

## The Role of CO<sub>2</sub> in Methanol Synthesis on Cu-Zn Oxide: An Isotope Labeling Study

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Methanol synthesis using H<sub>2</sub>, CO, and <sup>18</sup>O-labeled CO<sub>2</sub> was studied over a Cu-Zn oxide catalyst at 220°C and 17 atm in a batch reactor. In the absence of gaseous water, the rate of production of C <sup>18</sup>O was rapid. The rate of production of <sup>18</sup>O-labeled methanol was about 50% of that of <sup>16</sup>O-labeled methanol. The presence of gaseous water suppressed the production of [<sup>18</sup>O]methanol, but not C <sup>18</sup>O or [<sup>16</sup>O]methanol. The results indicated that there are at least four parallel reactions on the catalyst: CO-CO<sub>2</sub> exchange, CO hydrogenation, CO<sub>2</sub> hydrogenation, and water-gas shift. Exchange of lattice oxygen with oxygen in CO<sub>2</sub> also took place. There was no evidence for the production of methanol from the reaction of CO and water. © 1985 Academic Press, Inc.

### INTRODUCTION

Methanol production from a mixture of CO, CO<sub>2</sub>, and H<sub>2</sub> over a Cu-Zn oxide catalyst has been a subject of considerable interest. Much has been published regarding the nature of the catalyst (1-7), the kinetics of the reaction (8-11), and the mechanism (10-18). Regarding the mechanism, a number of proposals have been forwarded. Rozovskii and co-workers, in a series of publications on kinetics and <sup>14</sup>C isotope labeling experiments, concluded that the hydrogenation of CO<sub>2</sub> is the source of methanol, instead of the commonly believed hydrogenation of CO (14-16). Their proposal, however, has been largely neglected, although recently their results have been reproduced (19). In the later proposals where specific mechanistic steps were presented, the CO has been assumed to be the origin for methanol. Deluzarche *et al.* proposed that the reaction proceeds via a formate intermediate formed from the insertion of CO into a surface hydroxyl (20). Their proposal was based on their study with a zinc chromite catalyst. Herman *et al.* suggested that CO is hydrogenated via a hydroxycarbene type

of intermediate (2). Kung suggested a formyl intermediate in which both the carbon and the oxygen interact with the catalyst (21). In spite of these various proposals, there has been very little direct observation of the intermediates. In one infrared spectroscopic study, it was reported that a pair of weak bands at 2770 and 2661 cm<sup>-1</sup> was found under synthesis conditions that was attributed to a formyl species (17). Trapping of surface intermediates by reactive chemicals has been reported recently indicating that an aldehydic or hydroxycarbenoic intermediate is involved in methanol formation (10).

The role of CO<sub>2</sub> in the methanol synthesis reaction has been a subject of great interest. Klier *et al.* clearly demonstrated that at steady state, the presence of CO<sub>2</sub> has a greatly beneficial effect which was postulated as the stabilization of the active site by CO<sub>2</sub> (8). A particular CO/CO<sub>2</sub> ratio is required for optimal activity. This dependence on the feed composition was later found to be very different in the initial rate measurements at low conversions, which showed that the rate increased with increasing CO<sub>2</sub>/CO in the gas phase (22). There were also reports that at low conversions, the hydrogenation rate of CO<sub>2</sub> to

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methanol was faster than CO (11, 12). Infrared spectroscopic studies detected surface formate in CO<sub>2</sub> hydrogenation, which could be correlated to methanol production (11, 13).

In view of these conflicting reports, it appeared necessary to firmly establish the mechanistic role of CO<sub>2</sub> so as to confirm, reject, or modify the various conclusions on the effect of CO<sub>2</sub>. We report here the results of an investigation on the mechanism of this reaction using <sup>18</sup>O-labeled CO<sub>2</sub>, and monitoring the production of <sup>18</sup>O-labeled methanol. In addition to determining the contribution of CO<sub>2</sub> hydrogenation to methanol production, the results could also provide the rate of the water-gas shift reaction, the possibility of oxygen exchange with the lattice oxygen of the catalyst, and the possibility of oxygen exchange between CO and CO<sub>2</sub>, or other reactant molecules. Some of this information would not be obtainable using carbon labeling.

#### EXPERIMENTAL

Experiments were carried out at 220°C under a total pressure of about 17 atm (1 atm = 101.3 kPa) in a stainless-steel batch reactor as described before (22, 23). Briefly, the reactor had a volume of 63 ml. The contents of the reactor were mixed by a magnetically driven fan. The gaseous composition in the reactor was monitored by leaking the gas through a leak valve (Varian) into a UTI mass spectrometer chamber. The response characteristics of the system were such that if the gaseous composition was suddenly changed by a concentration jump, over 90% of the corresponding change in the mass spectrometer reading would be completed in less than 2 min. This time was fast compared to the reaction time in these measurements. The entire reactor was in an isothermal oven.

The mass spectrometer was computer-controlled. In every experiment, masses 48, 46, 44, 34, 33, 32, 31, 30, 28, 20, 19, 18, 17, and 2 were monitored. The cracking patterns of C <sup>16</sup>O<sub>2</sub> ( $m = 44$ ), CO, CH<sub>3</sub>OH,

and H<sub>2</sub>O were individually obtained. Those of C <sup>18</sup>O<sub>2</sub> ( $m = 48$ ), C <sup>18</sup>O <sup>16</sup>O ( $m = 46$ ), CH<sub>3</sub> <sup>18</sup>OH ( $m = 34$ ), C <sup>18</sup>O, and H<sub>2</sub> <sup>18</sup>O were assumed to be the same as the normal isotope species except for the shift in the mass number for the O-containing fragments. Scrambling of oxygen isotopes in methanol in the mass spectrometer was negligible because a zero rate of production of CH<sub>3</sub> <sup>18</sup>OH was detected in some experiments.

The preparation of the catalyst has been described (22). It was prepared according to Herman *et al.* (2). Its BET area after use was 18 m<sup>2</sup> g<sup>-1</sup>. Its CuO/ZnO ratio was 30/70 by weight. The catalyst was first reduced with a stream of 2% H<sub>2</sub> in N<sub>2</sub> at 1 atm and 250°C at a flow rate of about 30 ml/min for 12 h. Normally about 0.3 to 0.4 g of catalyst was used. It was established that diffusion in the catalyst bed was fast and did not affect the kinetics (22).

As before (22), each series of experiments (in a given day) began with the calibration for the mass spectrometer sensitivity of the species with a known gaseous mixture of CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>3</sub>OH. This calibration corrected for any mass discrimination by the leak valve and other instrumental effects. Following this calibration, the catalyst was conditioned by running the synthesis reaction using a mixture of 4.28% CO<sub>2</sub>, 32.5% CO, and 63.22% H<sub>2</sub> (Airco premixed) until the activity was constant, which usually took two to three experiments. Then various mixtures of various compositions, prepared in the premixer, were introduced. The conversion of each experiment, which usually lasted about 30 min, was so low that the methanol concentration was always less than 30% of the equilibrium concentration at the end of the experiment. Between experiments, the reactor was evacuated for 15 min. The catalyst was always preconditioned with the premixed mixture before each isotope experiment, unless otherwise specified.

The C <sup>18</sup>O<sub>2</sub> used was from Merck. Its composition was 77% C <sup>18</sup>O<sub>2</sub>, 22% C <sup>16</sup>O <sup>18</sup>O, and 1% C <sup>16</sup>O<sub>2</sub> as determined by mass

spectroscopy assuming equal mass spectrometer sensitivities.

Reduction of the mass spectrometer data involved corrections for the cracking patterns and the mass spectrometer sensitivities for the various species. They were then normalized to yield the mole fractions, and the partial pressures. The details have been reported in Ref. (23) with a few minor modifications.

Both the reactor and the premixer were made of the same type of stainless steel. They were also at the same temperature. Thus the activity of the premixer toward isotope mixing reactions could be directly used to indicate the activity of the reactor. Only one isotope mixing reaction was observed in the premixer, which was the oxygen exchange between CO<sub>2</sub> and H<sub>2</sub>O. This scrambling was very rapid and the isotope distribution attained roughly a statistical distribution between CO<sub>2</sub> and H<sub>2</sub>O within a few minutes when they were being kept in the premixer. An unsuccessful attempt was made to reduce this scrambling by first introducing water into the reactor, and then

followed with a mixture of H<sub>2</sub>, CO, and C <sup>18</sup>O<sub>2</sub>. Complete scrambling between CO<sub>2</sub> and H<sub>2</sub>O still took place within the first 2 min of the reaction. This explains the isotope composition in the feed of Experiments 3-19-S, 3-19-I, and 4-15-H.

RESULTS

Changes in the partial pressure of the various species in Experiment 3-19-O are shown in Fig. 1. The parent peaks were used for most species except H<sub>2</sub> <sup>16</sup>O, CH<sub>3</sub> <sup>16</sup>OH, and CH<sub>3</sub> <sup>18</sup>OH which used masses 17, 31, and 33, respectively. The feed conditions are listed in Table 1. As expected from the feed composition, the pressures of H<sub>2</sub>O, C <sup>18</sup>O, C <sup>16</sup>O<sub>2</sub>, C <sup>16</sup>O <sup>18</sup>O, CH<sub>3</sub> <sup>16</sup>OH, and CH<sub>3</sub> <sup>18</sup>OH all increased with time, while the pressures of C <sup>18</sup>O<sub>2</sub>, C <sup>16</sup>O, and H<sub>2</sub> all decreases. This trend continued during the course of the experiment except for C <sup>16</sup>O <sup>18</sup>O which showed a substantial curvature. These results are representative of all the experiments listed in Table 1 with two exceptions. The first exception was the behavior of C <sup>16</sup>O <sup>18</sup>O. In Experiments 3-30-

TABLE I  
Initial Rates of Formation of Various Products at 220°C on Cu-Zn Oxide

Expt	Feed composition (atm)					Rate of formation (10 <sup>-5</sup> mol/min-g)												
	H <sub>2</sub>	CO	C <sup>18</sup> O <sub>2</sub> <sup>a</sup>	H <sub>2</sub> O	CH <sub>3</sub> <sup>16</sup> OH	CH <sub>3</sub> <sup>18</sup> OH			C <sup>16</sup> O	C <sup>18</sup> O	C <sup>16</sup> O <sub>2</sub>	C <sup>16</sup> O <sup>18</sup> O	C <sup>18</sup> O <sub>2</sub>	H <sub>2</sub> <sup>16</sup> O <sup>c</sup>	H <sub>2</sub> <sup>18</sup> O	Sum <sup>d</sup> <sup>18</sup> O	Sum <sup>b</sup> C	Sum <sup>a</sup> O
3-19-K	11.7	4.56	0.24	0	0.22	0.13	0.59	-5.66	6.15	1.71	4.89	-8.4	0.42	0 <sup>e</sup>	-5.6	-1.0	-2.3	
3-19-O	11.4	4.59	0.27	0	0.19	0.17	0.89	-5.52	5.16	1.30	5.39	-9.61	0.27	0.52	-8.0	-2.9	-5.0	
2-21-M	12.3	5.07	0.14	0			0.43											
3-19-M	15.9	0	0.35	0	0.05	0.22	—	0.67	0.27	0.18	0.04	-1.93	0.36	1.03	-2.3	-0.4	-0.8	
3-19-Q	16.2	0	0.24	0	0.03	0.39	—	0.36	0.22	0.04	0.08	-2.20	0.45	1.17	-2.6	-1.1	-1.7	
3-30-F	11.6	5.4	0.12	0 <sup>b</sup>	0.23	0.04	0.18	-5.61	5.97	2.51	3.01	-5.21	-0.18 <sup>f</sup>	-1.84	-3.2	0.9	-0.8	
3-30-I	12.1	5.0	0.11	0 <sup>b</sup>	0.23	0.04	0.17	-5.84	5.75	2.47	2.69	-5.25	0.03	-1.84	-3.9	0.1	-1.5	
3-19-S	11.8	4.0	0.20 <sup>e</sup>	0.65 <sup>e</sup>	0.21	0.02	0.11	-10.9	10.9	4.85	0.0	1.44	0.94	-7.45	0.95	4.0	1.3	
3-19-I	11.5	4.5	0.13 <sup>f</sup>	0.20 <sup>f</sup>	0.19	0.01	0.07	-7.00	6.3	3.10	-1.03	-1.75	1.03	-3.86	0.0	1.9	1.4	
4-15-H	12	5.2	0.11 <sup>g</sup>	0.14 <sup>g</sup>	0.15	0.01	0.06	-5.07	4.94	1.80	-0.76	-1.21	1.39	-1.62	0.15	-0.1	-0.5	

<sup>a</sup> Also contained C <sup>16</sup>O <sup>18</sup>O which was about 30% of C <sup>18</sup>O<sub>2</sub>.

<sup>b</sup> Although water was not added, water was used in the feed in the experiments immediately preceding this. The background water was within the mass spectrometer background level.

<sup>c</sup> H<sub>2</sub> <sup>16</sup>O was detected using the fragment *m/e* = 17 because *m/e* = 18 was a cracking fragment of C <sup>18</sup>O<sub>2</sub>.

<sup>d</sup> <sup>18</sup>O balance. Negative means a net loss of oxygen-18 from the gas phase.

<sup>e</sup> The isotope compositions were (in atm): C <sup>18</sup>O<sub>2</sub>, 0.03; C <sup>16</sup>O <sup>18</sup>O, 0.10; C <sup>16</sup>O<sub>2</sub>, 0.07; H<sub>2</sub> <sup>18</sup>O, 0.25; H<sub>2</sub> <sup>16</sup>O, 0.40.

<sup>f</sup> The isotope compositions were (in atm): C <sup>18</sup>O<sub>2</sub>, 0.03; C <sup>16</sup>O <sup>18</sup>O, 0.07; C <sup>16</sup>O<sub>2</sub>, 0.03; H<sub>2</sub> <sup>18</sup>O, 0.08; H<sub>2</sub> <sup>16</sup>O, 0.12.

<sup>g</sup> The isotope compositions were (in atm): C <sup>18</sup>O<sub>2</sub>, 0.03; C <sup>16</sup>O <sup>18</sup>O, 0.04; C <sup>16</sup>O<sub>2</sub>, 0.04; H<sub>2</sub> <sup>18</sup>O, 0.05; H<sub>2</sub> <sup>16</sup>O, 0.09.

<sup>h</sup> Carbon and oxygen balance.

<sup>i</sup> Uncertainties in these were exceptionally high due to interference from the previous experiment.

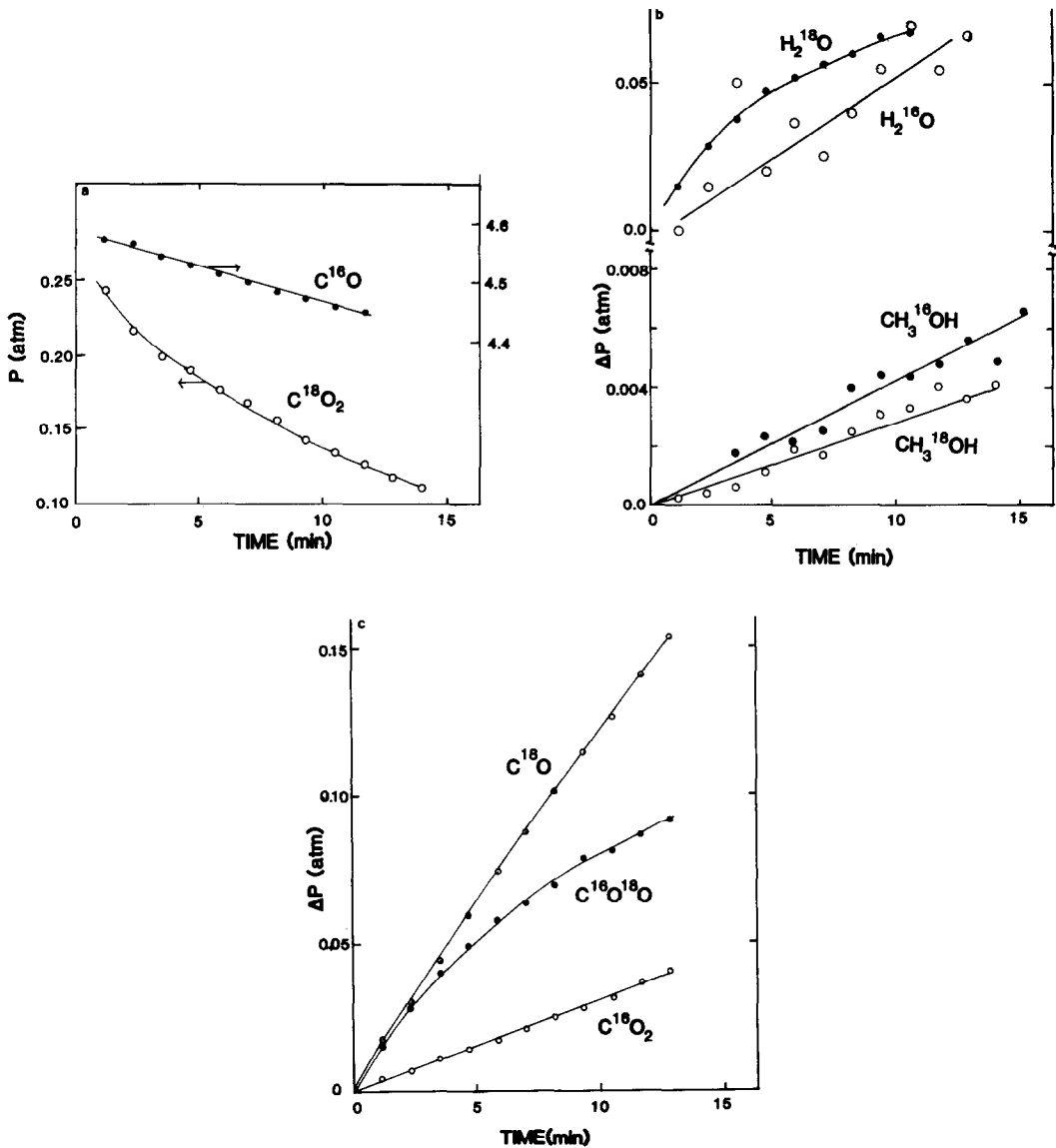


FIG. 1(a-c). Partial pressures and changes in partial pressures ( $\Delta P$ ) of the various species in the methanol synthesis reaction on 0.3472 g of catalyst at 220°C; Experiment 3-19-O; feed composition: 11.4 atm  $H_2$ , 4.59 atm CO, and 0.27 atm  $C^{18}O_2$ .

F and 3-30-I, the partial pressure of this species showed such a pronounced curvature that it attained a maximum value within the 30 min of the experiment. The second exception was the behavior of  $CH_3^{18}OH$  in the Experiments 3-19-M and 3-19-Q, which did not contain CO in the feed. There, the partial pressure of [ $^{18}O$ ]methanol showed an upward curvature as shown in

Fig. 2, indicating that the rate of its formation increased with time in the first few minutes.

The initial slopes of these curves were the rates of appearance (or disappearance) of the species at the feed composition. These rates are summarized in Table 1.

Uncertainties in these numbers varied among different species. A detailed discus-

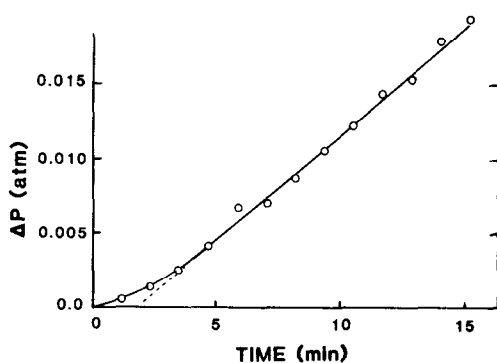


FIG. 2. Partial pressures of  $\text{CH}_3^{18}\text{OH}$  in Experiment 3-19-M, 0.3472 g of catalyst at  $220^\circ\text{C}$ .

sion is provided in the Appendix. In general, the uncertainties in the data decreased as  $\text{CO} > \text{H}_2\text{O} > \text{CO}_2 > \text{CH}_3\text{OH}$ , but the exact magnitudes depended on the experiments. However, the ratios of the rates of a given species containing different isotopes were much more accurate.

As mentioned under Experimental and in Ref. (22), the data at a given time were normalized so that the carbon, oxygen (disregarding isotope nature), and hydrogen conservation equations were satisfied. However, because of noise in the data as shown in Fig. 1, the set of initial slopes going through these data points did not have to exactly satisfy these conservation equations. In fact, how closely these slopes satisfied the conservation equations was usually determined by the most uncertain species of  $\text{CO}$  and  $\text{H}_2\text{O}$ . For the data shown in Table 1, the carbon and oxygen conservation were satisfied to within about 15%. The balance for the  $^{18}\text{O}$  isotope was generally poorer, but was still within the noise of the data. The exceptions were experiments which did not contain water in the feed (3-19-K and 3-19-O) which indicated the incorporation of  $^{18}\text{O}$  into the lattice.

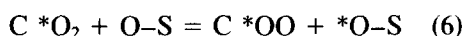
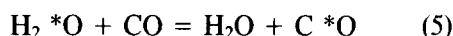
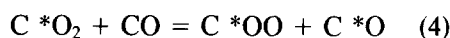
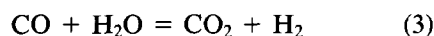
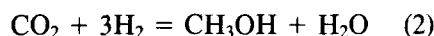
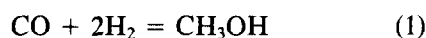
#### DISCUSSION

It is helpful to recognize that with a batch reactor, the results were obtained under low conversion conditions such that there were little changes in the gas-phase composition during reaction. This is exemplified

by the data in Fig. 1. Over 10 min of reaction, the total  $\text{CO}$  pressure remained essentially at 4.59 atm, and the total  $\text{CO}_2$  pressure dropped from about 0.28 to 0.24 atm. The changes in the isotopic contents of the reactants were more extensive, but the majority isotope of a component remained the majority throughout the experiment. In the data in Fig. 1, the  $^{18}\text{O}/^{16}\text{O}$  ratio in  $\text{CO}$  changed from zero to 0.13/4.48 (= 0.03) in 10 min. The  $^{16}\text{O}/^{18}\text{O}$  ratio in  $\text{CO}_2$  changed from 12/88 (0.14) to 17/31 (0.55). Similar changes in the other experiments can be calculated from the rate data in Table 1, noting that for our system,  $10^{-5}$  mol/min-g equals  $6.4 \times 10^{-3}$  atm/min-g. The only exception to this were the experiments with water. For these, the isotope scrambling between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  was so rapid that close to a statistical distribution of isotopes was attained in less than 2 min of the experiment.

It should also be mentioned that this discussion assumes that the isotope scrambling between  $\text{CO}$  and  $\text{CO}_2$  on the surface is not infinitely fast. Otherwise, oxygen labeling cannot trace the origin of the methanol. Although this possibility is not definitively excluded, there was no evidence for it.

From the discussions above, we proceed to interpret the results using the isotopic content of the feed directly in most experiments. The results presented can be understood with the following set of reactions, in addition to the O exchange between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  on the reactor wall:



Reactions (1) and (2) are the methanol production reactions. The methanol produced should be isotopically labeled as the reactant  $\text{CO}$  or  $\text{CO}_2$ . The possibility of metha-

nol production from the reaction of CO with surface hydroxyl will be discussed later. Reaction (3) is the water-gas shift reaction. When this reaction proceeds from right to left, the oxygen isotope of CO<sub>2</sub> is equally split between CO and H<sub>2</sub>O. Reactions (4) and (5) are oxygen exchange reactions between CO and CO<sub>2</sub> or H<sub>2</sub>O. Reaction (6) is the oxygen exchange between CO<sub>2</sub> and the solid. The species O-S may be an adsorbed oxygen, a lattice oxygen, or a surface hydroxyl close to an active site.

Since these were initial rate measurements, some reactions can be eliminated. For example,  $C^*O + 2H_2 = CH_3^*OH$  could not take place initially because there was no C\*O present in the feed, unless C\*O could be produced by reaction (3) or (4) and be hydrogenated rapidly to methanol before desorption. This latter possibility will be shown to be unlikely in the later discussion.

Reactions (1) and (2) are discussed first. First, the results of Experiments 3-19-K and 3-19-O showed that in the absence of water, methanol was produced from both CO<sub>2</sub> and CO. In fact, the CO<sub>2</sub> hydrogenation was very competitive with CO hydrogenation, although the CO<sub>2</sub> pressure was only  $\frac{1}{20}$  of the CO pressure. This agrees with the observations that under these reaction conditions (low conversion, absence of water in the feed), CO<sub>2</sub> hydrogenation was faster than CO hydrogenation (11, 12, 22). An alternate possibility is that [<sup>18</sup>O]methanol was formed from isotope exchange between C<sup>18</sup>O<sub>2</sub> and intermediates in the CO hydrogenation.

The latter possibility is not supported by the following evidence. In the absence of CO in the feed, the initial rate of [<sup>18</sup>O]methanol production greatly exceeded the rate of [<sup>16</sup>O]methanol. The small methanol-<sup>16</sup>O production rate was close to the uncertainty level, and might indicate that oxygen exchange between the lattice oxygen and the surface intermediates in CO<sub>2</sub> hydrogenation to methanol is slow. Assuming that CO<sub>2</sub> hydrogenation took place in the presence of CO, the [<sup>18</sup>O]methanol production

can be adequately accounted for by CO<sub>2</sub> hydrogenation without invoking the possibility of C<sup>18</sup>O<sub>2</sub> exchange with intermediates in CO hydrogenation.

If the catalyst had been pretreated with water (Experiments 3-30-F, 3-30-I), the total rate of methanol production was lower, as reported earlier (22). This decrease in rate was due to the suppression of the [<sup>18</sup>O]methanol production, leaving the [<sup>16</sup>O]methanol production unaffected. This suppression of [<sup>18</sup>O]methanol production suggested a suppression of the CO<sub>2</sub> hydrogenation rate. Presumably water was so strongly adsorbed as to block the CO<sub>2</sub> hydrogenation site. Indeed, we have reported earlier that the effect of water pretreatment can only be removed after prolonged evacuation (22).

This effect of adsorbed water also excluded the possibility that C<sup>18</sup>O<sub>2</sub> first forms C<sup>18</sup>O which is hydrogenated to [<sup>18</sup>O]methanol before desorption. This follows from the fact that while water suppressed [<sup>18</sup>O]methanol formation, it did not suppress the formation of C<sup>18</sup>O or the hydrogenation of CO.

The experiments containing water in the feed can be similarly explained. The following argument is more involved because of the isotope scrambling between H<sub>2</sub>O and CO<sub>2</sub>. Table 1 shows the isotopic distribution of CO<sub>2</sub> at the beginning of the experiments. Methanol produced from CO<sub>2</sub> hydrogenation would reflect these isotope distributions to yield a ratio of [<sup>18</sup>O]methanol to [<sup>16</sup>O]methanol close to unity. In other words, in the absence of water inhibition, the rate of [<sup>18</sup>O]methanol production should be about half of the same rates in Experiments 3-19-K and 3-19-O, which would be clearly higher than the observed rates. Thus the phenomenon of water inhibition was real. The above argument also suggests that in the experiments with water, the [<sup>16</sup>O]methanol production from C<sup>16</sup>O<sub>2</sub> would be small. Thus the [<sup>16</sup>O]methanol observed must be almost totally produced from CO hydrogenation. Com-

parison of [ $^{16}\text{O}$ ]methanol rates between experiments with and without water then shows that water had minimal effect on CO hydrogenation. The different effects of water on the CO and the  $\text{CO}_2$  hydrogenation reactions thus suggest that these two reactions are independent, and probably occur on different sites.

The three experiments using water in the feed also showed that the methanol cannot be formed from the reaction of CO and  $\text{H}_2\text{O}$ . This is because from the isotope content of the water in these experiments, the methanol produced would have a ratio of [ $^{18}\text{O}$ ]methanol/[ $^{16}\text{O}$ ]methanol of 1/2 to 1/3, which was quite different from the observed ratio.

Finally, it should be pointed out that the amount of water in the feed was about 10 times the amount of water at equilibrium using these feeds. The partial pressure of methanol for reaction (2) in equilibrium with the feed composition can be calculated to be about 0.2 atm. Thus our experiments were far from equilibrium.

In view of the strong effect of water, we must assume that even in Experiments 3-19-K and 3-19-O and 2-21-M where no water was added, the results could well be affected by some adsorbed water, since the catalyst had been pretreated with the synthesis mixture before these experiments. In other words, the rates of [ $^{18}\text{O}$ ]methanol might still be higher if the catalyst was very dry.

At this point, it is interesting to propose a scheme regarding the role of CO,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  in methanol synthesis over Cu-Zn-O. It is proposed that methanol can be produced *primarily* by two independent pathways—one involving the hydrogenation of  $\text{CO}_2$ , and the other the hydrogenation of CO. Using a feed of CO,  $\text{CO}_2$ , and  $\text{H}_2$  and at low conversions and low temperature, the hydrogenation of  $\text{CO}_2$  is the primary pathway because it is faster than the hydrogenation of CO (11, 12, 22). This explains the observation of Rozovskii (14-16) and Chinchén *et al.* (19). At high conversions,

however, significant amounts of water would be produced by both  $\text{CO}_2$  hydrogenation and the reverse water-gas shift reaction. The water preferentially suppresses  $\text{CO}_2$  hydrogenation, and methanol is then primarily produced from CO.

In addition to direct participation in the reaction mechanism, the presence of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is also important in maintaining the oxidation state, and thus the activity of the catalyst. This model can be used to explain the dependence of methanol production rate as functions of  $\text{CO}_2/\text{CO}$  and  $\text{H}_2\text{O}/\text{CO}$  (8, 10). In the absence of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , the feed of CO and  $\text{H}_2$  is too reducing, and the catalyst deactivates due to over-reduction. The activity of the catalyst is due to CO hydrogenation on the reduced site (such as  $\text{Cu}^+$ ) of the catalyst. The presence of an optimal amount of  $\text{CO}_2$  or  $\text{H}_2\text{O}$  maintains the oxidation state of the catalyst. At this point, the catalyst has both the reduced sites where CO hydrogenation occurs, and the oxidized site (such as  $\text{Cu}^{2+}$  which may be formed by oxidation of Cu metal) where  $\text{CO}_2$  hydrogenation occurs ( $\text{CO}_2$  is present in the feed or formed from  $\text{CO} + \text{H}_2\text{O}$ ). Methanol is produced from both sites. Beyond the optimal compositions, excess  $\text{H}_2\text{O}$ , either in the feed or produced by  $\text{CO}_2$  hydrogenation, suppresses the activity by suppressing the  $\text{CO}_2$  hydrogenation reaction.

The apparent independence of the CO and  $\text{CO}_2$  hydrogenation reactions could be the reason for the different claims on whether the Cu-Zn-O catalyst is active for CO hydrogenation (8, 11, 12, 18, 22). That different sites are involved implies that the relative contributions from the two hydrogenation reactions would depend on the detailed preparation and the pretreatment of the catalyst.

Discussions on the other reactions will be more qualitative because they involve CO,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  whose rates had higher uncertainties.

Next we discuss the water-gas shift reaction. In experiments without water, only

the reverse shift reaction could take place initially. This includes the first five experiments in Table 1. In the experiments without CO (3-19-M and 3-19-Q),  $^{18}\text{O}$ -labeled water was formed from both  $\text{CO}_2$  hydrogenation and the reverse shift reaction. Indeed, considering the large uncertainties in the water production rate, the  $\text{H}_2$   $^{18}\text{O}$  formation rate equaled the sum of the formation rates of [ $^{18}\text{O}$ ]methanol and  $\text{C}^{18}\text{O}$ . The small rates of formation of  $\text{C}^{16}\text{O}$  and  $\text{H}_2^{16}\text{O}$  may indicate the participation of lattice oxygen in the reactions. This will be further discussed later. They may also result from the desorption of previously adsorbed species.

As to the experiments with CO present (3-19-K and 3-19-O), if the formation rate of  $\text{H}_2$   $^{18}\text{O}$  was taken as due to  $\text{CO}_2$  hydrogenation and reverse water-gas shift, then the  $\text{C}^{18}\text{O}$  formation rate was too high to be accounted for by the reverse shift reaction. In fact, the rate of consumption of  $\text{C}^{18}\text{O}_2$  was also too high to be accounted for by these two reactions. Thus we propose the  $\text{CO}_2$ -CO oxygen exchange reaction (reaction (4)). In the presence of CO, this reaction was the fastest reaction. It accounted for most of the reaction of  $\text{C}^{16}\text{O}$  and  $\text{C}^{18}\text{O}_2$ , and for the production of  $\text{C}^{16}\text{O}^{18}\text{O}$  and  $\text{C}^{16}\text{O}_2$ . The behavior of these two latter species, as shown in Fig. 1, was indeed characteristic of a stepwise oxygen exchange process. This reaction interestingly was not affected by the presence of adsorbed water (3-30-F and 3-30-I). We have also investigated as to whether the presence of  $\text{H}_2$  was required by replacing  $\text{H}_2$  with He. The results are shown in Table 2. Clearly, this exchange proceeded readily as long as both CO and  $\text{CO}_2$  were present, independent of the methanol production or the water-gas shift reaction.

Water was added in the feed in the last three experiments in Table 1. Interpretation of the data was more involved because of the rapid isotope scrambling between  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Most of the data could be interpreted with reactions (1) to (4). There was

TABLE 2  
Exchange of Oxygen between CO and  $\text{CO}_2$  on  
Cu-Zn oxide

Expt	Feed composition (atm)			Initial product formation rate ( $10^{-5}$ mol/min-g)	
	He	CO	$\text{C}^{18}\text{O}_2$	$\text{C}^{16}\text{O}^{18}\text{O}$	$\text{C}^{18}\text{O}$
3-13-G	11.3	4.4	0.24	11.5	5.1
3-19-U	11.5	5.0	0.17	9.8	12.1
3-13-I	15.6	0	0.14	0	0.3
3-9-G	16.3	0	0.12	2.6	0.5

one exception, namely, the  $\text{C}^{18}\text{O}$  production rate was too high to be accounted for by  $\text{CO}$ - $\text{CO}_2$  exchange and the reverse water-gas shift. Thus it was assumed that reaction (5), oxygen exchange between CO and  $\text{H}_2\text{O}$ , also took place.

It is of interest to point out that the gas-phase  $^{18}\text{O}$  was not conserved in these initial rates in experiments without water. There was a net loss of  $^{18}\text{O}$ . The most likely explanation is that  $^{18}\text{O}$  was being incorporated into the catalyst, probably via reaction (6). If indeed  $^{18}\text{O}$  is being incorporated into the lattice, it might reappear in some of the products in normal isotope experiments subsequent to the  $^{18}\text{O}$  isotope experiments. Table 3 shows the rates of appearance of the labeled products in these experiments. The sequence of the experiments were identified by the alphabetical order. For example, Experiment 3-19-L in Table 3 followed Experiment 3-19-K in Table 1. The results showed that indeed  $^{18}\text{O}$ -labeled products were observed but at very small rates. This could mean that diffusion of lattice oxygen was rather rapid, only a small amount of  $^{18}\text{O}$  was incorporated into the lattice, or  $^{18}\text{O}$  was removed in some form during the evacuation between experiments. These possibilities could be distinguished with more accurate measurements than those possible here.

#### APPENDIX: UNCERTAINTIES IN THE RATES

The accuracies of the rates in Table 1 can



TABLE 3  
Formation of  $^{18}\text{O}$ -Containing Molecules in  
Experiments following an Isotope Experiment  
(Feed: 4.28%  $\text{CO}_2$ , 32.5%  $\text{CO}$ , 63.22%  $\text{H}_2$ )

Expt	Initial rate of formation ( $10^{-5}$ mol/min-g)					
	$\text{C}^{18}\text{O}$	$\text{C}^{16}\text{O}^{18}\text{O}$	$\text{C}^{18}\text{O}_2$	$\text{CH}_3^{18}\text{OH}$	$\text{H}_2^{18}\text{O}$	
3-19-N	0	0.31	0	0.04	-0.05	
3-19-P	0.09	0.09	0	—	0.26	
3-19-L	0.04	0.40	0	—	—	
3-30-G	0	0.18	0	0.01	0	

be discussed with respect to the uncertainties of the individual rates and of ratios of rates.

One of the most important factors determining uncertainties was the mass spectrometer sensitivities of the species. Uncertainties in the sensitivities were due to fluctuations in the operation conditions such as the mass spectrometer settings, the pumping speed, and the pressures of the species in the reactor. The sensitivities were obtained by calibration with a known composition in the reactor. Although calibrations were done every day, experience showed that the sensitivities varied by 10 to 20% between experiments. This contributed significantly to the uncertainties in the absolute magnitudes of the rates and limited the accuracies in the comparison of rates among species. However, the ratios of rates of the different isotopes of the same species were not dependent on the sensitivities, and were therefore more accurate, unless one of the isotopes was overlapped by the cracking from another component.

Uncertainties in the rates also depended on the magnitudes of the rates compared to the magnitudes of the partial pressures in the reactor, the background pressures in the mass spectrometer, the noise in the spectrometer signal for that mass unit, and in some cases the accuracies of the cracking patterns. The higher were the rates compared to the other parameters, the lower were the uncertainties. In general,

disregarding sensitivities, the uncertainties in the  $\text{C}^{16}\text{O}$  and  $\text{H}_2$  rates were high because their pressures were high, and the mass spectrometer background of these gases were also high. The uncertainties were about 30% for high rates, and up to 50% for low rates. The uncertainties in  $\text{C}^{18}\text{O}$  ( $m/e = 30$ ) rates were about 25% due to non-negligible contributions from the natural isotopic content of  $\text{CO}$  to this peak, the uncertainties in the cracking patterns of  $\text{C}^{18}\text{O}_2$  and  $\text{C}^{16}\text{O}^{18}\text{O}$  into this peak, and the build-up of  $\text{CO}$  in the mass spectrometer chamber due to inefficient pumping of  $\text{CO}$  compared to other gases. The uncertainties in the water rates were about 50%, primarily due to noise and the background pressure in the mass spectrometer. Those for  $\text{C}^{16}\text{O}_2$  and  $\text{C}^{18}\text{O}_2$  were about 30%, and those for  $\text{CH}_3^{16}\text{OH}$  and  $\text{CH}_3^{18}\text{OH}$  were about 10%. The uncertainties for the methanol rates were low because of the low background pressures for these masses.

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