JOURNAL OF CATALYSIS **111**, 445–449 (1988)

Higher Alcohol Synthesis over CuO/ZnO Catalysts: Relationship between Methanol and Higher Alcohol Syntheses

INTRODUCTION

Catalysts based on CuO/ZnO are active for the synthesis of both methanol and higher alcohols (*1–5*). The selectivity to higher alcohols can be promoted by alkalinization of the catalyst (*3, 5*), but methanol is always the principal reaction product. It is desirable, in order to develop greater selectivity toward higher alcohols, to know the relationship, if any, between methanol formation and higher alcohol formation. Although several schemes have been proposed for the formation of higher alcohols over metal oxide catalysts, and methanol has often been regarded (*7–9*) as an intermediate in the reaction, little work has been done to determine whether the synthesis of higher alcohols and that of methanol are related and in particular whether the same catalytic sites are involved in both syntheses.

In early mechanistic studies it was proposed that over methanol catalysts higher alcohols are formed either by stepwise condensation of methanol (*8, 9*) or by successive carbonylation (*2, 7*) of lower alcohols, starting with methanol. Analogous mechanisms were also proposed for other C_1 intermediates (formaldehyde (*10*), surface methoxide (*2*)). More recently, several schemes based on the addition of various intermediates to a growing alcohol chain have been proposed (*4, 5, 11*). None of these new schemes provide information about the relationship between methanol and higher alcohol formation, except for suggesting that any of the C_1 species proposed as intermediates in the higher alcohol synthesis may also be an intermediate in the methanol synthesis. Moreover, none of these mechanistic studies have addressed the question of whether the same sites are active for both methanol and higher alcohol formation. In fact, the nature of the active sites for the synthesis of the higher alcohols has received little attention, and that for the synthesis of methanol, although the subject of numerous studies (*12*), remains uncertain.

The objective of the work reported here is to establish whether the activity of CuO/ZnO catalysts for the methanol synthesis can be correlated with that for the synthesis of higher alcohols, and, if a relation exists between the two syntheses, to determine its nature.

EXPERIMENTAL METHODS

Materials. The CuO/ZnO catalysts were prepared according to the procedure of Herman *et al.* (*13*), by coprecipitation of mixed carbonates with Na_2CO_3 at pH 7.0 from solutions of the nitrates. After several washings to remove the residual sodium, the catalyst was dried at 140°C for 16 h and calcined at 350°C for 4 h. The catalyst was then tableted, crushed, and sieved to 16/40 mesh. The $CuO/ZnO/Al_2O_3$ catalyst (atomic ratio Cu/Zn/Al = 1/1/0.3) was a commercial sample (C-79) obtained from United Catalysts, Inc. The $\frac{1}{4}$-in. tablets were crushed, sieved to 16/40 mesh size, and calcined at 350°C for 4 h. The resulting catalyst granules were either used as cooled or impregnated by incipient wetness (10 cc solution/25 g catalyst) with sufficient aqueous solution of $Co(NO_3)_2 \cdot 6H_2o$ to add 0.3% cobalt to the catalyst. The catalyst

0021-9517/88 $3.00

was then dried at 140° for 16 h and calcined at 350°C to decompose the metal salt.

Hydrogen (Linde, 99.99%) was passed through a Deoxo purifier to remove traces of oxygen, followed by a 4A molecular sieve trap to dry the gas. Carbon monoxide (Matheson, 99.5%) was passed through an activated charcoal trap to remove possible metal carbonyls. Methanol (Fischer, 99.9%) was used as received.

Apparatus. Studies were performed using a fixed-bed single-pass reactor. Gas flows were measured and controlled with mass flow controllers. The gases were mixed and delivered to the reactor with a Whitey compressor. The pressure of the system was maintained at 65 atm for all experiments using a Moore regulator. Liquids were introduced to the reactor using an Eldex chromatography pump. The reactor effluent was cooled to 0–4°C to condense liquid products. The gas phase was passed through an analytical train consisting of a gas chromatograph and wet test meter.

Product analysis. The gas phase was analyzed at 20-min intervals using a modified Applied Automation/Perkin–Elmer gas chromatograph. Hydrogen was determined in a nitrogen carrier, while a helium carrier was used to analyze for CO, CO_2, CH_4, and other light hydrocarbons. Condensed liquids were analyzed using a Porapak Q column with a thermal conductivity detector, or a methyl silicone capillary column with a FID detector. The identity of each eluted component was confirmed with GC/MS.

Procedure. The catalyst charge, generally 1–5 cc of catalyst granules, was mixed with sufficient alundum to provide a 10-cc bed and loaded into a 0.75-in.-diameter 316 stainless-steel reactor with a 0.25-in. thermocouple well running axially through the catalyst bed. Following a 1-h purge in nitrogen while the temperature was raised to 200°C, a mixture of 3% hydrogen in nitrogen was admitted at 5000 GHSV for 4 h to reduce the catalyst. The pressure and temperature were then adjusted to reaction conditions. A catalytic run consisted of passing the reactants over the catalyst for a period of 16 h during which the liquids were collected. Following the experiment, the system was depressurized, the receivers were removed and drained, and the liquids were analyzed.

RESULTS AND DISCUSSION

The dependence of the higher alcohol synthesis activity on catalyst composition was studied over four catalysts with compositions ranging from CuO/ZnO = 20/40 to 50/50. In the present study, to promote the formation of higher alcohols, synthesis gas with $H_2/CO = \frac{1}{2}$ was used and the synthesis was carried out at 285°C. The yields of total alcohols are listed in Table 1, and the yields of both methanol and higher alcohols are plotted as a function of catalyst composition in Fig. 1. For both methanol and the higher alcohols a maximum in the activity was found at a composition CuO/ZnO = 30/70.

The measurements were also made with a feed containing 6% CO_2. The results listed in Table 1 and plotted in Fig. 1 indicate that the CO_2 also promotes the formation of higher alcohols, and confirm that a maximum in the rate of formation of higher alcohols occurs at the composition CuO/ZnO= 30/70. The data given in Table 1 show that the methanol synthesis activity was promoted by the presence of the CO_2; how-

TABLE 1

Effects of the Cu : Zn Ratio and of CO_2 on Alcohol Yields for CuO/ZnO Catalysts

Cu : Zn ratio	Feed $H_2 : CO : CO_2$	Temp. (°C)	Alcohol yield (g/g cat./h)	Surface area[a] (m^2/g)
20 : 80	100 : 200 : 0	288	0.46	32.4
30 : 70	100 : 200 : 0	289	0.57	33.3
40 : 60	100 : 200 : 0	284	0.18	14.5
50 : 50	100 : 200 : 0	288	0.10	8.9
20 : 80	100 : 188 : 12	284	1.19	
30 : 70	100 : 188 : 12	286	1.14	
40 : 60	100 : 188 : 12	286	0.53	
50 : 50	100 : 188 : 12	287	0.44	

[a] Surface area of used catalyst.

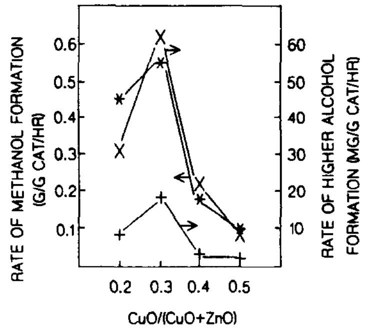

FIG. 1. Rate of formation of (∗) methanol and (+) higher alcohols with the feed containing no CO_2, and of (×) higher alcohols with the feed containing 6% CO_2, as a function of catalyst composition (285°C, 65 atm).

ever, the methanol yields were too close to the equilibrium values (*15*) for the results to be representative of the activities of the catalysts, and the maximum in the activity is not discernible. The promoting effects of small amounts of CO_2 in the feed for the synthesis of methanol over CuO/ZnO are already well documented (*13*).

The dependence of the methanol synthesis activity on the CuO/ZnO molar ratio was first investigated by Frolich *et al.* (*14*) using a CO_2-free feed with a H_2-to-CO volume ratio of 2.6 to 1. A maximum in the methanol synthesis activity was observed at a catalyst composition near CuO/ZnO = 30/70. More recently Herman *et al.* (*13*) have carried out a similar study using a feed with a H_2/Co ratio of 2.9/1 and containing 6% CO_2. They also observed a maximum in the methanol synthesis activity at a catalyst composition CuO/ZnO = 30/70; in addition a second maximum was observed at CuO/ZnO = 70/30. In the two previous studies a high H_2/CO ratio was used to maintain a high selectivity to methanol, so that in their experiments Herman *et al.* observed no carbon-containing product other than methanol.

The similarity in the influence of the catalyst composition and of CO_2 on the methanol synthesis and on the higher alcohol synthesis indicates that the two syntheses are related. It is not clear, however, whether they are related because they occur on the same sites or because methanol is an intermediate in the formation of the higher alcohols. In early work on the synthesis of higher alcohols the role of methanol as an intermediate was deduced either from the distribution of the product alcohols (*8*) or from the similarity between the products obtained from syngas and those obtained from methanol (*9*). Such similarity is illustrated in Table 2 for experiments over a $CuO/ZnO/Al_2O_3$ catalyst. Because of the rapid equilibration between methanol and CO and H_2, the conclusion that these results indicate that higher alcohols are formed from methanol is unwarranted. The data in Table 2 also show the complexity of the product distribution and point out the difficulty in deducing from this distribution

TABLE 2

Products Obtained from H_2 + CO and from CH_3OH + CO over the $CuO/ZnO/Al_2O_3$ Catalyst

Feed	H_2 + CO	CH_3OH + CO
H_2/CO[a]	0.33	0.25
GHSV[a]	3360	3817
Temperature (°C)	287	285
Products as weight percent of condensed liquids		
Water	0.6	2.7
Methanol	69.9	66.1
Methyl formate	0.4	0.5
Ethanol	6.3	8.2
Methyl acetate	2.0	3.7
1-Propanol	3.7	4.7
Butanone	0.2	0.5
Methyl propanoate	0.4	—
2-Methyl-1-propanol	4.7	6.5
3-Methyl-2-butanone	0.2	—
1-Butanol	1.4	2.0
2-Pentanone	3.8	0.6
2-Methyl-1-butanol	1.9	1.8
Methyl butanoate	1.0	—
Hexanones	1.7	1.3
sec-Hexanols	0.6	0.4
Heptanones	0.9	0.5
Octanones	0.2	0.4
Nonanones	0.2	—

[a] Effective H_2/CO ratio and GHSV assuming total dissociation of CH_3OH to CO + $2H_2$.

TABLE 3

Higher Alcohol Yields from H_2 + CO and CH_3OH + CO over $CuO/ZnO/Al_2O_3$ with and without Cobalt

Composition	Temp. (°C)	Feed $H_2:CO:CO_2:CH_3OH$	CH_3OH conv. (%)	C_{2+}(mg/g cat./h)
$CuO/ZnO/Al_2O_3$	273	100 : 188 : 12 : 0	—	33.
0.3% $Co/CuO/ZnO/Al_2O_3$	272	100 : 188 : 12 : 0	—	1.7
$CuO/ZnO/Al_2O_3$	288	0 : 140 : 0 : 19	82	63.
0.3% $Co/CuO/ZnO/Al_2O_3$	285	0 : 140 : 0 : 19	52	8.

the role played by methanol in the formation of the higher alcohols.

An alternative approach to determining whether the synthesis of methanol and that of the higher alcohols occur on the same sites is provided by the poisoning of the methanol synthesis sites. It has been reported (*16, 17*) that some transition metals, cobalt and rhenium in particular, poison the activity of $Cu/ZnO/Al_2O_3$ for methanol synthesis. For example, the addition of 0.3 wt% cobalt, corresponding to a cobalt surface coverage of 2%, reduced the methanol synthesis activity of a commercial methanol catalyst (UCI C-79) by nearly one order of magnitude (*6*). In the present study, over the same catalyst, but under conditions more suitable to the formation of higher alcohols (285°C, $H_2/CO = \frac{1}{2}$), the addition of the same amount of cobalt (0.3%) reduced the yield of higher alcohols by more than an order of magnitude, as shown in Table 3. The inhibition by cobalt of the formation of both methanol and higher alcohols provides additional evidence that over CuO/ZnO catalysts the synthesis of methanol and that of higher alcohols are related. However, it cannot be determined from these results alone whether the lower rate of the higher alcohol synthesis in the presence of the cobalt is due to direct poisoning by cobalt of the sites active for the formation of higher alcohols or is a consequence of the reduction in methanol concentration caused by the cobalt.

To distinguish between these two effects the synthesis was carried out with a higher concentration of methanol in the presence of cobalt than in its absence. This was accomplished by using methanol and Co as the feed. Over CuO/ZnO methanol decomposes into H_2 and CO, and higher alcohols are formed (see Table 2) either from methanol or from its decomposition products. As expected from the principle of microscopic reversibility, the addition of cobalt to the catalyst inhibited the decomposition of methanol (see Table 3), so that, while in the absence of cobalt equilibrium conversion of the methanol to CO and H_2 was achieved, in the presence of cobalt the conversion was significantly lower. Despite the presence of higher partial pressures of methanol in the catalyst bed when cobalt was present, the rate of formation of the higher alcohols was still lower by an order of magnitude than that with the unpoisoned catalyst. Therefore, the inhibition of higher alcohol formation by cobalt cannot be attributed to changes in the concentration of methanol; more likely, it is a consequence of poisoning by cobalt of the sites active for the higher alcohol synthesis.

The effectiveness of the cobalt, at such low surface concentrations, in inhibiting the methanol synthesis and the synthesis of the higher alcohols suggests that the cobalt interacts very specifically with sites that are active for the formation of both methanol and higher alcohols. Therefore, the two syntheses are related because they share a common catalytic site or, alternatively, because they take place through a common intermediate that is formed on the sites poisoned by cobalt.

CONCLUSIONS

The purpose of the work was to determine if the formation of methanol and the formation of higher alcohols are related over CuO/ZnO-based catalysts. Yields of both products displayed a similar dependence on the CuO/ZnO ratio of the catalyst and also increased upon the addition of CO_2 to the feed. The addition of small amounts of cobalt to the catalyst, which is known to poison methanol synthesis sites, also inhibited the formation of higher alcohols, when synthesis gas or when methanol and CO were used as feeds. These results indicate that the reactions leading to both products are related, probably through a common active site or common intermediate.

REFERENCES

1. Natta, G., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. 3, Chap. 8. Rheinhold, New York, 1955.
2. Natta, G., Colombo, U., and Pasquon, I., *in* "Catalysis" (P. H. Emmett, Ed.), Vol. 5, Chap. 3. Rheinhold, New York, 1957.
3. Smith, K. J., and Anderson, R. B., *Canad. J. Chem. Eng.* **61,** 40 (1983).
4. Smith, K. J., and Anderson, R. B., *J. Catal.* **85,** 428 (1984).
5. Vedage, G. A., Himmelfarb, P., Simmins, G. W., and Klier, K., *Prepr. Div. Pet. Chem. Amer. Chem. Soc.* **28,** 1261 (1983).
6. Elliott, D. J., and Pennella, F., *Prepr. Div. Pet. Chem. Amer. Chem. Soc.* **31,** 39 (1986).
7. Fischer, F., and Tropsch, H., *Brennst. Chem.* **4,** 276 (1931).
8. Graves, G. D., *Ind. Eng. Chem.* **23,** 1381 (1931).
9. Frolich, P. K., and Cryder, D. S., *Ind. Eng. Chem.* **22,** 1051 (1930).
10. Morgan, G. T., *Proc. R. Soc. London Ser. A* **127,** 246 (1931).
11. Mazanec, T. J., *J. Catal.* **98,** 115 (1986).
12. Chinchen, G. C., and Waugh, K. C., *J. Catal.* **97,** 280 (1986), and references therein.
13. Herman, R. G., Klier, K., Simmons, G. W., Finn, B. P., Bulko, J. B., and Kobylinski, T. P., *J. Catal.* **56,** 407 (1979).
14. Frolich, P. K., Fenske, M. R., Taylor, P. S., and Southwich, C. A., *Ind. Eng. Chem.* **20,** 1327 (1928).
15. Strelzoff, S., *Chem. Eng. Prog. Symp. Ser.* **66,** (98) 54 (1970).
16. Lin, F. N., and Pennella, F., *in* "Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals" (R. G. Herman, Ed.), p. 53. Plenum, New York, 1984.
17. Elliott, D. J., and Pennella, F., *J. Catal.* **102,** 464 (1986).

D. J. ELLIOTT

Phillips Petroleum Company
Bartlesville, Oklahoma 74004

Received July 14, 1987; revised January 20, 1988