

BEHAVIOR OF ZINC OXIDE AND ZINC OXIDE-CHROMIUM OXIDE CATALYSTS IN THE DECOMPOSITION AND SYNTHESIS OF METHANOL*

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Introduction

The search for a catalyst which will accelerate a given reaction is frequently conducted by studying the action of the prospective catalyst on the desired product. This procedure, while thermodynamically sound, does not always give conclusive results. This is especially true when mixed catalysts are being tested in the decomposition of a single substance which it is desired to synthesize from two reactants. Comparatively little work has been done on the action of mixed or promoted catalysts on the decomposition or transformation of a single substance. Unless the adsorption at the interfaces of mixed or promoted catalysts is different (quantitatively, at least) from the adsorption of simple catalysts, it is difficult to account for promoter action in the decomposition of a single substance.

Palmer¹ found that magnesium oxide and manganous oxide promote copper as a catalyst for the dehydrogenation of ethanol, provided that these promoters are present in amounts greater than 2.5 and 0.4 atomic percent, respectively. Smith and Hawk² found that zinc oxide, (prepared by precipitation with sodium carbonate from zinc nitrate solution, followed by drying and heating to form the oxide), was of the same activity in the decomposition of methanol as their most active $\text{ZnO-Cr}_2\text{O}_3$ preparation. Indeed, these authors found that the addition of chromium oxide in any proportion other than 8 $\text{ZnO-1 Cr}_2\text{O}_3$ resulted in a catalyst markedly less active than the most active zinc oxide catalyst.

During the course of a research not primarily concerned with the purposes of this paper, some data on the behavior of zinc oxide and zinc oxide-chromium oxide catalysts in the decomposition of methanol were obtained in this laboratory by A. W. Gauger, and in the synthesis by the writer.

Methanol Decomposition

Methanol was heated in a copper container immersed in a water-bath. The flow of vapor from this container was controlled by means of a brass valve, from which the methanol passed through a flowmeter kept in an oven at 100°C , and thence into the catalyst chamber. The latter consisted of a Pyrex U-tube heated by means of an electrical resistance furnace.

The gases and vapors from the catalyst passed through a condenser immersed in a methanol-solid CO_2 bath, thence through two water scrubbers,

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¹ Proc. Roy. Soc., **101A**, 175 (1922).

² J. Phys. Chem., **32**, 420 (1928).

and finally through a flow-meter. The off-gases were, unfortunately, not analyzed. The percent decomposition was calculated from the amount of methanol recovered.

The catalysts were prepared as follows:—

(1) 200 grams of zinc oxide¹ were mixed with 22 grams of chromic acid, and enough water added to form a thick paste. 100 grams of 4-8 mesh pumice were mixed with the paste, and the mixture dried at 150°C.

(2) 242 grams of zinc carbonate were dissolved in formic acid, and the solution mixed with 50 grams of asbestos. The mixture was evaporated to dryness, and dried at 150°C.

Both catalysts were treated at 200°C with hydrogen saturated with methanol at room temperature, for several hours before use.

TABLE I
Methanol Decomposition

Catalyst No.	Wt. grams	Apparent Volume cc.	Temp. °C.	Space Velocity per hour	% Decomposition
1	185	543	300	110	3
1	185	543	365	110	80
2	193	400	300	111	4
2	193	400	342	108	78

It will be observed from Table I, that these catalysts were of approximately equal activity. Catalyst No. 2 was of greater apparent density than No. 1, and because of this and the difference in the character of the supports used, a rigorous comparison of the data is not permissible. However, if the large increase in activity usually associated with promotion existed, a much greater variation in the percent decomposition would have been observed.

Synthesis of Methanol

The earliest published work on the use of zinc oxide (per se) as a catalyst for methanol synthesis was that of Patart.² Using "pure" zinc oxide as a catalyst at 400-420°C, and 150-200 atmospheres pressure of $2\text{H}_2 + 1\text{CO}$, the liquid condensate was of 0.896 specific gravity at 19°C, and contained about 80% methanol, the bulk of the remaining 20% being water. The data given are insufficient to calculate space velocity or space-time-yield. The method of preparation of the catalyst is not described. An equally laconic reference to the use of zinc oxide was published in a description of experiments at the Badische Anilin und Soda Fabrik.³ Dreyfus⁴ also mentions the use of zinc oxide. Woodruff and Bloomfield⁵ state: "Zinc oxide—per se—has no catalytic effect on the methanol reaction."

¹ Baker's C. P. chemicals were used without further purification.

² *Chimie et Industrie*, 13, No. 2, 182 (1925).

³ *Die Metallbörse*, 48, 1317 (1925).

⁴ *Eng. Pat.* 262, 494 (1926).

⁵ *U. S. Pat.* 1,608,643 (1926).

Zinc and chromium oxides are separately listed by Mittasch and Schneider¹, and the mixed catalyst specifically claimed for methanol synthesis by Mittasch and Pier.²

The data given below on the synthesis of methanol were obtained by using $4\text{H}_2 + 1\text{CO}$ gas at 3000 lbs. pressure. The reactants were prepared passing "blue water-gas" (obtained from an ordinary water-gas generator) mixed with steam over a water-gas shift catalyst so that the H_2/CO ratio was changed from about 1.1 to 1.9. After scrubbing with caustic soda solution, the gas was diluted with electrolytic hydrogen until a ratio of $4\text{H}_2/1\text{CO}$ was obtained.

The reaction vessel was made of chrome-vanadium steel, and was lined with copper, heating being accomplished by an electric furnace surrounding the converter. The volume of the catalyst space was 42 cc. The catalyst temperature was measured by means of a concentric thermocouple³ imbedded in the catalyst. The temperature of the furnace was controlled by a Walton Torrey thermoregulator.

The converter off-gases were led into a pressure condenser, and thence at atmospheric pressure to a gas meter.

Table II gives the results obtained using zinc oxide catalysts and catalyst No. 1 ($\text{ZnO-Cr}_2\text{O}_3$). The latter was prepared as described above, except that the pumice was omitted, and the catalyst used in the form of a fine granular powder. The preparation of the various forms of zinc oxide is described below. All of these were used as granular powders of approximately the same screen analysis as Catalyst No. 1. All tests were made after the catalyst had been treated with $9\text{H}_2 + 1\text{CH}_3\text{OH}$ at 300°C for 12 hours.

TABLE II
Methanol Synthesis
Space Velocity per hour = 4000 in all cases

Catalyst No.	Temp °C.	Space Time Yield ⁴
1	330	660
3	330	360
3A	330	Inactive
	350	"
3B	330	290
3C	330	Slightly Active
	350	88
3D	330	360

The product obtained was in all cases better than 95% methanol by volume. Each of the space-time-yield figures represents an average value taken for determinations made about once per hour for at least three hours

¹ U. S. Pat. 1,201,850 (1916).

² U. S. Pat. 1,558,559 (1925).

³ This was a copper-constantan couple made by passing an electrically insulated constantan wire thru a piece of copper tubing and welding at one end. The other end was silver soldered into a threaded brass spindle. The latter was screwed into a T attached to the stem of the converter, the reactants being admitted thru the other end of the T.

⁴ S. T. Y. = lbs. of CH_3OH per cubic foot of catalyst per 24 hours.

and in some cases (Catalyst No. 1, and No. 3) the tests were prolonged to 200-300 hours. The average deviation from the mean S.T.Y. varied for the different catalysts from 5% to 10%.

Preparation of Zinc Oxide Catalysts

(No. 3) 200 grams of zinc oxide were mixed with one liter of water, and sufficient concentrated nitric acid added to dissolve the oxide. An excess of ammonia was added to form $\text{Zn}(\text{NH}_3)^{++}$. 200 grams of NaOH dissolved in 500 cc. of water were added, and the mixture boiled until no odor of ammonia could be detected. After filtration and washing (until no test for nitrates was obtained in the wash waters), the filter cake was dried at 200°C.

(No. 3A) 200 grams of zinc oxide were mixed with one liter of water, and an equivalent quantity of concentrated nitric acid added. 600 grams of 28% ammonia were added, and the resulting mixture filtered. The filter cake was washed and dried as in No. 3.

(No. 3B) Identical with preparation of No. 3, except that the addition of ammonia was omitted.

(No. 3C) Zinc formate was prepared in the form of a fine crystal powder.

(No. 3D) 81 grams of zinc oxide were dissolved in one liter of a dilute acetic acid solution containing 120 grams of acetic acid. A solution of 171 grams of $\text{Ba}(\text{OH})_2$ in two liters of water was mixed with the zinc acetate solution and the mixture filtered. The filter cake was washed until no test for acetates was obtained in the wash waters, and subsequently dried at 200°C.

Of two preparations of chromium oxide catalysts, one made by soaking pumice in molten CrO_3 , and the other by precipitation of $\text{Cr}(\text{OH})_3$, the latter was found to be only slightly active (about 20 S.T.Y. at 330°C), and the former inactive.

The slight activity of chromium oxide, combined with the fact that the most active zinc oxide catalysts gave only about 50% of the yield obtained from the $\text{ZnO-Cr}_2\text{O}_3$ catalyst, indicates that the $\text{ZnO-Cr}_2\text{O}_3$ interfaces enhance the activity of zinc oxide in methanol synthesis. The fact that no such increase in activity is observed in the decomposition of methanol may be due to the fact that the experiments on the decomposition were made at atmospheric pressure instead of at the partial pressure corresponding to the conditions in the synthesis. However, it seems improbable that twenty atmospheres pressure of CH_3OH would change the primary adsorption characteristics of either ZnO or $\text{ZnO-Cr}_2\text{O}_3$ catalysts.¹

Regarding the mechanism of the synthetic reaction very little can be stated, because of insufficient data. The variation of the space-time-yield with space velocity (see Table III) is characteristic of any contact reaction

¹ This statement is based upon the work of Palmer and Constable (Proc. Roy. Soc. 98A, 13, (1920); 99A, 412 (1921); 101A, 178 (1922); 106A, 250 (1924); 107A, 255, 270 (1925); 108A, 355 (1925)) who showed that the rate of dehydrogenation of ethanol is independent of the pressure. This is due to the fact that the reaction proceeds in a unimolecular layer on the catalyst surface. It is probable that catalysts for the decomposition of methanol would be similarly unaffected by an increased pressure of CH_3OH .

in which the conversion is relatively high, and hence the data are insufficient to indicate whether the adsorption of the methanol formed retards the synthesis.

TABLE III
Space-Velocity:
Space-time-yield Relationship

Temperature = 330°C	Pressure = 3000 lbs. of 4H ₂ + 1 CO gas	Catalyst No. 1
Space velocity per hour	Space time yield	% Conversion of CO to CH ₃ OH
2180	476	52
2430	500	50.5
2860	566	46
4080	663	40
4550	790	41
5480	900	38
5520	874	39
7850	1110	33
7900	1120	33
8260	1230	30
11600	1450	30
13500	1530	27
14900	1535	24.5
17000	1660	23
19200	1910	23.5
25300	2260	21

No data on the change of S.T.Y. with pressure are available for this catalyst. The change of S.T.Y. with temperature is complicated by the extraordinarily narrow range of temperature in which Catalyst No. 1 may be used without deterioration due to sintering. Thus this catalyst is practically inactive at temperatures appreciably below 300°C, and at 350°C the S.T.Y. is lower than that obtained at 330°C. Rapid measurements at 350°C indicate a somewhat larger yield than at 330°C.

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Summary

The addition of chromium oxide to a zinc oxide catalyst in certain proportions increases the activity of the catalyst for methanol synthesis, but does not affect its activity for methanol decomposition (at atmospheric pressure).

Some data describing the characteristics of a ZnO-Cr₂O₃ catalyst in the synthesis of methanol are given.