Effects of Space Velocity on Methanol Synthesis from $CO_2/CO/H_2$ over Cu/ZnO/Al$_2$O$_3$ Catalyst

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Abstract−The space velocity had profound and complicated effects on methanol synthesis from $CO_2/CO/H_2$ over Cu/ZnO/Al$_2$O$_3$ at 523 K and 3.0 MPa. At high space velocities, methanol yields as well as the rate of methanol production increased continuously with increasing CO_2 concentration in the feed. Below a certain space velocity, methanol yields and reaction rates showed a maximum at CO_2 concentration of 5-10%. Different coverages of surface reaction intermediates on copper appeared to be responsible for this phenomenon. The space velocity that gave the maximal rate of methanol production also depended on the feed composition. Higher space velocity yielded higher rates for CO_2/H_2 and the opposite effect was observed for the CO/H$_2$ feed. For $CO_2/CO/H_2$ feed, an optimal space velocity existed for obtaining the maximal rate.

Key words: Methanol Synthesis, Cu/ZnO/Al$_2$O$_3$ Catalyst, Space Velocity, Surface Coverage, N$_2$O Titration

INTRODUCTION

Carbon dioxide is the most important "greenhouse gas" which may cause the global warming. Various measures have been proposed to stabilize the atmospheric CO_2 concentration which include chemical fixation and recycling the emitted CO_2 [Mizuno and Misono, 1991]. Conversion of CO_2 to methanol by catalytic hydrogenation (Reaction 1) has been recognized as a promising route for the purpose because of a potentially large demand for methanol as a fuel and a basic chemical [Arakawa et al., 1992].

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \tag{1}$$

The process is closely related to the established methanol synthesis technology from CO/H$_2$ (Reaction 2) because current industrial feeds contain *ca.* 5-10 vol% of CO_2 in addition to CO/H$_2$ [Bart and Sneeden, 1987; Waugh, 1992].

$$CO + 2H_2 \rightarrow CH_3OH \tag{2}$$

The processes are operating at 50-100 bar and 220-250 °C with catalysts composed of Cu/ZnO/Al$_2$O$_3$ or Cu/ZnO/Cr$_2$O$_3$ [Bart and Sneeden, 1987; Waugh, 1992].

In our previous study [Lee et al., 1993] of the effect of CO_2/CO ratios in the feed on the methanol synthesis over Cu/ZnO/Al$_2$O$_3$, an unusual effect of the space velocity was observed. At high space velocities (or short contact times), methanol yield increased continuously as increasing amount of CO was replaced by CO_2. At low space velocities, methanol yields showed an initial sharp increase, reached a maximum, and then decreased. Different surface oxygen coverages of copper surface during the synthesis reaction were proposed to be responsible

for this phenomenon. The present paper investigates the effect of space velocity on the surface coverage of the catalyst by reaction intermediates and the catalytic performance in methanol synthesis from $CO_2/CO/H_2$ over a commercial Cu/ZnO/Al$_2$O$_3$.

EXPERIMENTAL

A commercial ICI catalyst Cu/ZnO/Al$_2$O$_3$ (39.8/23.5/36.7 wt%) was crushed and sieved to obtain 100/140 mesh powders. The catalyst was reduced in a 20% H$_2$-He flow (34 μmol s^{-1}) at atmospheric pressure and 523 K for 4 h. Specific surface area was determined by the N$_2$ BET method on a Micromeritics constant-volume adsorption system (Accusorb 2100E). The exposed copper surface area was measured by the N$_2$O titration at 333 K following the procedure described by Chinchen et al. [1987].

The detailed procedure for the methanol synthesis reaction has been described elsewhere [Lee et al., 1993]. The reaction was typically carried out at 523 K and 3.0 MPa. The space velocity (F/W=feed gas volume at STP/catalyst volume/h) was varied by changing the flow rate of $CO_2/CO/H_2$ gas mixtures. 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.

After the synthesis reaction, the reactor was depressurized and flushed with He near ambient temperature. The exposed copper surface after 4 h of the synthesis reaction (Cu$_{rxn}$) was determined by the N$_2$O titration assuming a copper atom density of 1.47×10^{19} m^{-2} [Chinchen et al., 1987]. The used catalyst was then reduced (post-reduction) under the same condition as for the initial reduction in order to clean the copper surface, and then the N$_2$O titration was performed again to obtain total

copper surface area (Cu$_{tot}$) of the working catalyst. The N$_2$O titration to obtain Cu$_{tot}$ was carried out after post-reduction rather than for fresh catalysts before the reaction in order to avoid complication due to sintering of copper catalysts during the reaction. The "oxygen coverage" of the catalyst (θ_O) was defined as (θ_O= (Cu$_{tot}$−Cu$_{rxn}$)/2 Cu$_{tot}$. The definition reflected the assumption that an oxygen atom would titrate two surface copper sites and give a saturated monolayer coverage of 0.5 [Chinchen et al., 1987].

RESULTS

The commercial Cu/ZnO/Al$_2$O$_3$ catalyst (ICI) was employed to eliminate the potential complications caused by different catalyst preparations. It had BET surface area of 64.3 m^{2}g^{-1} and copper surface area of 19.3 m^{2}g^{-1} after reduction. The copper area is greater by a factor of *ca.* 3 than the area of the catalyst with the similar composition prepared in our previous study [Lee et al., 1993].

Methanol synthesis was carried out at 523 K and 3.0 MPa. The general trend of approaching a steady state was similar to the one we reported earlier for laboratory catalysts [Lee et al., 1993]. The effect of CO/CO$_2$ composition on methanol yield (CO$_x$ conversion×methanol selectivity) is shown in Fig. 1 for different space velocities (F/W). The hydrogen concentration relative to carbon oxides (H$_2$/CO$_x$) was fixed at 4 except for the F/W of 73,000 *l*/kg/h where the H$_2$/CO$_x$ value of 8 was employed. For the two low space velocities, methanol yield showed an initial sharp increase, reached a maximum at CO$_2$ concentration of *ca.* 5-10% in CO$_2$/CO mixture, and then decreased. For high space velocities, the methanol yield increased monotonically as CO was progressively replaced by CO$_2$. The effect of the different H$_2$/CO$_x$ ratios for the F/W of 73,000 *l*/kg/h was not apparent. In all cases, the rate of CO$_2$ hydrogenation was faster than that of CO hydrogenation. This is evident when methanol yields at 0% CO$_2$ are compared with those at 100% CO$_2$ in Fig. 1 for each space velocity. The same behavior was observed in

Fig. 2. Rate of methanol production as a function of space velocity and feed gas composition for methanol synthesis over Cu/ZnO/Al$_2$O$_3$. Reaction conditions: T=523 K, P=3.0 MPa, H$_2$/CO$_x$=4 except for F/W=73,000 *l*/kg/h (H$_2$/CO$_x$= 8).

our previous study over laboratory catalysts. For example, a plot similar to that for F/W of 54,000 *l*/kg/h in Fig. 1 was obtained for the F/W of 6,000 *l*/kg/h over the laboratory catalyst with the same composition. This indicates that the rate of methanol synthesis over the commercial catalyst is higher by a factor of 9, although its copper surface area is larger by a factor of only *ca.* 3.

The same set of data was plotted for the specific rate of methanol production (mol-methanol/kg-catalyst/h) in Fig. 2. The maximum rate was achieved at the F/W of 54,000 *l*/kg/h and 5-10% CO$_2$ in CO/CO$_2$ mixture. The next highest rate was obtained for the F/W of 108,000 *l*/kg/h, yet, because of different dependence on CO/CO$_2$ composition, the maximum rate in this case occurred when pure CO$_2$ was employed as a feed. During this experiment, the concentration of water in the reactor outlet
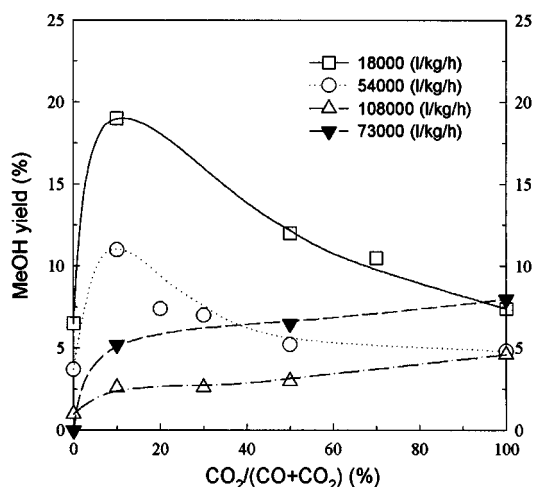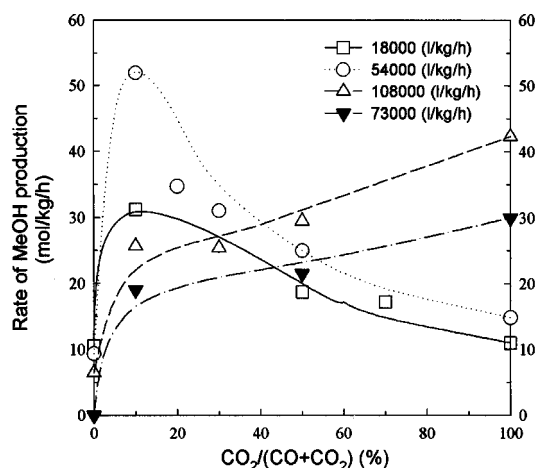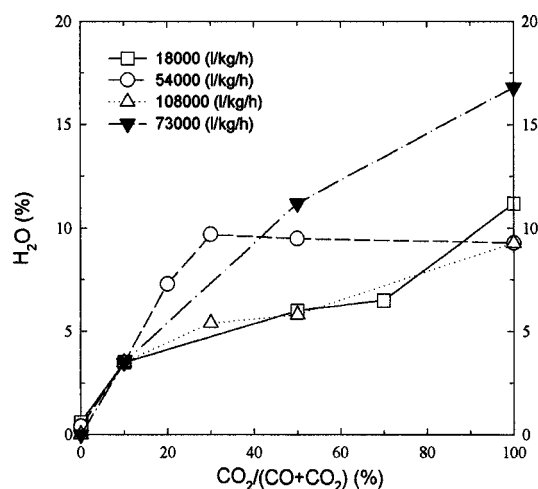

Fig. 1. Yields of methanol as a function of space velocity and feed gas composition for methanol synthesis over Cu/ZnO/Al$_2$O$_3$. Reaction conditions: T=523 K, P=3.0 MPa, H$_2$/CO$_x$=4 except for F/W=73,000 *l*/kg/h (H$_2$/CO$_x$=8).

Fig. 3. Change in water concentration as a function of space velocity and feed gas composition for methanol synthesis over Cu/ZnO/Al$_2$O$_3$. Reaction conditions: T=523 K, P= 3.0 MPa, H$_2$/CO$_x$=4 except for F/W=73,000 *l*/kg/h (H$_2$/CO$_x$=8).
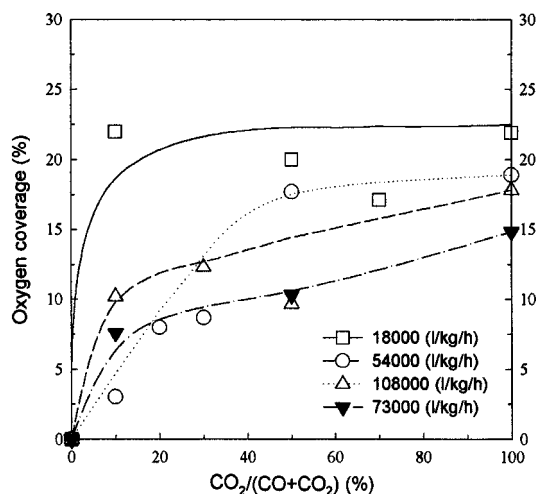
Fig. 4. Surface oxygen coverage as a function of space velocity and feed gas composition for methanol synthesis over Cu/ZnO/Al$_2$O$_3$. Reaction conditions: T=523 K, P=3.0 MPa, H$_2$/CO$_x$=4 except for F/W=73,000 l/kg/h (H$_2$/CO$_x$=8).

was measured and is shown in Fig. 3. In all cases, the concentration of water increased with increasing CO$_2$ concentration in the feed. The variation with CO$_2$ concentration was particularly large for the F/W of 73,000 l/kg/h where the H$_2$/CO$_x$ of 8 was used.

As mentioned, the "oxygen coverage" during the reaction (θ_O) was measured by difference between N$_2$O titrated copper sites after reaction and those after post-reduction. Fig. 4 shows the oxygen coverage as a function of CO$_2$ concentration in the feed for different space velocities. In general, θ_O values increased as CO$_2$ concentration increased and were saturated at low space velocities while they increased continuously at high space velocities. Their absolute values were larger for lower space velocities. A higher H$_2$ concentration appeared to result in smaller θ_O values as shown for the F/W of 73,000 l/kg/h.
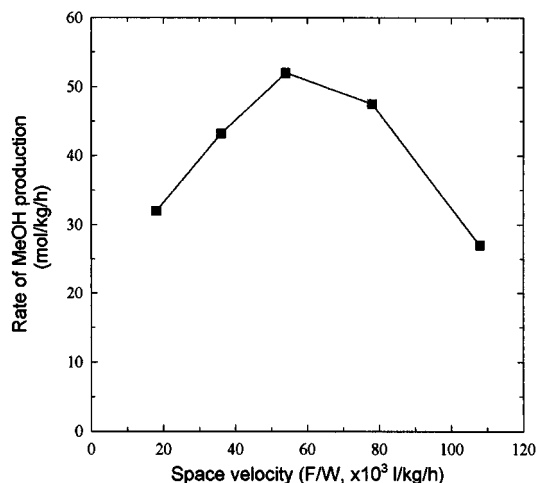

Fig. 5. Rates of methanol formation as a function of space velocity for methanol synthesis over Cu/ZnO/Al$_2$O$_3$ with synthesis gas containing 10 vol% CO$_2$. Reaction conditions: T=523 K, P=3.0 MPa, H$_2$/CO$_x$=4.

Table 1. Effect of space velocity on CO$_2$ hydrogenation[a]

F/W (l/kg/h)	Conversion (%)	Rate of CH$_3$OH production (mol/kg/h)	CH$_3$OH	Selectivity (%) CO	CH$_4$	Water content (%)
18000	16.9	11.5	42.3	57.0	0.7	11.2
54000	7.0	21.9	65.2	33.7	1.0	9.2
108000	7.1	42.0	61.7	37.5	0.8	9.2
73000	13.5	30.2	61.8	37.6	0.6	16.6

[a]523 K, 3.0 MPa, H$_2$/CO$_2$=4 except for F/W=73,000 (H$_2$/CO$_2$=8).

Table 2. Effect of space velocity on CO hydrogenation[a]

F/W (l/kg/h)	Conversion (%)	Rate of CH$_3$OH production (mol/kg/h)	CH$_3$OH	Selectivity (%) CO	CH$_4$	Water content (%)
18000	6.84	10.2	93.0	5.9	1.1	0.54
54000	1.98	8.36	87.5	9.5	3.0	0.42
108000	0.79	6.47	84.6	9.3	6.2	0.03
73000	0.15	0.11	20.9	3.0	76.1	0.0

[a]523 K, 3.0 MPa, H$_2$/CO=4 except for F/W=73,000 (H$_2$/CO = 8).

Examination of Fig. 2 indicates that there exists an optimal space velocity that gives rise to the maximal specific rate of methanol formation. This is demonstrated in Fig. 5 where the rate is plotted against space velocity with a constant CO$_2$ concentration of 10%. Note that this CO$_2$ concentration gave the maximum rates for low space velocities. The maximal rate was obtained for the F/W of 54,000 l/kg/h.

Effects of space velocity were further examined for methanol synthesis from CO$_2$/H$_2$ and CO/H$_2$, respectively, and results are summarized in Tables 1 and 2. From CO$_2$/H$_2$, a higher space velocity caused a higher rate and an improved methanol selectivity. The effect of higher H$_2$ concentration was not significant on the rate of CH$_3$OH production (Table 1). On the contrary, a higher space velocity brought about a reduced reaction rate and a slightly deteriorated methanol selectivity from CO/H$_2$. The high H$_2$ concentration drove the reaction from methanol synthesis to methane synthesis. As expected, water concentration during the synthesis with CO/H$_2$ feed was much lower than for the CO$_2$/H$_2$ feed.

DISCUSSION

The space velocity has profound and complicated effects on methanol synthesis from CO$_2$ containing feeds. At high space velocities (or short contact times), methanol yield as well as reaction rate increased continuously as increasing amount of CO was replaced by CO$_2$. Below a certain space velocity, methanol yield and reaction rate show a maximum at CO$_2$ concentration of 5-10%. The similar observation has been made for laboratory catalysts as discussed in our previous publication [Lee et al., 1993]. In the work, we proposed that different coverages of copper surface by atomic oxygen might be responsible for the

effect. Now, the results in this work suggest that this is indeed the case, with a modified interpretation of so-called "oxygen coverage" measured by N_2O titration as follows.

What N_2O titration really measures is the "exposed copper surface area" before and after the H_2 treatment following 4 h of the reaction. The difference should be the coverage of copper surface by reaction intermediates during the reaction. The surface intermediate had initially been thought as atomic oxygen O* on copper surface formed from CO_2 according to the following stoichiometry [Bowker et al., 1988].
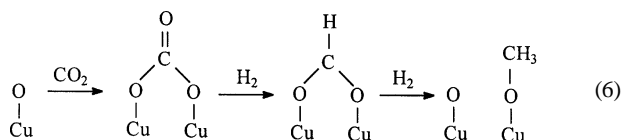
$$CO_2 + 2H_2 \rightarrow CH_3OH + O^* \qquad (3)$$

It is balanced by two reactions of oxygen removal.

$$CO + O^* \rightarrow CO_2 \qquad (4)$$

$$H_2 + O^* \rightarrow H_2O \qquad (5)$$

The surface oxygen on copper has been proposed to take part in the methanol synthesis both as reactant and as a promoter for the adsorption of CO_2, H_2O and H_2 [Chinchen et al., 1987]. Szany and Goodman [Szannyi et al., 1991] showed that methanol synthesis was faster over an oxidized Cu(100) than over an clean Cu(100). Recently, Fujitani et al. [1994] demonstrated an excellent correlation between the specific activity for methanol synthesis from CO_2/H_2 and the oxygen coverage for copper catalysts on various metal oxides supports measured by the N_2O titration. Despite the claimed beneficial effects of O* on the methanol synthesis reaction, bare copper surface is also needed for efficient synthesis, especially for hydrogen activation. Hence, there is usually an optimal level of oxygen coverage [Fujitani et al., 1994].

Recent transient experiments [Muhler et al., 1994], however, convincingly demonstrated that actual oxygen coverage of copper under the industrial methanol synthesis conditions over Cu/ZnO/Al_2O_3 catalysts was less than 2% of a monolayer. Hence, the "oxygen coverage" measured by N_2O titration cannot be the actual population of oxygen on copper surface. The DRIFT study of Bailey et al. [Bailey et al., 1995] showed that the surface composition of the operating Cu/ZnO/Al_2O_3 catalysts predominantly consisted of carbonates and formates. Hence, the "oxygen coverage" should be interpreted now as the coverage by these surface intermediates. In a proposed mechanism of methanol synthesis from CO_2/H_2 [Arakawa et al., 1992], the following intermediates are involved:

$$(6)$$

Thus, the abundant intermediates and surface atomic oxygen constitute the same reaction pathway and, hence, most of the mechanistic arguments made above regarding the surface oxygen could also be applied to carbonate or formate species. In the following discussion, the term "oxygen coverage" is still employed following the convention with its new interpretation kept in mind.

At high space velocities, the yield and the reaction rate of methanol increase with increasing CO_2 concentration in the same manner as surface oxygen coverage does. This monotonic change suggests that the population of the surface intermediates is below the optimal level throughout the whole CO_2/CO range. As the space velocity is further reduced, CO_2 conversion increases, which would result in a higher surface coverage for the same CO_2/CO feed. Thus, the optimal level of surface coverage is crossed in the middle of CO_2/CO composition range where the maximum rate is observed.

In methanol synthesis from CO_2/H_2 over Cu or Cu/ZnO promoted by various oxides, Fujitani et al. [1994] found the optimum oxygen coverage of 0.16-0.18, which gave the maximum synthesis rate. A similar value can be obtained from Fig. 4. An interesting point to note is that Fujitani et al. and our previous work [Lee et al., 1995] achieved this optimum surface coverage for CO_2/H_2 feed by adding a catalyst modifier to Cu/ZnO catalyst, while the present work did it by changing CO_2/CO feed composition for a given Cu/ZnO/Al_2O_3 catalyst. Fujitani et al. [1994] ascribed the presence of the optimum oxygen coverage to the requirement for both Cu^+ and Cu^o for efficient methanol synthesis over copper-based catalysts, suggesting that the oxygen on the surface of copper might stabilize Cu^+ which was a possible active center [Herman et al., 1979; Sheffer and King, 1989; Nonneman and Ponec, 1990; Klier et al., 1982]. A similar argument could also be employed with the new interpretation of the oxygen coverage. Thus, an optimum coverage by reaction intermediates leads to the maximum reaction rate following the Sabatier principle of volcano curve [Rootsaert and Sachtler, 1960].

Although it has been a controversial question for a long time in the mechanism of methanol synthesis over copper catalysts, it is now generally accepted that the primary carbon source of methanol is CO_2 [Chinchen et al., 1987; Ya Rozovskii, 1989]. Carbon monoxide participates in the synthesis only after it is first converted to CO_2 by the water gas shift reaction. Based on this mechanism, the presence of the maximum mathanol yield and rate in Figs. 1 and 2 could be viewed as a promotional effect of CO in CO_2 hydrogenation by controlling the surface oxygen coverage through the reaction 4. This view represents an interesting contrast to a conventional view that CO is the primary source of methanol and CO_2 is a promoter at low concentrations that prevents the over-reduction of copper and an inhibitor at high concentrations due to its strong adsorption [Klier et al., 1982]. Under high space velocities where oxygen coverage is small, this effect is not important and the methanol yield and reaction rate increase monotonically with increasing concentration of CO_2, the main reactant.

Water plays complicated roles in methanol synthesis. It inhibits the reaction by adsorbing strongly on active sites in competition with CO_x [Liu et al., 1984]. Indeed, serious deactivation was observed when water was added in the feed mixture. In Fig. 3, water concentration increases with increasing CO_2 concentration in the feed. Yet, the dependence of water concentration on space velocity is complicated. For example, similar water concentrations were observed for F/W of 18,000 and 108,000 l/kg/h. Because the yield of methanol was much higher for F/W of 18,000 l/kg/h, the extra methanol observed for the lower space velocity must have come from the synthesis that does not pro-

duce water, namely CO, through the reaction 2. Therefore, water concentration in the reactor does not provide any information that could help understand the effect of space velocity displayed in Figs. 1 and 2.

From a practical point of view, it is desired to employ a space velocity that yields the maximum rate of methanol production. Examination of Fig. 5 and Tables 1 and 2 indicates that the optimal space velocity depends on the employed feed composition. For CO_2/CO feed containing 10% CO_2, F/W of 54,000 l/kg/h gives the maximal rate. In CO_2 hydrogenation (Table 1), higher space velocities show improved selectivity for methanol and increased rates of methanol formation. The reduced formation of CO may be attributed to the suppression of secondary reactions forming CO from methanol such as its decomposition or steam reforming [Okamoto et al., 1988]. In contrast, the rate is higher for lower space velocity for CO hydrogenation (Table 2). This may reflect the requirement of CO to be first converted to CO_2 by the water gas shift reaction for efficient methanol synthesis.

CONCLUSIONS

The surface coverage of copper by reaction intermediates is an important variable in methanol synthesis from CO_2/H_2 over copper-based catalysts. This could be controlled by changing reaction conditions (space velocity in particular) or by adding a modifier to the catalysts. This could serve as a new guideline in designing an improved catalyst or modified reaction conditions for methanol synthesis from CO_2/H_2.

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