agreement with that of Randall

and Gerard  $(1\beta)$ , which gives for the free energy of formation of methane from reaction 5

### $\Delta F^{\circ}_{298\cdot 1} = -11,582$ cal.

#### Literature Cited

- (1) Adams, J. Am. Chem. Soc., 36, 65 (1914).
- (2) Berthelot, Ann. chim. phys., [3] 67, 52 (1863).
- (3) Bone and Coward, (a) J. Chem. Soc., 93, 1197 (1908); (b) 97, 1219 (1910).
- (4) Bone and Jerdan, Ibid., (a) 71, 41 (1897); (b) 79, 1042 (1901).
- (5) Coward and Wilson, Ibid., 115, 1380 (1919).
- (6) Fonda and Van Aernem, J. IND. ENG. CHEM., 14, 539 (1922).
- (7) Lewis and Randall, (a) J. Am. Chem. Soc., 37, 458 (1915); (b) "Thermodynamics and Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.
- (8) Mayer and Altmayer, (a) Ber., 40, 2134 (1906); (b) J. Gasbel., 52, 238 (1909).
- (9) Medsforth, J. Chem. Soc., 123, 1452 (1923).
- (10) Pring, Ibid., 97, 498 (1910).
- (11) Pring and Fairlie, *Ibid.*, **101**, 91 (1912).
  (12) Pring and Hutton, *Ibid.*, **89**, 1591 (1906).
- (13) Randall and Gerard, IND, ENG, CHEM., 20, 1335 (1928)

# Catalysts for the Formation of Alcohols from Carbon Monoxide and Hydrogen

# V-Decomposition and Synthesis of Methanol with a Zinc-Copper-Chromium Oxide Catalyst<sup>1</sup>

# M. R. Fenske and Per K. Frolich

DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

REVIOUS papers (1, 3, 4, 5) have reported the properties of zinc-copper and zinc-chromium oxide catalysts used both in the decomposition of methanol at atmospheric pressure and in its synthesis under high pressure from carbon monoxide and hydrogen. While there is no literature on the ternary mixture of zinc-copperchromium oxides, except the multitudinous combinations mentioned in various patents, it follows from the results obtained with the zinc-copper and zinc-chromium mixtures

A study of the properties of a catalyst composed of the oxides of copper, zinc, and chromium in the molal ratio of 49:43:8 has brought out that this ternary mixture possesses considerably higher activity for both the decomposition and synthesis of methanol than any of the binary systems Cu-Zn and Cr-Zn discussed in previous papers. The ternary catalyst is active at low temperature, gives high conversion, and stands up well in the synthesis of methanol. In the decomposition experiments there is a tendency for the catalyst to deteriorate with time, but its activity may be restored by oxidation and subsequent reduction.

The reduction of the catalyst with methanol vapor is apparently preceded by decomposition of the alcohol into carbon monoxide and hydrogen. The carbon monoxide appears to be the active reducing agent while the hydrogen comes through unchanged.

that a combination of all three oxides should offer an interesting problem for investigation.

This paper presents a study of a catalyst prepared from a mixture of oxides containing the metals in the proportion  $Cu_{49}Zn_{43}Cr_8$ , this composition having been chosen as the one representing the highest activity of the several combinations tested in preliminary experiments on synthesis of methanol. While the mixture was prepared from the simple metallic oxides, it is difficult to say what the final state of oxidation was in the reduced catalyst (3).

# **Decomposition Experiments at Atmospheric Pressure**

PROCEDURE—The present catalyst was prepared from copper nitrate, zinc nitrate, and chromic acid anhydride. The nitrates were dissolved in hot water and precipitated separately with ammonium hydroxide. They were washed

Received July 26, 1929.

anol over the catalyst, starting at 150° C. and gradually raising the temperature until the operating temperature was reached.

The reduction period usually was about  $1^{1/2}$  hours. For heating the reactor a fused salt bath of sodium and potassium nitrates was used (Figure 1). An ordinary mercury thermoregulator, C, operating a relay which in turn varied the current through the hot plate, E, kept the temperature to within 1° C. The reaction tube, A, about 1.5 cm. in diameter and 17 cm. long, contained the catalyst and was connected by the heated tube, D, to the bulb, B, containing the methanol. The flow of methanol through the reaction tube was maintained reasonably constant by immersing the bulb B in a water bath kept at a constant temperature. Varying the temperature of the bath varied the rate of flow of the methanol. The tube F served to introduce oxygen, hydrogen, or any other gases, the exit tube, G, being connected to a trap to condense the undecomposed methanol.

three to four times by decantation, after which the gels of zinc and copper hydroxides were mixed together and washed on a Büchner funnel with 4 liters of hot water. Into this gel the chromium oxide was stirred and thoroughly mixed.

The resulting material was supported on a piece of 60mesh copper gauze (10 by 15 cm.) and dehydrated at 110° C. The gauze was then rolled up and placed in the reaction tube. Reduction was effected by passing a slow stream of carefully dehydrated meth-



The resulting gas was analyzed in a Williams gas-analysis apparatus for carbon dioxide. carbon monoxide, oxygen, nitrogen, methane, and hydrogen. The last two gases were determined by the explosion method.

EFFECT OF TEMPERATURE—Figure 2 shows the effect of temperature on the decomposition of methanol using the zinc-copper-chromium oxide catalyst. Although the space velocity was low, it is evident that the catalyst possessed marked activity, even at 220° C., while 90 per cent of the methanol was decomposed at 285° C., showing this catalyst



to be considerably more active than the zinc-copper or zincchromium mixtures (1, 4, 5), previously studied. In fact, on comparing the zinc-copper-chromium oxide catalyst with one consisting of 73.1 mol per cent zinc oxide and 26.9 mol per cent chromium oxide described in an earlier paper (1), it appears that the binary catalyst decomposed about 40 per cent of the methanol at 340° C., whereas the ternary mixture gave the same decomposition at a temperature about 100° C. lower at comparable space velocities.

From Figure 2 it will be seen that at temperatures above 250° C. and a space velocity of 25 cc. of gaseous methanol (at N. T. P.) per hour per cubic centimeter of catalyst the decomposition, as evidenced by the percentage of carbon monoxide in the gas, was almost entirely into carbon monoxide and hydrogen (33 per cent CO and 67 per cent  $H_2$ ) in accordance with the over-all reaction

# $CH_{1}OH = CO + 2H_{2}$

Had formaldehyde and methyl formate resulted to any great

extent, as in the case of the zinc-copper catalysts (4). the gas would contain more than 67 per cent hydrogen considering that the formaldehyde and methyl formate are removed before analysis:

$$\begin{array}{c} \text{CH}_3\text{OH} \longrightarrow \text{CH}_2\text{O} + \text{H}_2\\ \text{Formaldehyde}\\ \text{CH}_3\text{OH} \xrightarrow{1/2} \text{H}_2 \text{CO}_2 \text{.} \text{CH}_3 + \text{H}_2\\ \text{Methyl formate} \end{array}$$

That these products do result at lower temperatures is indicated by a somewhat higher percentage of hydrogen and lower carbon monoxide content of the exit gas. This is more noticeable in Figure 4 than in Figure 2. Since the carbon dioxide curve in Figure 2 decreases with temperature, and also with time of run, its presence is probably due to further slow reduction of the catalyst.

LIFE OF CATALYST. REVIVIFICATION—The activity of the zinc-copper-chromium oxide catalyst decreases gradually as time goes on and approaches an asymptotic value. Table I illustrates this effect for a space velocity of about 110 cc. of gaseous methanol (at N. T. P.) per hour per cubic centimeter of contact material. The catalyst can be rejuvenated, however, by oxidation and subsequent reduction, as Figure 3 shows. Here the lower curve represents the activity observed after a catalyst had been in use for some time, while the upper curve resulted after admission of a slow stream of oxygen at 150–180° C. followed by reduction with methanol vapor at 180° C.

	Table I—D	ecomposit	ion of Me	thanol	
TIME FROM	CH <sub>2</sub> OH EXIT GAS COMPOSITION				
START	DECOMPOSED	CO2	CO	CH4	$H_2$
Hours	Per cent	Per cent	Per cent	Per cent	Per cent
	TEMPERATURE, 255° C.				
0	86	13.7	19.4	0.6	65. <b>6</b>
1.4	64	6.6	23.7	0.9	68.8
3.4	43	7.5	21.5	0.9	69.5
6.0	37	10.0	18.0	0.7	71.2
10.5	32	5.8	28.2	• • •	66.0
	TEMPERATURE, 285° C.				
1	86	4.8	29.8	0.9	64.6
$\overline{2}, 5$	64	2.6	31.2	1.2	64.5
7.0	$\overline{51}$	1.0	32.0	1.5	65.3

Repeating this operation did not cause any further increase in activity as measured by the percentage of methanol decomposed plotted in Figure 3. However, Figure 4 brings out a change in mechanism of the decomposition reaction





upon successive oxidations and reductions. The increase in the carbon monoxide concentration of the exit gas at low temperature shows that these treatments increased the portion of the methanol being decomposed into carbon monoxide and hydrogen. In other words, the increased activity resulting from the first oxidation and reduction led to more complete decomposition of the alcohol with less formaldehyde and methyl formate production. In spite of the fact that the percentage of methanol decomposed was not altered by the second oxidation and reduction, Figure 4 shows a further increase in the carbon monoxide concentration with a corresponding depression of formaldehyde and methyl formate.

An experiment was also made in which a catalyst was poisoned by passing ordinary illuminating gas over it all night at 160-170° C. After a test made the next morning had shown it to be entirely inactive, it was oxidized by passing oxygen through the reactor starting at 195° C. and gradually increasing the temperature up to 300° C. Subsequent reduction with methanol vapor brought the activity of the catalyst back to about 70 per cent of its original value. It is reasonable to assume that the poisoning was caused by the sulfur compounds present in the illuminating gas and that the sulfur thus combined with the catalyst as metallic sulfides was more or less completely removed by the oxidation process.



Figure 4—Effect of Successive Oxidations and Reductions on Zinc-Copper-Chromium Catalyst on Decomposition of Methanol Space velocity = 110

MECHANISM OF REDUCTION OF CATALYST—From Figure 4 it is also seen that reduction of the catalyst and catalytic decomposition of the methanol took place simultaneously, as evidenced by the occurrence of both carbon dioxide and carbon monoxide in the gas. Considerable reduction took place at  $180^{\circ}$  C. and as the temperature increased the carbon dioxide content of the exit gas decreased, indicating that the reduction of the catalyst was becoming more complete. That the carbon dioxide was due to reduction of the metallic oxides, and did not result from decomposition of the metallo alone, was demonstrated by the absence of the other products which are invariably associated with production of carbon dioxide from methanol (1). The products consisted essentially of hydrogen and the oxides of carbon, with only an insignificant amount of methane.

The fact that the ratio of  $H_2$  to (CO + CO<sub>2</sub>) is very nearly 2:1-i. e., the ratio in which hydrogen and carbon monoxide are formed by decomposition of methanol-points to carbon monoxide as the reducing agent. Had hydrogen entered into the reduction process to any considerable extent, it would have been removed from the gaseous products as water and the above ratio would not have been maintained. A more elaborate study of the early stage of the reduction process (2) led to the following conclusions: Starting with the metallic oxide mixture, the initial reduction may involve the complete oxidation of methanol into carbon dioxide and water, which would give a carbon dioxide content of 100 per cent in the gaseous products. As soon as the reduction has started, however, active spots are formed which decompose the methanol into carbon monoxide and hydrogen, and as these gases, perhaps in a nascent state, pass over the unreduced catalyst, the carbon monoxide rather than the hydrogen acts as the reducing agent with formation of carbon dioxide. This explanation is substantiated by the fact that even the smallest sample of gas resulting from the initial stage of reduction at temperatures from  $220^{\circ}$  C. and above always contained close to two-thirds hydrogen, while the remaining one-third was composed essentially of carbon monoxide and carbon dioxide. The smaller this initial sample of gas the higher was the carbon dioxide content, although the carbon monoxide never disappeared completely.

REDUCTION OF CATALYSTS WITH MIXTURES OF CARBON MONONIDE AND HYDROGEN-In order to prove whether carbon monoxide was actually oxidized in preference to hydrogen, as in the case of catalysts of the hopcalite type used in gas masks for combustion of carbon monoxide to dioxide (6) or the catalysts which have been developed for final clean-up of carbon monoxide from the gases used in the ammonia synthesis (7), mixtures of carbon monoxide and hydrogen were passed over the freshly prepared oxide mixture at different temperatures. With mixtures containing from 30 to 58 per cent carbon monoxide and the remainder hydrogen, no reaction could be detected below 80° C. At 100° C. 3 per cent of the carbon monoxide was converted into dioxide while the hydrogen was untouched. At 250° C. 5.7 per cent carbon monoxide went to dioxide with the hydrogen still coming through unchanged.

On the basis of these results it is safe to conclude that the carbon monoxide is the reducing agent and that the hydrogen is unchanged whether it be used in the elementary state or is formed from methanol. While it might be inferred that any water formed by oxidation of the hydrogen could react with carbon monoxide according to the water gas reaction  $H_{10} + C_{10} = H_{10} + C_{10}$ 

$$H_2O + CO = H_2 + CO_2$$

thus preventing any net change, it is highly improbable that this reaction should go quantitatively at the low temperatures employed.

# Synthesis Experiments at High Pressure

PROCEDURE—The apparatus and experimental procedure used in the studies on synthesis of methanol at high pressure with this catalyst are described elsewhere (8). Two reactions were used in series, the tests being confined to the second reactor with the first serving as a final purifier for the gas in order to remove iron carbonyl and traces of sulfur compounds. The pressure used was 3000 pounds per square inch (204 atmospheres) and the reactor contained 40 cc. of catalyst supported on copper shot to secure uniform temperature distribution.

GENERAL RE-SULTS—Figure 5 shows the percentage conversion of carbon monoxide to methanol as a function of temperature. It is seen that in the synthesis of methanol under high pressure from carbon monoxide and hydrogen the conversions are high



Inlet gas composition = 20.4% CO and 72% H<sub>2</sub> Space velocity = 3900 on basis of entering gas Pressure = 204 atmospheres

for this catalyst and that it is active at low temperatures. These facts are in good agreement with the data obtained in the decomposition experiments at atmospheric pressure.

The curve for efficiency is the carbon monoxide converted to methanol divided by the total carbon monoxide reacting and shows the extent of side reactions. Of the carbon monoxide going to products other than methanol, the larger part went to formation of methane by the reactions: November, 1929

$$\begin{array}{l} 2\text{CO} + 2\text{H}_2 = \text{CH}_4 + \text{CO}_2 \\ \text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} \end{array}$$

Of these two the first reaction predominated, as evidenced by material balances on the runs. This checks the results previously obtained with a mixture of the oxides of zinc, copper, and aluminum (8).

The methanol formed was 99 to 100 per cent pure, the remainder being chiefly water.

METHANOL EQUILIBRIUM—The equilibrium conversions for these conditions as calculated from the data of Smith and Branting ( $\theta$ ) are also indicated in Figure 5. The equilibrium constant was determined from the relationship  $-\Delta F = RT \ln K$  and the equation given by these authors for the free energy change accompanying the reaction

 $CO + 2H_2 = CH_3OH$ 

$$\Delta F = -20,857 + 41.17 \text{ log } T - 0.01423 T^2 - 54.42 T$$

These data indicate equilibrium to be reached in the experiment at 322° C. with the following partial pressures in the exit gas, 11.7, 122, and 43.3 atmospheres for carbon monoxide, hydrogen, and methanol, respectively. Substituting the fugacity of methanol gives a value of about 40 atmospheres instead of 43.3, and on this basis the equilibrium constant becomes  $2.3 \times 10^{-4}$  at  $322^{\circ}$  C.



Figure 6—Continues Run with 7inc-Copper-Chromium Catalyst with Reactors I and II in Series Pressure = 204 atmospheres

Assuming the value thus calculated to be correct, equilibrium was reached in spite of the relatively high space velocity employed. This points to a catalyst of considerable activity.

A marked deviation between the calculated and observed values below 322° C. will be noted in Figure 5. The rather unexpected decrease in carbon monoxide converted to methanol in this temperature range should not be construed to mean that Smith and Branting's data are in error, for it must be remembered that the present experiments did not aim at equilibrium conditions and this leaves room for other interpretations. It is better to consider these results as a qualitative confirmation of their equilibrium determinations which were made at atmospheric pressure.

LIFE of CATALYST—Figure 6 shows the results of a 48hour test on this catalyst with reactors I and II in series. It will be noticed from the upper curve that the activity in chamber II remained constant at a high level over practically the entire period with only a slight tendency to drop off toward the end of the run. Judging from the performance of chamber I, it may be assumed that this drop was due to some poisonous constituents, probably sulfur compounds in the gas, escaping into the second reactor.

A comparison with life tests on a catalyst composed of the oxides of zinc, copper, and aluminum (8) shows that the present mixture is less susceptible to poisoning and yet gives approximately twice the conversion of carbon monoxide into methanol at 20° C. lower temperature under otherwise constant conditions.

# Conclusions

When compared with the results of previous investigations, the present study brings out the superiority of the zinccopper-chromium oxide catalyst (49 Cu: 43Zn: 8Cr) to binary mixtures of zinc-copper and zinc-chromium as evidenced by tests on decomposition of methanol. The same has been shown to hold with regard to the synthesis of the alcohol from water gas. In previous papers in which the activity of a catalyst for decomposition of methanol has been correlated with its activity for the synthesis by the reverse reaction, it has been pointed out that in order for a catalyst to be active in the synthesis of methanol from carbon monoxide and hydrogen, it should yield these products and not formaldehyde or methyl formate in the decomposition reaction. In other words, a catalyst which decomposes methanol into carbon monoxide is capable of converting carbon monoxide back into methanol by the reverse reaction, whereas catalysts which decompose the alcohol into intermediate products rather than carbon monoxide do not possess any marked tendency to build up methanol from water gas. In view of this, it might have been predicted that the present mixture of the oxides of copper, zinc, and chromium would be a good catalyst for the synthesis, because it gives unusually high yields of carbon monoxide by the decomposition of methanol.

The higher activity of this catalyst is further evidenced by its performance at relatively low temperatures as well as by the fact that it gives methanol conversions approaching Smith and Branting's equilibrium values even at a moderately high space velocity.

The catalyst seems to stand up well in operation in the high-pressure synthesis, but has a tendency to deteriorate on age in the decomposition of methanol at atmospheric pressure. However, the activity may be restored by oxidation and subsequent reduction with methanol vapor. Although such experiments were only conducted in connection with the decomposition work, it may be expected that the same method of revivifying the catalyst would be applicable to the methanol synthesis at high pressure.

It has been shown that the carbon monoxide resulting from decomposition of methanol vapor is the active agent in reducing the catalyst, while the hydrogen apparently does not take part in the reduction process as shown by experiments in the temperature range of  $80^{\circ}$  to  $250^{\circ}$  C. No attempt has been made to ascertain how far the reduction proceeds. However, by comparison with previous work it may be assumed that the copper oxide is practically completely reduced while the zinc oxide loses only a relatively small portion of its oxygen content. It has been suggested by other experimenters that the chromium is present in such mixtures in the form of a suboxide.

# Acknowledgment

The experimental work on synthesis of methanol with the present catalyst was done in this laboratory about four years ago and the writers are indebted to various members of the laboratory staff for active participation in this phase of the work.

#### Literature Cited

- (1) Cryder and Frolich, IND. ENG. CHEM., 21, 867 (1929).
- (2) Doctor's Thesis (1928), M. I. T. Library, gives further details.
- (3) Frolich, Davis, and Fenske, IND. ENG. CHEM., 21, 109 (1929).
- (4) Frolich, Fenske, and Quiggle, *Ibid.*, **20**, 694 (1928)
- (5) Frolich, Fenske, Taylor, and Southwick, *Ibid.*, **20**, 1327 (1928).
- (6) Green, "Industrial Catalysis," p. 114, MacMillan, 1928.
- (7) Green, Ibid., p. 110.
- (8) Lewis and Frolich, IND. ENG. CHEM., 20, 285 (1928).
- (9) Smith and Branting, J. Am. Chem. Soc., 51, 134 (1929).

Temperature =  $281^{\circ}$  C. Space velocity = (S. V.) calculated on basis of gas entering each chamber