

## The Rate of Methanol Production on a Copper-Zinc Oxide Catalyst: The Dependence on the Feed Composition

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The initial rates of formation of methanol over a copper-zinc oxide catalyst were measured in a batch reactor at 195 to 225°C and 17 atm pressure. The measurements were made in the absence of mass and heat transport influence. The rates were found to increase with increasing CO<sub>2</sub>/CO ratio in the feed, and were suppressed by the presence of water. The differences between these observations and those in previous work were discussed. © 1984 Academic Press, Inc.

### INTRODUCTION

Methanol synthesis on a copper-zinc oxide catalyst has been extensively studied with respect to the solid state properties of the catalyst (1-4), the adsorption properties (5), the reaction mechanism (6-9), and the kinetics (10-13). In a very extensive kinetic study, Klier *et al.* measured the rate of methanol production in an integral reactor as a function of the CO/CO<sub>2</sub> ratio in the reactant feed (12). They observed a sharp maximum at a CO/CO<sub>2</sub> of about 28/2. The data were interpreted assuming that the active site of the catalyst undergoes a redox reaction with the gas-phase CO and CO<sub>2</sub>. When the CO<sub>2</sub> content is too low, the reduced and inactive form of the active site dominates. When the CO<sub>2</sub> content is too high, the competitive adsorption of CO<sub>2</sub> blocks the active site. Thus an optimum CO/CO<sub>2</sub> ratio is observed. Using this model and the assumption that methanol is formed by the reaction of adsorbed CO with adsorbed H<sub>2</sub>, a rate expression was derived which fit the experimental rate data well. Furthermore, reasonable values of adsorption enthalpies and entropies could be calculated using the kinetic model. In a later

study, CO<sub>2</sub> was replaced by water and a similar optimal water content was observed (13). Furthermore, a significant shift of water into CO<sub>2</sub> was also observed.

Because of the use of an integral reactor in Klier's study, the carbon conversions were relatively high, especially in the experiments at higher temperatures in which the methanol yield approached the equilibrium yield. The high conversion introduced a number of possible complications to the kinetic measurement. The rate of the reverse reaction of methanol decomposition could be significant and could contribute to the observed kinetics. The rate of the competing water-gas shift reaction could be high and result in the production of water (or CO<sub>2</sub>) the effect of which has to be considered. The large change in the gas-phase composition along the reactor also could complicate analysis of the data. To obtain the kinetics of the methanol synthesis reaction without these complications, we performed initial rate measurements using a batch reactor. Results of the study are reported here.

### EXPERIMENTAL

All measurements were conducted in a constant-volume stainless-steel reactor with a volume of 63 ml. The inside of the

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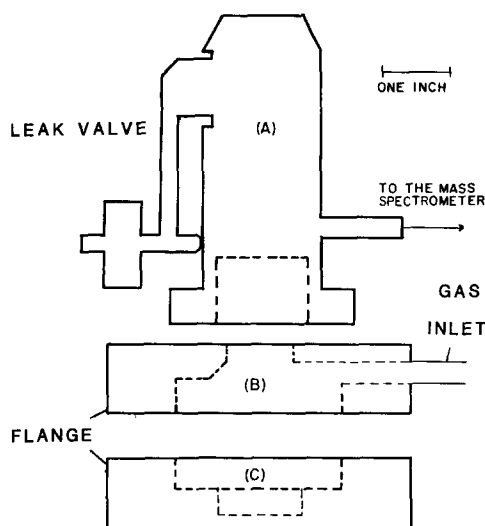


FIG. 1. Schematic drawing of the batch reactor. (A) Leak valve, (B) upper flange, (C) lower flange.

reactor was made up of two connecting concentric cylindrical sections (see Fig. 1). The inside diameter and the height of the bottom section were 6.5 and 2.6 cm, respectively, and those of the upper section were about 3.5 and 2.7 cm, respectively. The content of the reactor was stirred by a magnetically driven fan which had blades at two different levels. The lower blades were about 1 cm above the catalyst bed, and the upper blades were about 1.5 cm above the lower blades. The lower blades were extended almost to the perimeter of the reactor. The extent of mixing in the reactor was determined by monitoring the response of the mass spectrometer signal to a step change in the gas composition in the reactor without any catalyst. Typically, the response was like an exponential decay, and the signal relaxed to within the noise level of the measurement in about two minutes. At the top of the reactor was a leak valve (Varian Vacuum Products) which fed a small amount of the reaction mixture into a mass spectrometer chamber. A UTI 100 C quadrupole mass spectrometer was used. The selection of mass numbers and the collection of data were performed by an Apple II plus computer interfaced with the mass

spectrometer. One mass intensity was collected every 5 s, and all five components ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CH}_3\text{OH}$ , and  $\text{H}_2\text{O}$ ) were monitored in every experiment by monitoring masses 44, 31, 28, 18, 15, and 2. These intensities were converted to mole fractions in the reactor after correcting for the cracking patterns and the sensitivity factors which were independently determined. In all experiments, the mass 15 intensity could be accounted for by the cracking of  $\text{CH}_3\text{OH}$ . Thus  $\text{CH}_4$  was not detected as a significant product.

The entire reactor was situated in an oven equipped with forced-air circulation. The temperature gradient along the reactor was less than  $2^\circ\text{C}$ . At the beginning of each series of experiments, a mixture of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_3\text{OH}$ , and  $\text{H}_2$  at about 17 atm (1 atm = 101.3 kPa) was introduced into the reactor to calibrate the mass spectrometer sensitivity factors. This was repeated three times before rate measurements were made and was done twice at the end of the series. For the rate measurements, a mixture of the desired composition was prepared in a premixer before being expanded into the reactor. A transducer (Viatran) measured the reactor pressure before and after the experiment, and was isolated from the reactor during reaction. All experiments were conducted at  $16.8 \pm 0.2$  atm pressure which decreased by less than 0.2 atm throughout the experiment. Each experiment lasted for 30 to 35 min. The experiments in each series were performed one after another immediately after evacuation of the gas mixture of the previous run, and introduction of the gas mixture for the new run. Between series of experiments, the catalyst was left in contact with the reaction mixture at 1 atm at reaction temperature.

The catalyst was prepared according to the method of Herman *et al.* (1). It was precipitated from a copper nitrate (Alfa) and zinc nitrate (Alfa) solution (total cation concentration was 1 M) by dropwise addition of a 1 M sodium carbonate (Alfa) solution at 85 to  $90^\circ\text{C}$  to a final pH of about 7.

The resulting mixture was cooled for 2 h while stirring. The precipitate was then filtered and washed with glass-distilled water five times, dried in air at 72°C, then calcined in air at 350°C for 3 h. Between 150 and 350°C, the calcination temperature was raised by 50°C every 30 min. The resulting catalyst was a black powder of 80–120 mesh. Its BET area was 21 m<sup>2</sup>g<sup>-1</sup>, which was reduced to 18 m<sup>2</sup>g<sup>-1</sup> after use. Its CuO/ZnO ratio was 30/70 by weight, assuming that the precipitation of Cu and Zn was complete. The catalyst was loosely spread out in a Teflon tray placed at the bottom of the reactor to form a bed of less than 3 mm thick. It was reduced with a 2% H<sub>2</sub> in N<sub>2</sub> mixture at 1 atm and 250°C. Reduction at 200°C gave the same results. Two methods of reduction were used. In one, the reduction was performed in a batch system and a fresh charge of H<sub>2</sub>/N<sub>2</sub> was introduced every 30 min after the previous charge was evacuated. This procedure was repeated eight times. At the end of the eighth time, the catalyst was left in the H<sub>2</sub>/N<sub>2</sub> mixture overnight. The reduction was considered complete because the activity remained the same for one charge of the catalyst after repeating this reduction procedure. In the second method, the catalyst was reduced in a flowing stream of H<sub>2</sub>/N<sub>2</sub> mixture for 12 h. This method was used only once and it produced a catalyst that was slightly more active than the first method. Otherwise the behavior of the catalysts was independent of the reduction method.

H<sub>2</sub> (Air Products, high purity), CO<sub>2</sub> (Linde, bone dry), and CO (Linde, high purity) were used without further purification. H<sub>2</sub>O was introduced by vaporizing liquid doubly distilled water that was purified by pumping. A premixed mixture of 4.28% CO<sub>2</sub>, 32.5% CO, and 63.22% H<sub>2</sub> (Airco) was used in every series of experiments as a test on the deactivation of the catalyst.

#### RESULTS

Since the activity of the catalyst depends on its oxidation state which in turn depends on the composition of the gas mixture, pre-

TABLE I  
Slow Deactivation of the Cu-Zn-O Catalyst

Date	Initial CH <sub>3</sub> OH production rate (10 <sup>-5</sup> mol/min-g)
Nov. 14	1.80 (fresh catalyst)
Nov. 16	1.73
Nov. 23	0.86
Nov. 25	0.74
Nov. 29	0.85
Dec. 3	0.75

liminary experiments were performed to test for the reproducibility of the system by introducing a reactant feed of the same composition in consecutive experiments. It was found that for a fresh charge of catalyst, reproducible rates were obtained after two or three experiments. However, a slow deactivation was observed when the rates were compared from day to day. An example is shown in Table 1. The activity of the catalyst decreased by about 60% before a steady state was reached, after a total reaction time of 15 to 20 h at 17 atm. An initial transient was also reported in steady state kinetic measurements (12). While the activity changed, the dependence of the rate on the feed composition did not change. Such deactivation was not noticed among the experiments within each series (in one day). An example is shown in Table 2. In these experiments, the composition of the reactant feed was randomly varied, and the initial rate of methanol production varied smoothly with the composition (see also Fig. 3).

As described, each series of experiments began with three calibration runs for the mass spectrometer. In the first one or two rate measurements immediately after the calibration, the methanol production rate was found to be higher than the steady state rates. The excess methanol was attributed to the displacement of adsorbed methanol

TABLE 2

Rates of Methanol and Water Formation in One Series of Experiments Cu-Zn-O (30/70)  
 $P = 16.9 \pm 0.1$  atm,  $T = 228^\circ\text{C}$ , 0.2810 g Catalyst

Experiment	Initial gas composition (%)			CH <sub>3</sub> OH rate (10 <sup>-5</sup> mol/min-g)	H <sub>2</sub> O rate (10 <sup>-5</sup> mol/min-g)
	H <sub>2</sub>	CO	CO <sub>2</sub>		
11-F	63.22	32.5	4.28	1.54	1.33
11-G	63.22	32.5	4.28	1.60	1.41
11-H	59.23	30.45	10.32	1.50	3.09
11-I	70.05	27.74	2.21	1.27	1.30
11-J	69.73	12.24	18.03	2.00	9.88
11-K	70.25	20.95	8.80	1.50	3.33
11-L	69.99	0	30.01	2.49	11.24
11-M	70.02	16.22	13.76	1.70	4.57

by the feed gases (probably CO<sub>2</sub>). Once this excess adsorbed methanol was displaced, reproducible rates were obtained as is shown by the data in Table 2.

Because the catalyst was placed in a tray at the bottom of the reactor, there was no forced convection through the catalyst bed. Transport of reactants and products in and out of the bed had to be by diffusion. The influence of catalyst-bed diffusion on the measured rate was minimized by making the bed as thin as possible to less than 3 mm thick. The absence of such influence was confirmed by measuring the initial rate using different amounts of catalysts (i.e., different bed thickness). Such experiments were conducted at both 198 and 225°C. In both cases, the steady state rate of a catalyst was first obtained using a H<sub>2</sub>-CO<sub>2</sub> feed mixture (70 : 30). Then about half of the catalyst was removed. The remaining catalyst was again reduced in a H<sub>2</sub>/N<sub>2</sub> mixture, and the rate measurements were performed using the same feed. It was found that the initial rate of methanol production was reduced by about 60%. This proportional decrease in rate suggested that catalyst-bed diffusion was much faster than the chemical transformation rate. That the rate was reduced by slightly more than half was attributed to the deactivation of the catalyst after exposure to air and the second reduction.

Diffusion limitation in the catalyst pores was not tested. However, we believe that pore diffusion limitation was not important because (1) the catalyst used has a low BET area and therefore large pores, (2) the catalyst was a fine powder, and (3) the rate of methanol production was slow. In fact, because of the slow reaction rate, the heat released by the reaction was small and there was no temperature gradient expected in the catalyst bed.

An example of the data showing the partial pressures of the components in the reactor is shown in Fig. 2. They were calculated from the mass spectrometer intensities by first correcting for the cracking pattern and the mass spectrometer sensitivities, and then normalizing the data to fit the mass conservation equations. The data for all the other experiments were similar to these except for different magnitudes and signs of the slopes. The rate of change of the H<sub>2</sub> partial pressure was always negative because it was a reactant. That for the CH<sub>3</sub>OH partial pressure was always positive because it was a product. That for H<sub>2</sub>O was positive if it was not being introduced in the feed, and could be either negative or positive if it was introduced in the feed, depending on whether the CO/CO<sub>2</sub> ratio was high or low, respectively. Similarly, the rates of change of CO and CO<sub>2</sub> partial pres-

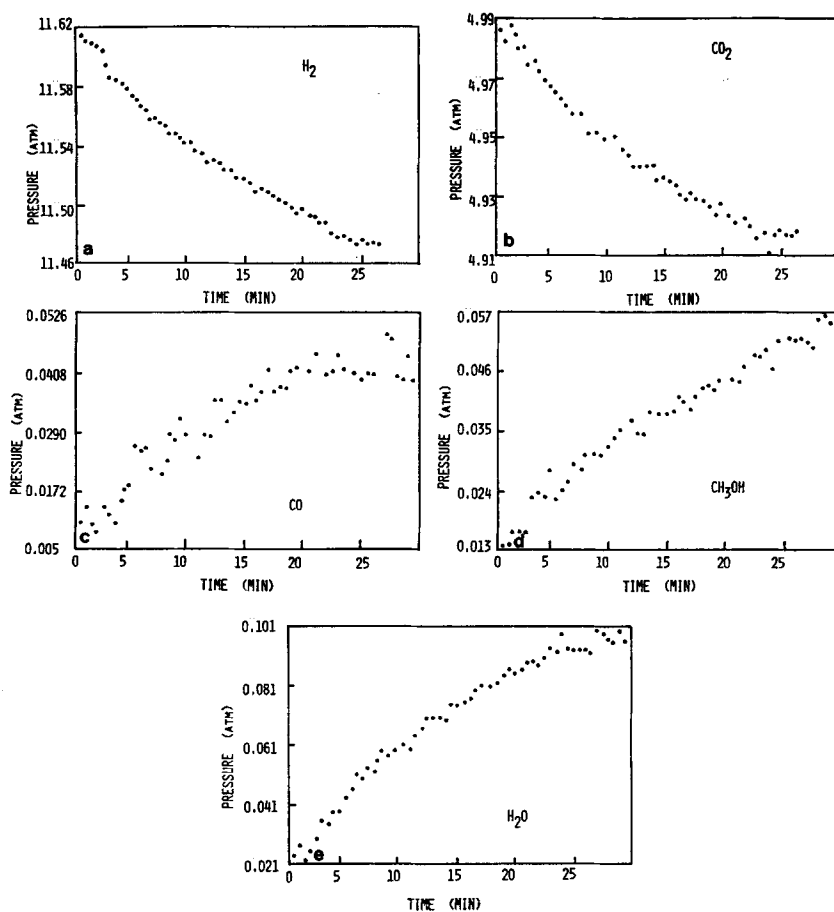


FIG. 2. The partial pressures of gases in the reactor as a function of time. Reaction conditions: 16.65 atm, 198°C, a feed composition of 70% H<sub>2</sub>, 30% CO<sub>2</sub>. (a) H<sub>2</sub>, (b) CO<sub>2</sub>, (c) CO, (d) CH<sub>3</sub>OH, (e) H<sub>2</sub>O; 0.3578 g of catalyst was used.

pressures depended on the feed composition.

The dependence of the initial rates of CH<sub>3</sub>OH production on the CO/CO<sub>2</sub> ratio in a 70% by volume of H<sub>2</sub>, 30% CO + CO<sub>2</sub> feed is shown in Fig. 3. The CO/CO<sub>2</sub> ratios were varied randomly in these experiments. The 225°C data were obtained with a fresh charge of catalyst, and the 195°C data were obtained with a steady state catalyst. The difference shown in the rates between the two temperatures were larger than the real difference because of the deactivation phenomenon described earlier. The trend was clear, however, that independent of the degree of deactivation, the rate was higher at a higher CO<sub>2</sub> partial pressure. Similar to

CH<sub>3</sub>OH, the initial rates of H<sub>2</sub>O production also increased with increasing CO<sub>2</sub> partial pressure. This is illustrated by the data in Table 2. It is due to the increased rates of reverse water gas shift and of hydrogenation of CO<sub>2</sub> to methanol and water with increasing CO<sub>2</sub> pressure.

The dependence of the initial rate of methanol production on the partial pressure of water in the feed was also investigated. The results are shown in Figs. 4 and 5 for the 195 and 225°C experiments. The data in each of these figures were obtained in one series of experiments in which the water partial pressure was varied randomly. The dotted lines in the figures show the rates in

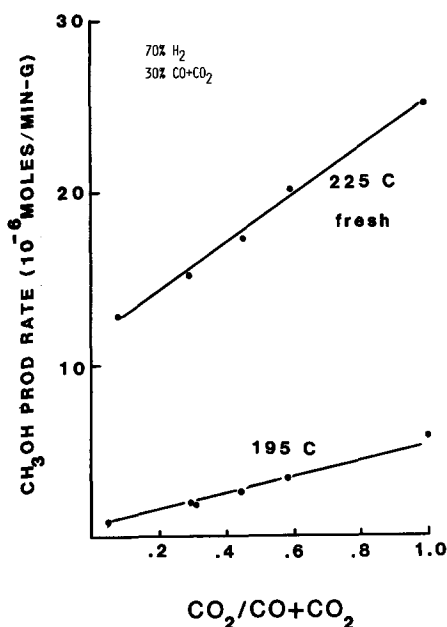


FIG. 3. The initial rates of methanol production as a function of the  $\text{CO}/\text{CO}_2$  ratio in the feed. Feed composition: 70%  $\text{H}_2$ , 30%  $\text{CO} + \text{CO}_2$ . The 225°C data were for a fresh charge of catalyst. The 195°C data were for a steady state catalyst.

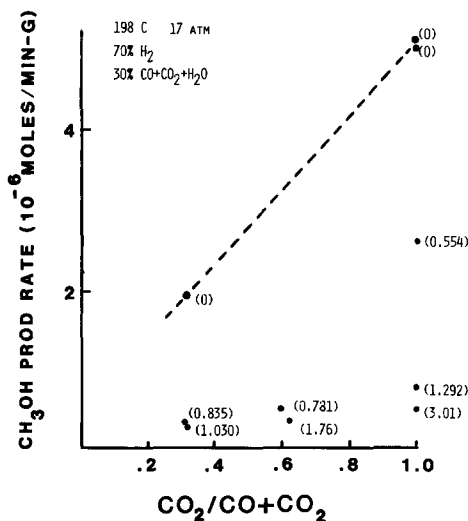


FIG. 4. The influence of water on the initial rates of methanol production at 198°C. Other reaction conditions: 17 atm, a feed composition of 70%  $\text{H}_2$ , 30%  $\text{CO} + \text{CO}_2 + \text{H}_2\text{O}$ . Numbers in the brackets denote the initial mole fractions of  $\text{H}_2\text{O}$ ; 0.3578 g of catalyst was used.

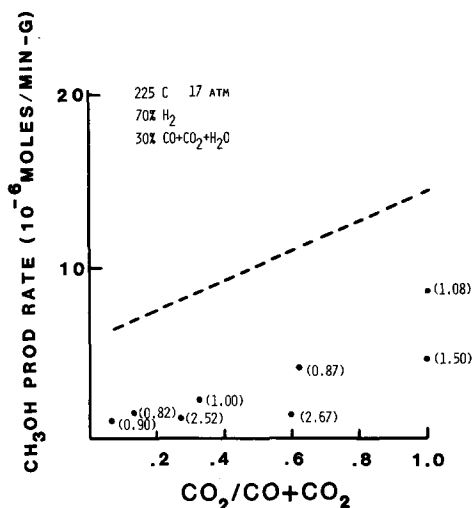


FIG. 5. The influence of water on the initial rates of methanol production at 225°C. Other reaction conditions: 17 atm, a feed composition of 70%  $\text{H}_2$ , 30%  $\text{CO} + \text{CO}_2 + \text{H}_2\text{O}$ . Numbers in the brackets denote the initial mole fractions of  $\text{H}_2\text{O}$ . The dotted line denotes the rate in the absence of water; 0.2810 g of catalyst was used.

the absence of water. For the 225°C data, experiments with no water were performed with 63%  $\text{H}_2$  instead of 70%  $\text{H}_2$ . The rates thus obtained were used to confirm the normal behavior of the catalyst. The dotted line shown was drawn using data from other series of experiments using 70%  $\text{H}_2$  feed compositions. It was noted that if water was used in a previous experiment, the rate in the experiment immediately following using  $\text{H}_2$  and  $\text{CO}_2$  but no water in the feed would be about 10 to 50% lower, depending on the amount of water used, than the same experiment on a catalyst that had not been exposed to water deliberately. The rate would return to normal after two to three experiments without added water.

#### DISCUSSION

It has been established that the rate data reported here were free of influence by mass and heat transfer processes. They were initial rates at the feed compositions that were introduced into the reactor. Over the 30-min interval when the rate data were gathered, the conversion was low (<3%)

such that in all cases examined, except when the feed did not contain CO, the partial pressure of methanol increased linearly with time. This indicated that the gas composition in the reactor only changed slightly, and that the reverse reaction of methanol decomposition was not important in these measurements. When only CO<sub>2</sub> and no CO was used, the methanol formation rate was the highest and a carbon conversion of 3% was reached. Coupled with the fact that the equilibrium partial pressure of methanol was the lowest, the reverse reaction of methanol decomposition was the most likely in these experiments. For the 198°C experiments, the equilibrium partial pressure of methanol was 0.555 atm. The methanol pressure increase showed at most a slight curvature, as shown in Fig. 2. For the 225°C experiment, the curvature was more noticeable as the equilibrium partial pressure of methanol was lower, being 0.259 atm (which corresponded to 5.15% carbon conversion).

Since the experiments were performed in a batch reactor, the catalyst might not have reached a truly steady state. Results in these experiments showed that either the catalyst responded to the changing gas-phase composition very rapidly or very slowly. This is because in every sequence of experiments performed, the gas-phase compositions were varied randomly. After accounting for the catalyst deactivation, the rates of methanol formation for the same feed composition were always reproducible, and did not depend on the preceding experiment except when water was used. In the latter case, the activity of the catalyst was lower, and was restored only after two or three experiments. If the nature of the catalyst responded rapidly to the gas-phase composition, the data represented the true behavior of the catalyst. If the catalyst responded very slowly, the data would be for a catalyst equilibrated with the standard mixture of 63.2% H<sub>2</sub>, 32.5% CO, and 4.3% CO<sub>2</sub>. There was evidence that the catalyst responded rapidly. In an experiment using a feed of 16 atm H<sub>2</sub>

and 0.4 atm CO<sub>2</sub> (instead of the normal 5 atm CO<sub>2</sub>), the rate of production of methanol showed an induction period such that in the first 3 min, the rate was close to that for the previous experiment. After 3 min, the rate increased to what was expected without CO in the feed. It should be emphasized that under discussion are the reversible changes of the catalyst in response to the gas composition. Such changes include changes in the degree of *surface* oxidation and amounts and nature of adsorbates. There could well be slow irreversible changes on exposure to certain gas compositions, such as *bulk* reduction of the catalyst. Such slow irreversible changes would not be detected in these experiments, but would show up in steady state flow reaction measurements.

Data in Figs. 4 and 5 showed the inhibition effect of water. The extent of inhibition increased with increasing water partial pressure. This suggested that water is competitively adsorbed on the active site of the catalyst. The suppression of activity should not be due to deactivation by oxidation by water of the catalyst. This is because CO<sub>2</sub> is a stronger oxidizing agent than water, yet addition of CO<sub>2</sub> enhanced and not suppressed the reaction. This inhibition by water was also observed by Vedage *et al.* for high water partial pressures (13).

The increase of the rate with increasing CO<sub>2</sub> pressure shown in Fig. 3 is somewhat surprising in view of the results of Klier *et al.* (12) who showed that on essentially the same catalyst, the methanol formation rate reached a maximum at a CO/CO<sub>2</sub> ratio of about 28/2. There are a number of differences between their measurements and ours. First, their experiments were performed at a higher pressure of 75 atm. The catalyst could behave differently although this does not seem likely. At higher pressure, condensation of methanol, water, and CO<sub>2</sub> in the catalyst pores is possible. If such condensation did occur, diffusional effect would influence their observed kinetics. Second, their experiments were conducted in an integral reactor and their conversions

were much higher than ours. It is possible that the reverse reaction of methanol decomposition occurred in their experiments. In other words, the decrease in rate beyond the maximum on increasing CO<sub>2</sub> pressure could be a consequence of the much lower equilibrium methanol yield at a high CO<sub>2</sub> pressure. This equilibrium limitation was not present in our experiments. Third, because of the integral nature of their reactor, the gas-phase composition changed along their reactor. In particular, because of the production of water by the water-gas shift reaction and CO<sub>2</sub> hydrogenation, the rate of methanol production they measured did not correspond to the feed composition in the same way as that in our experiments. Since the rate of water production increased with the CO<sub>2</sub> content in the feed (see Table 2) and that water inhibited the reaction, this could result in the decrease in methanol formation rate with increasing CO<sub>2</sub> content in their experiments. While these are possible explanations of the differences, the answer can only be obtained by a detailed study of the effect of the different operating conditions.

If indeed the effect of water is the explanation, which is the most likely, the optimal CO/CO<sub>2</sub> and CO/H<sub>2</sub>O ratios observed earlier (12, 13) could be explained as follows. In the absence of CO<sub>2</sub> or H<sub>2</sub>O, the catalyst is excessively reduced so that it is rather inactive. Addition of a small amount of CO<sub>2</sub> or H<sub>2</sub>O prevents the reduction and maintains a highly active catalyst. As the amount of CO<sub>2</sub> increases, the amount of water produced also increases. This decreases the catalyst activity probably by competitive adsorption of water on the active sites. That water is strongly adsorbed on the active site is suggested by the fact that the activity of the catalyst was lower in experiments immediately after those in which water was used.

In conclusion, using initial rate measurements, methanol synthesis on a Cu-Zn-O catalyst was found to be enhanced by CO<sub>2</sub> and suppressed by H<sub>2</sub>O. The observation pointed to the important role of CO<sub>2</sub>, but it

did not provide any mechanistic information. The large difference in the dependence of the rates on the feed composition obtained in this study and in an earlier study using an integral reactor pointed to the sensitivity of the catalyst behavior to the gas phase environment. It also illustrated once again the danger of deriving mechanistic information from kinetic data.

#### ACKNOWLEDGMENT

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*Note added in proof.* It has been reported that the hydrogenation of CO<sub>2</sub> is faster than CO below 250°C at low conversion over Cu-Zn oxide. This is in agreement with our observations. [R. Kieffer, E. Ramarosan, A. Deluzarche, and Y. Trambouze, *React. Kinet. Catal. Lett.* **16**, 207 (1981); B. Denise and R. P. A. Sneeden, *J. Mol. Catal.* **17**, 359 (1982).]

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