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A Comparative Study of Methanol Synthesis from CO_2/H_2 and CO/H_2 over a $Cu/ZnO/Al_2O_3$ Catalyst

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Methanol synthesis from CO_2/H_2 and CO/H_2 has been compared over a $Cu/ZnO/Al_2O_3$ catalyst. Methanol synthesis was much faster with CO_2/H_2 than with CO/H_2, particularly at low temperatures. A trace amount of CO_2 improved the rates significantly. Thus it appeared that CO_2 was the primary source of methanol with $CO/CO_2/H_2$ feed. When space velocities were varied, both of the previously conflicting observations on the effect of CO_2/CO composition, i.e., monotonical increase in synthesis rate vs the presence of a maximum rate as CO_2 concentration increased, were observed. The different conversion levels and consequent difference in surface oxygen coverage and/or water appeared to be responsible for the different effects. The more oxidized surface state of copper obtained for CO_2/H_2 was more active and stable in methanol synthesis than the overreduced surface obtained for the CO/H_2 feed. Due to the promotional and inhibition effects of water for CO/H_2 and CO_2/H_2 feeds, respectively, higher space velocities yielded higher synthesis rates for CO_2/H_2 and the opposite effect was observed for the CO/H_2 feed.

INTRODUCTION

Carbon dioxide is the most important "greenhouse gas" which may cause global warming. Its concentration has been increasing steadily due to the ever—increasing energy usage of modern society. One estimate indicates that the CO_2 concentration in the atmosphere will double from pre—Industrial Revolution levels by a year between about 2025 and 2075 (*1*). Various measures have been proposed to stabilize the atmospheric CO_2 level which include chemical fixation and recycling the emitted CO_2. Conversion of CO_2 to methanol by catalytic hydrogenation (Reaction 1) has been recognized as one of the most promising processes for this purpose because of a potentially large demand for methanol as a fuel and a basic chemical (*2*).

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (1)$$

Methanol synthesis by hydrogenation of CO_2 is closely related to methanol synthesis by CO hydrogenation (Reaction 2) because typical feedstocks for current industrial methanol synthesis contain ca. 5 vol% CO_2 in addition to CO and H_2.

$$CO + 2H_2 \rightarrow CH_3OH \quad (2)$$

The processes are operating at 50–100 bar and 220–240°C with catalysts composed of $Cu/ZnO/Al_2O_3$ or $Cu/ZnO/Cr_2O_3$ (*3*). Fundamental aspects of the process and catalysts have been extensively studied and the results are summarized in recent reviews (*4–7*). However, there is still controversy over many important questions such as the roles of catalyst components, the reaction steps leading to methanol and whether CO or CO_2 is the main source of methanol. The last question is particularly relevant when one considers methanol synthesis as a means of CO_2 recycling.

The mechanism that stipulates CO as the direct precursor to methanol was first proposed by Boomer and Morris (*8*) in 1932. Carbon dioxide is considered to function to

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control the surface composition, oxidation state, and dispersion of copper in the catalyst and to transform to methanol only after being converted to CO by the reverse water–gas shift reaction (*9–10*). However, Russian workers (*11–14*) claimed that methanol was made predominantly from CO_2. Recently, Chinchen *et al.* (*15, 16*) demonstrated by isotope labeling experiments over a $Cu/ZnO/Al_2O_3$ catalyst that, under realistic industrial reaction conditions (50 bar, 250°C), essentially all the methanol was made from CO_2 of a $CO/CO_2/H_2$ feed and that this remained true down to a very low CO_2/CO ratio. The results are in complete agreement with those of the Russian workers (*11–14*) which were obtained under similar conditions and with similar catalysts.

In spite of these rather convincing evidences, the matters are not completely settled yet (*17*). Of particular interest are apparently conflicting effects of CO_2/CO ratio in the feed on the rate of methanol formation. Klier and co-workers (*10, 18*) observed a maximum synthesis rate at CO_2/CO ratio of 1/14. They claimed that at lower CO_2 concentration the catalyst was deactivated by overreduction and at higher concentration the synthesis was retarded by a strong adsorption of the gas. On the other hand, Liu *et al.* (*19*) reported that the rate increased monotonically as CO_2 concentration increased. It has also been reported that CO_2 converts to methanol at greater rates than CO (*20, 21*). Most recently, Chanchlani *et al.* (*17*) observed both effects. Namely, below 250°C, CH_3OH synthesis rates exhibited monotonical increase with increasing CO_2 concentration, while a maximum rate was observed at higher temperatures. This observation was interpreted as being due to a change in the importance of CO and CO_2 as the source of methanol in the synthesis.

In order to evaluate the potentialities of CO_2 recycling by methanol synthesis from CO_2/H_2, it is desired to understand fundamental nature of the reaction, especially in comparison with more common synthesis from CO/H_2. Hence, this work compares the methanol synthesis from CO_2/H_2 and CO/H_2 over a conventional $Cu/ZnO/Al_2O_3$ catalyst. The reaction kinetics and the state of catalyst are investigated under two synthesis gas mixtures. Furthermore, the effect of CO_2 concentration in synthesis with $CO/CO_2/H_2$ is reexamined. If CO_2 is indeed the sole source of CH_3OH in the synthesis from $CO/CO_2/H_2$ over $Cu/ZnO/Al_2O_3$ catalyst, it would have an important implication in CH_3OH synthesis from CO_2/H_2, the ultimate goal of this work.

EXPERIMENTAL

The catalyst used in this study was prepared by a conventional coprecipitation method (*9*). It was precipitated from an aqueous solution of $Cu(NO_3)_2 \cdot 2.5H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ (all Alfa, total cation concentration 1 *M*) by dropwise addition of a 1 *M* aqueous solution of Na_2CO_3 (Alfa) at 80°C to a final pH of 7. The precipitate was then filtered, dried, and then calcined in air at 350°C for 12 h. The resulting catalyst has the composition of $CuO/ZnO/Al_2O_3$ = 49/36/15 by weight. It was ground and sieved to obtain mesh sizes of 100–140.

Specific surface area was determined by the N_2 BET method on a Micromeritics constant–volume adsorption system (Accusorb 2100E). Exposed copper surface area was measured by the N_2O titration following the procedure described by Chinchen *et al.* (*22*). To examine the bulk structure of the catalyst, the powder X-ray diffraction (XRD) was performed on Rigaku Dmax-B diffractometer with Cu$K\alpha$ radiation. Temperature-programmed reduction (TPR) was performed in a flow reaction system with 25 mg of the catalyst. After the methanol synthesis with CO/H_2 or CO_2/H_2 at 250°C for 24 h, the catalyst was flushed by He at 150°C for 1 h in order to remove weakly adsorbed species on the catalyst. After switching the gas to 5% H_2 in N_2, temperature was raised at a rate of 200°C h^{-1}. The consumption of H_2 was monitored by a thermal conductivity detector.

Methanol synthesis was conducted in a pressurized flow reactor which was an in-house modification of a commercial Sotelem RDP-830 reaction system. The reactor was a stainless steel U-tube with a volume of 3 ml. It was housed in an electric furnace controlled by a temperature controller and a local thermocouple located at the exterior wall of the reactor. The reactor pressure was regulated by a backpressure regulator. The flow rate and composition of feed gases were adjusted by controlling the flow rate of individual gases by mass flow controllers which were calibrated by a bubble flow meter. CO (99.95%), H_2 (99.98%) were passed through MnO/SiO_2 and molecular sieve traps and CO_2 (99.98%) was used as received.

Prior to catalytic reaction, typically 0.5 g of the calcined catalyst was reduced in flowing 20% H_2 in He at atmospheric pressure (34 μmol s^{-1}) at temperatures increasing at a rate of 150°C h^{-1} up to 250°C and then in pure H_2 (27 μmol s^{-1}) at 250°C for 3.5 h. The reaction products were analyzed by an on-line gas chromatograph (Hewlett-Packard 5890) equipped with a 2.5 m long Porapak T column and a thermal conductivity detector. The stainless steel line between reactor and GC was heated by a heating tape at 130°C to avoid condensation of some products.

RESULTS

The reduced catalyst had the BET surface area of 35 m^2 g^{-1}. The exposed copper area determined by the N_2O titration was 5.3 m^2 g^{-1} which corresponded to a particle size of 63 nm if copper particles assumed a spherical shape.

To understand the fundamental difference between methanol synthesis from CO_2/H_2 and CO/H_2, the reactivity and the state of the catalyst were compared under otherwise identical reaction conditions. In all cases, the reaction was carried out at 30 bar over $Cu/ZnO/Al_2O_3$ with the composition of 49/36/15 (wt%). In Fig. 1, approaches to steady states are compared. In CO_2/H_2, the reduced catalyst showed slight decrease in CO_2 conversion with time on stream and reached a steady state within 5 h. The behavior in CO/H_2 was much more complex. It showed slight increase in the beginning followed by decrease in CO conversion. It took more than 20 h to reach a steady state. Hence, the steady state rate data reported in this paper were those obtained after 12 and 24 h on stream for CO_2/H_2 and CO/H_2, respectively. In both cases, there was no significant change in methanol selectivity.

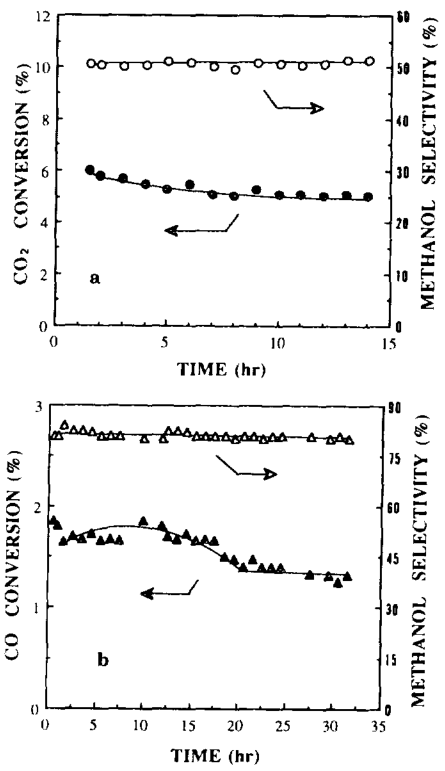

FIG. 1. Approach to steady states during methanol synthesis over $Cu/ZnO/Al_2O_3$ catalyst with CO_2/H_2 (a) and CO/H_2 (b). Catalyst loading = 0.25 g; P = 30 bar; T = 250°C; total flow rate = 100 μmol s^{-1}; H_2/CO_x = 4.

As shown in Fig. 2, an increase in H_2 concentration resulted in higher CO_x (x = 1 or 2) conversions both in CO_2/H_2 and CO/H_2. However, methanol selectivity showed opposite trends for two gas mixtures; an

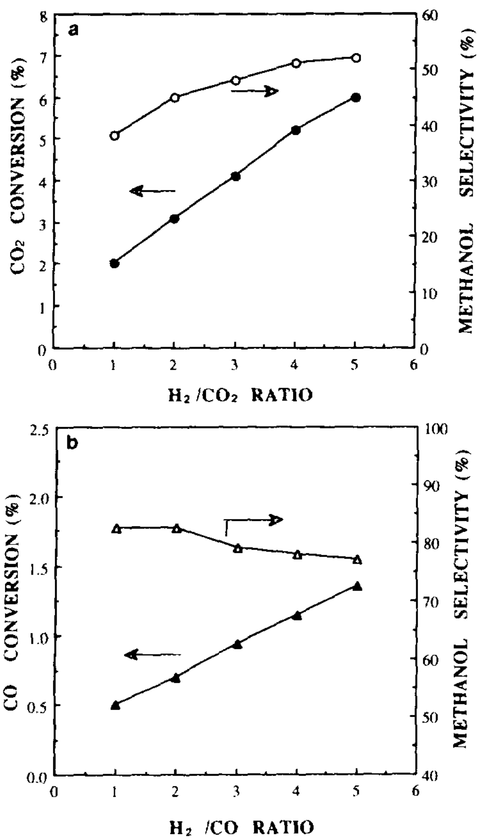

FIG. 2. Dependence of CO_2 (a) or CO (b) conversion and methanol selectivity on H_2/CO_x feed ratio. Catalyst loading = 0.25 g; P = 30 bar; T = 250°C; total flow rate = 100 μmol s^{-1}.

increase for CO_2/H_2 and a decrease for CO/H_2 at higher H_2 concentrations. In general, carbon oxide conversion for CO_2/H_2 was higher, but methanol selectivity was lower than for CO/H_2. Most of the selectivity loss was due to the interconversion of carbon oxides. Thus methanol and CO were produced with almost the same yields (% conversion × % selectivity) from CO_2/H_2. Significant amount of methane (up to the yield of 0.1%) and small amount of ethane were also detected from synthesis with CO/H_2, particularly at higher H_2/CO ratios.

The effect of reaction temperature on methanol yield is shown in Fig. 3. Also shown are calculated equilibrium yields for synthesis with CO_2/H_2 and CO/H_2. The equilibrium yields were higher for CO/H_2 below 300°C. The sequence of temperature change was random in order to avoid potential systematic errors due to catalyst deactivation. Experimental methanol yields showed a maximum in both cases. Since these points are far enough from the calculated equilibrium lines, it is unlikely that the maxima are due to thermodynamic equilibria. Reduction in methanol yields at high temperatures was not caused by the loss of activity, but by the loss of selectivity. In high temperature synthesis, the major product with CO_2/H_2 was CO and significant amount of methane. Meanwhile, synthesis with CO/H_2 showed CO_2 and C_1–C_5 hydrocarbons. These hydrocarbons satisfied the Schulz–Flory distribution by showing a straight line in a plot of ln (mol%) vs carbon chain length. The catalysts which underwent synthesis with CO/H_2 at temperatures above 290°C indicated carbon deposition on their surface by X-ray photoelectron spectroscopy (Perkin–Elmer PHI 5400) analysis. In the whole temperature range tested here, CO_2 hydrogenation always gave higher methanol yields than that of CO.The difference was greater at lower temperatures

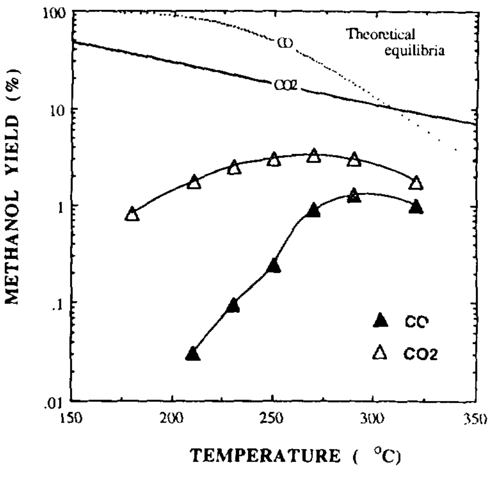

FIG. 3. Temperature dependence of methanol yield in synthesis with CO_2/H_2 and CO/H_2. Catalyst loading = 0.25 g; P = 30 bar; total flow rate = 100 μmol s^{-1}; H_2/CO_x = 4.

where more than one-order-of-magnitude difference was observed.

Effect of CO/CO_2 composition is shown in Fig. 4 for three space velocities (F/W) expressed as (1 feed gas at STP)/(kg catalyst) (h). The concentration of H_2 was fixed at 80 mol% and relative composition of CO/CO_2 was varied continuously. The rate of methanol formation was very slow with CO/H_2 at F/W of 36,000 liter/kg/h and increased monotonically as CO was progressively replaced by CO_2. At F/W of 12,000 liter/kg/h, the trend was similar, yet the rate with CO_2/H_2 was higher than with CO/H_2 by only a factor of 2. At F/W of 6000 liter/kg/h, the methanol yield showed a sharp maximum at CO_2 concentration of ca. 5% in CO/CO_2 mixture. Since the methanol yields depended on H_2 concentration as shown in Fig. 2 and theoretical requirements of H_2 are different for CO and CO_2 (Eqs. 1 and 2), similar experiments of varying CO/CO_2 ratio were performed by maintaining stoichiometric H_2 concentrations, i.e., $[H_2] = 2 \times [CO] + 3 \times [CO_2]$. As shown in Fig. 5, a similar effect was observed, monotonical increase in methanol yield with increasing CO_2 concentration for the high F/W, and the presence of a maximum at the low F/W. Again, thermodynamic equilibrium was not responsible for these effects as shown in Fig. 5. Carbon monoxide used in the present study contained ca. 150 ppm of CO_2 as an impurity. When purer grade CO containing CO_2 less than 50 ppm was used, methanol formation was negligible as indicated by the lower points for 0% CO_2 in Fig. 5 (F/W = 12,000 liter/kg/h). The result showed that even trace amounts of CO_2 can accelerate methanol formation significantly.

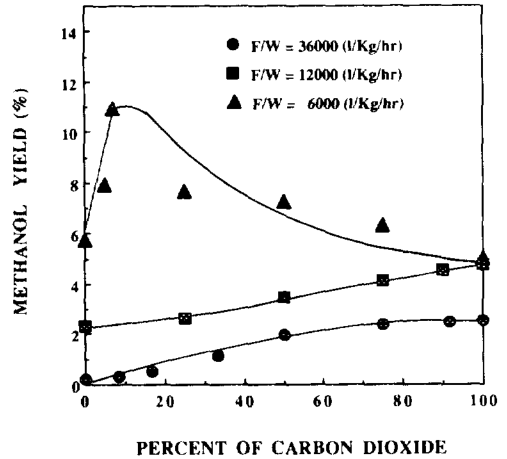

FIG. 4. Yields of methanol as a function of space velocity and feed has composition containing 80 mol% H_2. Catalyst loading = 0.5 g; P = 30 bar; T = 250°C.

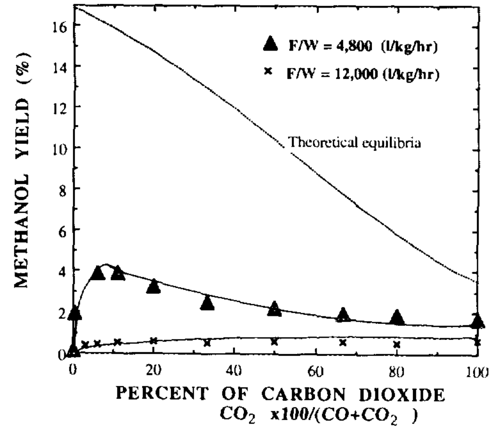

FIG. 5. Yields of methanol as a function of space velocity and feed gas composition containing H_2 according to stoichiometric relation, i.e., $[H_2] = 2 \times [CO] + 3 \times [CO_2]$. Catalyst loading = 0.5 g; P = 13 bar; T = 240°C. The lower point for 0% CO_2 (F/W = 12,000 liter/kg/h) was obtained with purer grade CO containing less than 50 ppm of CO_2 as an impurity.

During the experiment shown in Fig. 4, the concentration of water in the reactor outlet was measured by GC. Although quantification of water by GC is known to be subject to significant errors, Fig. 6 clearly shows that the concentration of water increases with increasing CO_2 concentration for all F/W values. During the experiment, it was found that the results depended on the sequence of changing gas composition. As shown in Table 1, reproducible results were obtained when the experiment was started with synthesis gases containing CO_2. As demonstrated for $CO/CO_2/H_2$ = 6.7/13.3/80, fresh catalyst and the catalyst

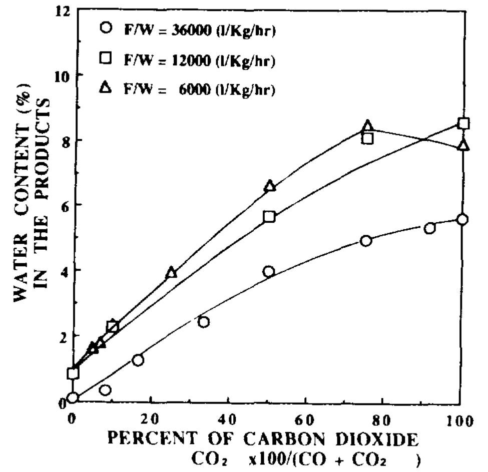

FIG. 6. Change of water concentration in the reactor outlet during the experiments shown in Fig. 4.

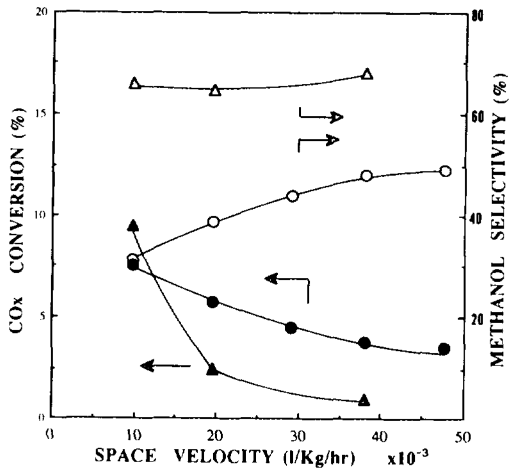

FIG. 7. Effect of space velocity on CO_x conversion and methanol selectivity for synthesis with CO_2/H_2 (○, ●) and CO/H_2 (△, ▲). Catalyst loading = 0.5 g; P = 30 bar; T = 250°C; H_2CO_x = 3.

which had been used for synthesis with other compositions of CO/CO_2 gave the same results for a new composition of the gases. On the other hand, the catalyst appeared to be deactivated irreversibly once it contacted CO/H_2 atmosphere.

Effects of space velocity on CO_x conversion and methanol selectivity are shown in Fig. 7. With CO/H_2, CO conversion decreased rapidly with increasing space velocity, while methanol selectivity remained unchanged. The decrease in CO conversion was so rapid that the rate of the reaction (CO conversion × space velocity) actually decreased as the space velocity was increased. On the other hand, CO_2 conversion decreased much more slowly and methanol selectivity increased with space velocity. Figure 8 shows the same data expressed in methanol yield (CO_x conversion × methanol selectivity) together with yields of other products. The decrease in CO_2 conversion and improvement in methanol selectivity compensate each other and made the methanol yield almost invariant (Fig. 8A). Rapid decrease in CO yield was responsible for the improved methanol selectivity. As a result, the rate of the reaction increased almost linearly with space velocity for synthesis with CO_2/H_2. As shown in Fig. 8B, methanol yield showed the same trend as CO conversion as expected. The yields of CO_2 and CH_4 also decreased with space velocity.

TABLE 1

Carbon Conversion to Methanol over $Cu/ZnO/Al_2O_3$ for Different Sequence of Changing Feed Gas Composition[a]

Feed gas composition/% $CO/CO_2/H_2$	Methanol yield/%	
	$CO_2/H_2 \rightarrow CO/H_2$	$CO/H_2 \rightarrow CO_2/H_2$
0/20/80	2.52[b]	0.85
1.7/18.3/80	2.48	0.73
3.3/16.7/80	2.37	—
6.7/13.3/80	1.97, 2.1[c]	0.25
10/10/80	1.15	0.18
15/5/80	0.53	—
18.3/1.7/80	0.30	0.53
20/0/80	0.21	0.28[b]

[a] Catalyst loading = 0.5 g; P = 30 bar; T = 250°C; feed gas flow rate = 200 μmol s^{-1}.

[b] Steady state yields after 24 h on stream.

[c] Over fresh catalyst without previous run under other gas composition.

Figure 9 compares the XRD patterns of calcined (Fig. 9a), reduced (Fig. 9b), and used catalysts for synthesis with CO_2/H_2

(Fig. 9c) or with CO/H_2 (Fig. 9d) at 250°C for 24 h. The samples for Fig. 9b–9d were passivated in a flowing O_2 (1 vol%)–He mixture at room temperature (RT) for 0.5 h before exposure to atmosphere for XRD measurements. The calcined sample showed monoclinic CuO with predominant {111} planes together with hexagonal ZnO and a trace of $CuAlO_2$. Upon reduction, peaks related to CuO disappeared and (111), (200), and (220) planes of cubic metallic copper appeared. The XRD patterns did not change at all after synthesis with CO_2/H_2 or CO/H_2. Thus metallic copper remained to be the only crystalline phase once it was reduced.

Temperature-programmed reduction (TPR) is a useful technique to examine the reducibility and degree of reduction of a catalyst. Figure 10 shows the TPR results for two samples used for methanol synthesis at 250°C for 24 h with CO/H_2 (Fig. 10a) or CO_2/H_2 (Fig. 10b). The catalyst used for CO/H_2 reaction showed a single H_2 consumption peak. The catalyst used for CO_2/H_2 showed a peak at the same temperature as for CO/H_2 and an additional peak at a lower temperature. Furthermore, the peak intensity was higher for the catalyst used for CO_2/H_2, indicating that the catalyst was more oxidized. The high temperature peak observed for both catalysts were also observed for the calcined catalyst, but in much higher intensity. Hence, the peaks in Fig. 10 are most likely originated from the oxygen species bonded to copper on or near the surface.

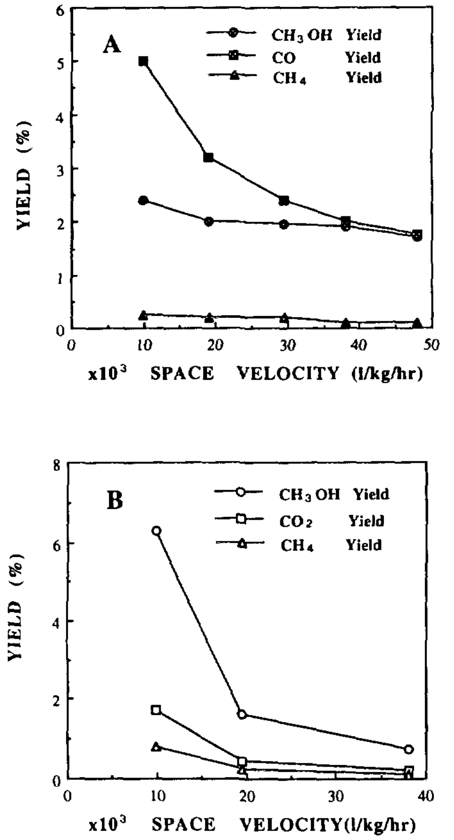

FIG. 8. % yields of major products during experiments shown in Fig. 7: (A) CO_2/H_2, (B) CO/H_2.

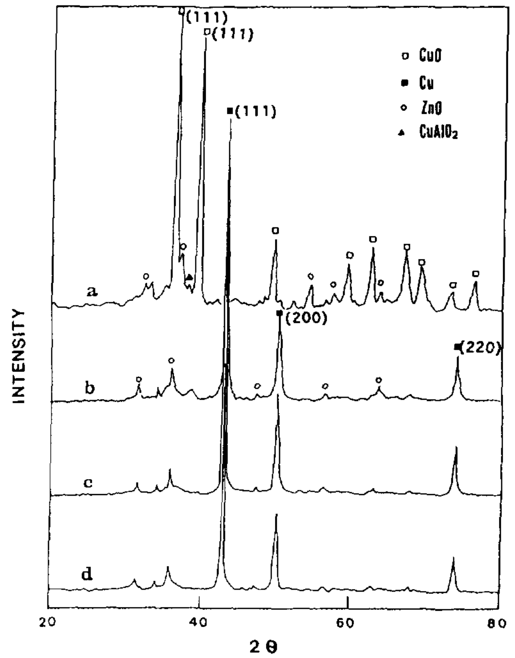

FIG. 9. XRD patterns of $Cu/ZnO/Al_2O_3$: (a) Calcined, (b) reduced in 20% H_2/He at 250°C for 3.5 h, (c) after synthesis with CO_2/H_2 at 250°C for 24 h, and (d) after synthesis with CO/H_2 at 250°C for 24 h. All the samples were passivated in flowing 1% O_2/He at room temperature before exposure to air.

DISCUSSION

As discussed in the Introduction, there has been a continued debate in the literature

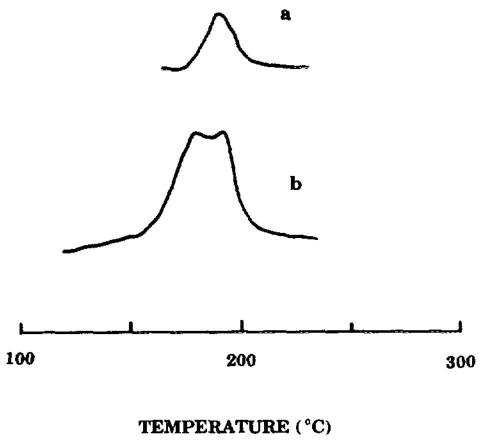

FIG. 10. TPR spectra of $Cu/ZnO/Al_2O_3$ after methanol synthesis at 250°C for 24 h in CO/H_2 (a) and CO_2/H_2. Sample loading = 25 mg; flow rate of 5% H_2/N_2 = 15 μmol s^{-1}; heating rate = 150°C h^{-1}.

on the primary source of methanol when both CO and CO_2 are present in the feed gas. Most of the recent experimental data indicate that CO_2 is the major source under usual synthesis conditions over $Cu/ZnO/Al_2O_3$ catalysts (*11–17, 19, 21*). However, there is still an opinion that CO hydrogenation could be important under some conditions such as at high temperatures (*17*). Figure 3 shows that CO_2 hydrogenation is much faster than that of CO, especially at low temperatures. This effect is in good agreement with previous reports (*20, 21*). The difference would be larger if the traces of CO_2 or H_2O usually contained in CO are absolutely excluded as exemplified in Fig. 5. Two rates are comparable only at the reaction temperatures above 300°C. Russian workers (*11, 23*) have also reported that no detectable activity of methanol synthesis was observed for CO_2-free syngas over $Cu/ZnO/Al_2O_3$. This has been attributed to the difference in catalyst (*24*). Yet it seems more probable that different purity of CO gas was responsible for the many different results reported on the activity of copper catalysts for methanol synthesis with CO/H_2. Hence, when both CO and CO_2 are present over $Cu/ZnO/Al_2O_3$, CO_2 must be the major source of methanol on this simple kinetic ground. One complication on this kinetic argument is, as discussed later, that CO/H_2 also deactivates the catalyst due to over-reduction as shown in Table 1. This difference in catalyst has to be considered in addition to the difference in reaction pathway.

In synthesis with CO/H_2, the contribution of CO_2 route, if present, should be minimal because the chance for the CO_2 formation is small. Water gas shift reaction cannot proceed without water in the system. However, the presence of hydrocarbons in the products and deposited carbon on the catalyst surface at high temperatures indicates that Fischer–Tropsch and Boudouard reactions have proceeded to some extent.

$$2CO \rightarrow CO_2 + C \qquad (3)$$

$$CO + H_2 \rightarrow -(CH_x)_n- + H_2O \qquad (4)$$

The water formed can now initiate the water gas shift reaction. Indeed, significant amounts of water and CO_2 (with selectivity near 10%) were detected in the reactor outlet (Fig. 8). During methanol synthesis, the CO_2-to-CO conversion with CO_2/H_2 feed was more pronounced than CO-to-CO_2 conversion with CO/H_2 feed, and this was the main reason that methanol selectivity was always better for the synthesis with CO/H_2. Under this condition, CO is known to transform to methanol via a formyl intermediate (–CHO) formed by a reaction between adsorbed CO and H, whereas CO_2 route involves a formate intermediate (–HCOO) (*7, 25, 26*). This difference in reaction mechanism may be responsible for the different response to H_2/CO_x ratio in Fig. 2. When CO/CO_2 coexists, CO_2 becomes a dominant reactant and CO participates in the synthesis mainly after being converted to CO_2 by water gas shift reaction.

$$CO \underset{H_2}{\overset{H_2O}{\rightleftharpoons}} CO_2 \xrightarrow{H_2} CH_3OH \qquad (5)$$

The H_2O could come from the methanol synthesis and the reverse water gas shift reaction.

Probably the most interesting observation made in the present work is the effect of CO_2 concentration in $CO/CO_2/H_2$ mixture on the yield of methanol as presented in Figs. 4 and 5. Note that the rates of methanol formation could be obtained by multiplication of the yield and space velocity. As mentioned earlier, there are conflicting reports on the effect of CO/CO_2 composition in the literature (*10, 18, 19*). With increasing CO_2 concentration, methanol synthesis rate increases monotonically, or shows a sharp peak at a low CO_2/CO ratio. Our results show that both effects could be observed at different space velocities. The potential interference of thermodynamic equilibrium or different H_2 requirement for CO and CO_2 was eliminated. The observation should be different in nature from that of Chanchlani *et al.* (*17*) since the reaction temperature was fixed in the present work. This observation has not been previously reported to the best of our knowledge.

At high space velocities (or short contact times), methanol yield increases continuously as increasing amount of CO is replaced by CO_2. The results are in complete agreement with those of Liu *et al.* (*19*). This can be easily understood if CO_2 is the primary source of methanol. Under this condition of small conversions, any secondary reactions are negligible and the behavior reflects true kinetic effects of methanol synthesis from $CO/CO_2/H_2$. Thus, concentration of water may be too small to drive CO-to-CO_2 conversion by the water gas shift reaction, and the contribution of CO to the methanol synthesis is insignificant. As the space velocity is lowered (F/W = 12,000 liter/kg/h in Fig. 4), the effect of CO/CO_2 composition becomes smaller. In particular, a substantial increase in methanol yield is achieved without CO_2 in CO/H_2. As shown in Fig. 6, the concentration of water increases significantly at this space velocity. It is expected that water gas shift reaction is equilibrated under this condition for the most part of CO/CO_2 composition (*17*).

As the space velocity is further decreased ($F/W < 6{,}000$ liter/kg/h in Figs. 4 and 5), methanol yields show an initial sharp increase, reach a maximum, and then decrease. At the same CO_2 concentration, the rate of methanol synthesis at this maximum in Fig. 4 is greater than those for higher space velocities by factors of ca. 2.5 and 3.5. These results are now in a qualitative agreement with those of Klier *et al.* (*10, 18*). From the basic assumption that CO was the primary source of methanol, they claimed that at lower concentration of CO_2 the catalyst was deactivated by overreduction and that at higher concentration of CO_2 the synthesis was retarded by a strong adsorption of CO_2. However, Liu *et al.* (*19*) attributed the decrease at higher CO_2 concentration to, among other things, an inhibition by water which adsorbs strongly on the active sites in competition with CO_x. Indeed serious deactivation was observed when water was added in the feed gas mixture (*18, 19*). In Fig. 6, the water concentration increases rapidly as CO_2 concentration is raised. However, it does not change much when the space velocity is reduced from 12,000 to 6,000 liter/kg/h. Therefore, different behavior for synthesis at F/W of 12,000 and 6,000 liter/kg/h cannot be explained solely in terms of strong adsorption of water.

Since gas phase water concentrations are similar for synthesis with F/W of 6,000 and 12,000 liter/kr/h, the extra methanol observed for the lower space velocity must have come from the synthesis that does not produce water, namely CO, probably through reaction 2. This means that relatively more CO is consumed for synthesis and that real CO_2/CO ratio in the reactor must be higher at the lower space velocity for the same initial CO_2/CO ratio. This will lead to higher surface oxygen O^* concentrations. This O^* plays important roles in methanol synthesis by promoting the adsorption of CO_2 and also its hydrogenolysis to methanol (*27*). However, bare copper surface is also needed for efficient synthesis, especially for activation of hydrogen. As indicated in Fig. 2, hydrogen activation appears to be an important step in methanol synthesis. Hence, there may exist an optimal level of oxygen coverage. If the oxygen coverages at low conversions are below this optimum throughout the whole CO_2/CO range, the rate must show a monotonous increase as CO_2 concentration is raised. Indeed, the surface concentration of O* was found to increase with increasing CO_2 concentration in the feed gas at low CO_x conversions (*28*). At high CO_x conversions, however, the optimal level of O* could be located in the middle of CO_2/CO composition range due to the increased consumption of CO for the methanol synthesis, and then the rate maximum for low space velocities could be accounted for. Recently, Saito *et al.* (*29*) reported that, for various copper-containing catalysts, a plot of areal rates of CH_3OH formation from CO_2/H_2 at 250°C against oxygen coverage of copper surface showed a volcano-shape curve, with the maximum rate at oxygen coverage of 0.30–0.35.

Although this argument has yet to be proved in our system, the possibility has to be considered together with the effect of water. If the hypothesis is indeed true, the effect is kinetically a promotional effect of CO in methanol synthesis from CO_2/H_2. The methanol synthesis with CO_2/H_2 leaves O* on the catalyst surface whenever a molecule of methanol is formed.

$$CO_2 + 2H_2 \rightarrow CH_3OH + O^* \qquad (6)$$

The O* could be scavenged either by H_2 or CO and the latter is reported to be more important under industrial conditions (*16*). Thus, under certain conditions, the presence of CO is desirable to regenerate clean copper sites which may be required for hydrogen adsorption.

There seems to be two causes for low synthesis rates below the maxima in Fig. 4 and 5. One is the intrinsically lower rate for synthesis with CO/H_2 as discussed above. The other is the irreversible deactivation of the catalyst in CO_2-free feed. The second point is demonstrated by Table 1. Klier and co-workers (*10*, *18*) called this effect as overreduction of copper. The chemical state of reduced $Cu/ZnO/Al_2O_3$ is modified further during the reaction as evidenced by the long induction periods in Fig. 1 particularly in CO/H_2 feed. The bulk remains as metallic copper as indicated by XRD, yet the surface seems to undergo modification depending on the composition of feed mixture. Although definitive statement cannot be made on the surface state of the working catalyst, TPR demonstrated that substantial difference in chemical state existed between the catalysts used for synthesis with CO_2/H_2 and CO/H_2 and that more oxidized copper surface was maintained in CO_2/H_2. The results indicate that partially oxidized copper surface is required for high activity and stability for methanol synthesis. The identity of active copper species has been a subject of continued controversy in the literature (*4–7*).

As indicated in Figs. 7 and 8, CO_2/H_2 and CO/H_2 respond differently to changing space velocities. For CO_2/H_2, methanol selectivity improves with increasing space velocity mainly because of the reduction in CO formation. This indicates that, in addition to the reverse water gas shift reaction, a part of CO comes from secondary reactions of methanol such as its decomposition or steam reforming (*30*). In any case, the rate of methanol production increases with space velocity. In contrast, the rate is higher for lower space velocity in the synthesis with CO/H_2. This indicates that CO need to be first converted to CO_2 by the water gas shift reaction for rapid synthesis. It is interesting to note that water plays the role of promoter for CO/H_2 feed and that of inhibitor for CO_2/H_2 feed.

CONCLUSION

Over $Cu/ZnO/Al_2O_3$, methanol synthesis is much faster with CO_2/H_2 than with CO/H_2 *and thus* CO_2 should be regarded as the primary source of methanol with $CO/CO_2/H_2$ feed. Previous conflicting reports on the effect of CO_2/CO composition, i.e., monotonical increase in synthesis rate vs the presence of a maximum rate as CO_2 concentration is raised, could be accounted for by different CO_x conversion levels. Consequent difference in surface oxygen coverage and/or water may be responsible for the different effects. More oxidized surface state of copper obtained for CO_2/H_2 feed is more active and stable than overreduced surface obtained for CO/H_2 feed. Due to the promotional and inhibition effects of water for CO/H_2 and CO_2/H_2 feed, respectively, higher space velocities yield higher synthesis rate for CO_2/H_2 and the opposite effect is observed for CO/H_2 feed.

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