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# Influence of Reaction Conditions on Methanol Synthesis and WGS Reaction in the Syngas-to-DME Process

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**Abstract:** A series of CuO-ZnO catalysts (with different Cu/Zn molar ratios) were prepared, and evaluated under the reaction conditions of syngas-to-dimethyl ether (DME) with three sorts of feed gas and different space velocity. The catalysts were characterized by X-ray diffraction (XRD) and temperature-programmed reduction (TPR). The experiment results showed that the reaction conditions of syngas-to-DME process greatly affected the methanol synthesis and WGS reaction. The influence caused by Cu/Zn molar ratio was quite different on the two reactions; increasing of percentage of CO<sub>2</sub> in feed gas was unfavorable for catalyst activity, and also inhibited both reactions; enhancement of reaction space velocity heavily influenced the performance of the catalyst, and the benefits were relatively less for methanol synthesis than for the WGS reaction.

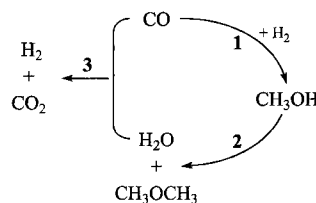
**Key words:** copper; zinc; Cu/Zn molar ratio; methanol; dimethyl ether; water gas shift reaction; syngas; dehydration

## 1. Introduction

Dimethyl ether (DME) is not only an important chemical product, but also a promising clean energy and environmental protective product [1–3]. At present, DME is produced by a two-step method, which means that, to begin with, methanol is produced from syngas, then, it is dehydrated to form DME. Recently, a direct method called syngas-to-dimethyl ether (STD) process has received more attention [4,5]. Economy valuation showed that the STD process was more competitive and promising [6].

The main reaction net in the STD process can be depicted as follows (shown in scheme 1). Methanol formed by CO hydrogenation (reaction 1) is dehydrated to form DME and H<sub>2</sub>O (reaction 2), and then H<sub>2</sub>O reacts with CO to form CO<sub>2</sub> and H<sub>2</sub> (reaction 3), which is also well known as water gas shift reaction

(WGS). It should be stressed that reaction 2 and reaction 3 cooperate to consume methanol synthesized from reaction 1, therefore, the equilibrium of reaction 1 is promoted shifting remarkably to the right.



**Scheme 1.** The reaction net in syngas-to-dimethyl ether (STD) process

A double function catalyst that has two parts: methanol synthesis component and methanol dehydration component, is used in STD processing. The former is mainly a copper-zinc-based catalyst and the latter is a zeolite or Al<sub>2</sub>O<sub>3</sub> [7,8].

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As observed in scheme 1, both methanol synthesis and the WGS reaction occur in the STD process. The former is crucial for DME production, while the latter produces  $\text{CO}_2$ , which is the main byproduct. Therefore, to enhance the DME yield and decrease the production of  $\text{CO}_2$ , it is imperative to study the effect of reaction conditions on the two reactions, but few researches have been reported. As is well known, a copper-zinc-based catalyst is not only useful for methanol synthesis [9], but is also valid to WGS reaction [10,11]. In this work—based on five copper-zinc catalysts with different Cu/Zn molar ratios—the influence of STD reaction conditions including Cu/Zn ratio, the content of  $\text{CO}_2$  in feed gas and space velocity on the two reactions were investigated in detail.

## 2. Experimental

### 2.1 Catalyst preparation

Solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with different Cu/Zn molar ratios (4/1, 2/1, 1/1, 1/2, 1/4) and solution of  $\text{Na}_2\text{CO}_3$  were added to 200 ml deionized water simultaneously, drop by drop, for over a period of 20 min at constant pH (8.0) and temperature (353 K) with violent stirring. The precipitates were aged for 0.5 h under stirring at the same temperature. Then, they were filtered out, washed and dried at 373 K for 2 h, calcined in air at 573 K for 2 h. The final powder was mixed with HZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3=38$ , purchased from Nankai University, China) at a mixing ratio of 2:1 (mass). The mixture was moulded under pressure into tablets, which were then crushed into granules and sieved to 20–40 meshes.

For convenience, the catalysts were denoted by an abbreviation: CZH(X), where 'C' denotes CuO, 'Z' denotes ZnO, 'H' denotes HZSM-5 and 'X' denotes Cu/Zn molar ratio, where  $X=0.25, 0.5, 1, 2, 4$ , respectively.

### 2.2 Measurement of catalyst activity

Catalytic activity measurements were carried out in a tubular fixed-bed stainless reactor system with a packed catalyst of 1 ml. Before evaluation, the catalysts had been reduced in a flow of pure hydrogen under the following heating program: heated up from room temperature to 473 K in 4 h and then kept at 473 K for 2 h, heated up to 523 K in 1 h and kept at 523 K for 1 h, and finally, cooled down to room

temperature. Then, the synthesis gas ( $\text{H}_2/\text{CO}/\text{CO}_2$ ) was fed into the reactor. The reaction conditions were:  $p=2$  MPa,  $\text{SV}=3000\text{ h}^{-1}$  or  $8000\text{ h}^{-1}$ . Program-heating reactions were employed at every temperature pot and samples were analyzed after 1 h stabilization. The products were analyzed by on-line HP 6890 chromatography with a TCD detector, with pure hydrogen ( $>99.99\%$ ) as the carrier gas.

### 2.3 Catalyst characterization

X-ray diffraction (XRD) was recorded on a Rigaku D/Max RB diffractometer (Cu  $K\alpha$  radiation, 40 kV, 40 mA, scanning range:  $5^\circ$ – $60^\circ$ ). Temperature-programmed reduction (TPR) was carried out in a quartz-glass reactor with 0.1 g catalysts. To begin with, the sample was pretreated at 673 K for 1 h in a 20 ml/min stream of pure He. Then the temperature was lowered to 303 K. Finally the catalyst was reduced in a flow of 5% $\text{H}_2$ -95%Ar gas, heating from room temperature to 1173 K at a ramping rate of 5 K/min.

## 3. Results and discussion

### 3.1 The result of phase analysis by XRD

Figure 1 shows XRD pattern of catalyst after calcination. When Cu/Zn molar ratio is 1/4, there are only peaks ascribed to ZnO ( $2\theta=31.6^\circ, 34.2^\circ, 36.1^\circ$ ,

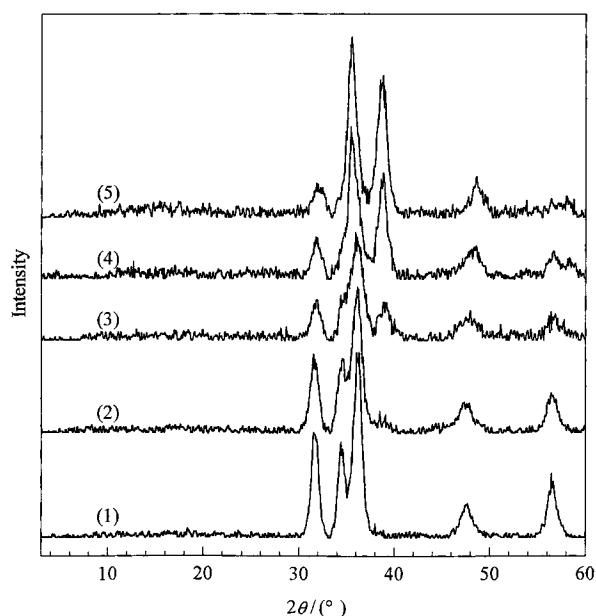
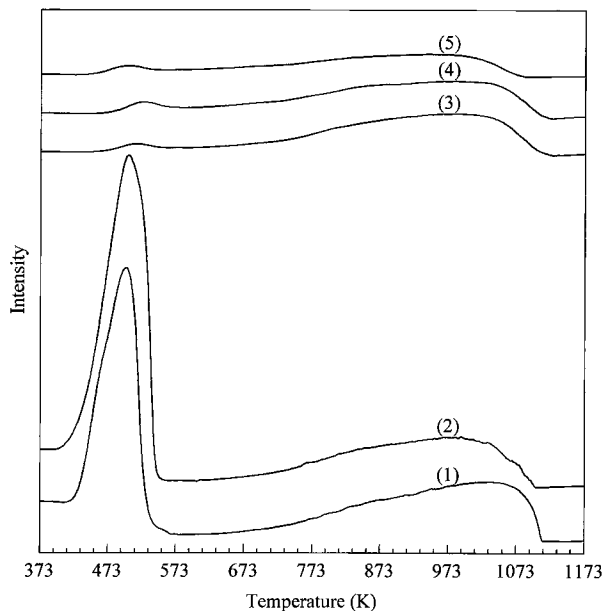


Figure 1. XRD patterns of CuO-ZnO/HZSM-5 catalysts with different Cu/Zn molar ratios: (1) 1/4, (2) 1/2, (3) 1/1, (4) 2/1, (5) 4/1

56.6°), suggesting that copper was highly dispersed in the catalyst. When Cu/Zn ratio reaches 1/2, peaks at 35.6° ascribed to CuO can be observed as a weak shoulder. As regards the sample of Cu/Zn molar ratio being 1/1, both peaks assigned to CuO and ZnO became clearly weaker and wider. According to Fujitani *et al.* [12] and Fujita *et al.* [13], at this Cu/Zn ratio, the aurichalcite phase was the main catalyst precursor, in which Zn atoms mixed with Cu atoms atomically. So after calcination, CuO and ZnO were contacted very closely and were dispersed well into each other. In the case of Cu/Zn molar ratio being 2/1, 4/1, peaks belonging to CuO ( $2\theta=35.6^\circ$ ,  $38.7^\circ$ ) can be clearly observed, while peaks for ZnO decrease gradually with increasing Cu/Zn ratio.

### 3.2 The result of TPR

Figure 2 shows the TPR pattern of catalysts with different Cu/Zn ratio. Two reduction peaks at 473–528 K and 943–1033 K can be observed over all the five catalysts, which can be attributed to the reduction of CuO and ZnO respectively. As CuO was



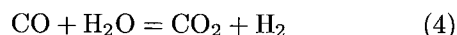
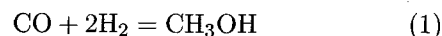
**Figure 2.** TPR profile of CuO-ZnO/HZSM-5 catalysts with different Cu/Zn ratios: (1) 4/1, (2) 2/1, (3) 1/1, (4) 1/2, (5) 1/4

reduced prior to ZnO, and the reduction temperature of CuO and ZnO varied with Cu/Zn ratio, it can be inferred that there should be an interaction between Cu and ZnO. As per Batyrev *et al.* [14], they have indicated that Cu crystallites are covered by partially reduced  $\text{ZnO}_x$  species in the reduction range of 450–

800 K; at reduction temperatures above 800 K, surface alloy of CuZn might appear. With increasing the content of ZnO, the top reduction peak temperature of CuO increased gradually to higher temperatures, indicating that the interaction was strengthened, especially when Cu/Zn ratio was 1/1 or 1/2. This result suggested that when Cu/Zn ratio was about 1/1, more  $\text{Cu}^{2+}$  species could have dissolved in the ZnO lattice, for the appearance and increase of aurichalcite in catalyst precursor phase [15].

### 3.3 Catalytic activity test

The possible reactions included in the STD process can be depicted as follows:



It can be seen that  $\text{CO}_2$  takes part in methanol synthesis and is produced by the WGS reaction. Many researches have proved that  $\text{CO}_2$  also influenced the CO hydrogenation reaction [16,17]. Therefore,  $\text{CO}_2$  is the bridge relating methanol synthesis and WGS reaction and we investigated the influence of  $\text{CO}_2$  concentration in feed gas on the two reactions. The compositions of feed gases are shown in Table 1. The  $\text{H}_2/\text{CO}$  molar ratio are very close to each other, but the percentage of  $\text{CO}_2$  varies from 1.2% to 23.5%. Additionally, we also investigated the effect of the Cu/Zn ratio and space velocity on the two reactions mentioned above.

**Table 1.** Feed gas composition in the STD process

Feed gas	$V(\text{H}_2)/\%$	$V(\text{CO})/\%$	$V(\text{CO}_2)/\%$	$n(\text{H}_2)/n(\text{CO})$
A	63.5	35.3	1.2	1.8
B	60.5	30.3	9.2	2.0
C	51.8	24.7	23.5	2.1

#### 3.3.1 Product distribution of STD reaction

Before analyzing, we have given the typical product distribution under our experimental conditions (as shown in Table 2). It can be seen that DME and  $\text{CO}_2$  are the main products, indicating that they are most favorable to be produced by thermodynamics [6]. There was no methanol remaining in the products, meaning that the acidity of zeolite, guaranteed that

the methanol thoroughly dehydrated to DME. Therefore, it can be deduced that the rate for methanol dehydration was much greater than that for methanol synthesis, and the yield of DME reflected the amount of methanol formed in the reaction. CO<sub>2</sub> formed by WGS reaction was the main byproduct besides DME, and the result of our experiment showed that there

was only a little water remaining in the products, indicating that the WGS reaction was more favorable on thermodynamics [18]. In addition, it can be seen that there was a small amount of CH<sub>4</sub> and C<sub>2</sub> (ethene and ethane), which should be ascribed to the further dehydration of DME on the strong acidic sites of HZSM-5 [4].

**Table 2. Product distribution over CuO-ZnO/HZSM-5 catalysts with different Cu/Zn molar ratios**

Feed gas	$n(\text{Cu})/n(\text{Zn})$	Product selectivity (%) <sup>a</sup>				
		CH <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub>	DME	CH <sub>3</sub> OH
A	0.25	1.31	37.48	5.76	55.46	—
	0.5	1.06	35.65	3.92	59.36	—
	1	1.02	35.28	3.41	60.29	—
	2	1.06	35.83	3.34	59.77	—
	4	1.02	35.62	3.72	59.63	—
B	0.25	1.89	38.17	5.31	54.63	—
	0.5	1.26	38.52	3.40	56.82	—
	1	1.19	36.22	2.93	59.66	—
	2	1.37	37.22	2.87	58.55	—
	4	1.43	37.53	3.13	57.91	—
C	0.25	2.45	29.49	5.57	62.48	—
	0.5	1.57	30.91	3.67	63.85	—
	1	1.32	31.93	2.95	63.81	—
	2	1.70	31.92	3.36	63.01	—
	4	1.68	31.16	3.42	63.74	—

Reaction conditions: 2 MPa, 533 K, 3000 h<sup>-1</sup>, 1 ml catalyst.

<sup>a</sup>Product selectivity was calculated based on carbon balance.

In order to clearly elucidate the influence of reaction conditions on the methanol synthesis and WGS reaction, we introduced a parameter: the ratio of DME to CO<sub>2</sub> (DME/CO<sub>2</sub>), which was calculated based on carbon balance as follows:

$$\text{DME/CO}_2 = S_{\text{DME}} / (S_{\text{CO}_2} \times 2)$$

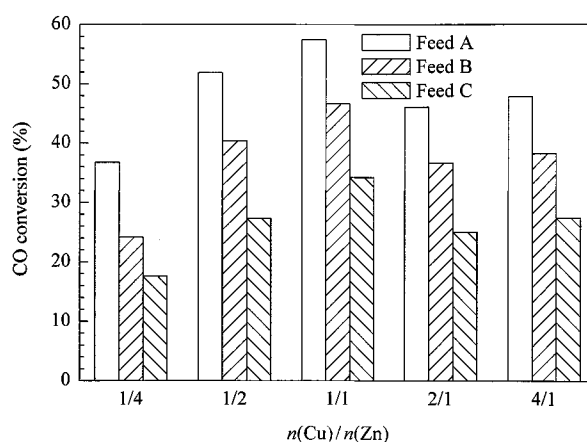
$S_{\text{DME}}$  and  $S_{\text{CO}_2}$  are denoted to the selectivity for DME and CO<sub>2</sub> in the outlet gas respectively ( $S_{\text{CO}_2}$  refers to the CO<sub>2</sub> produced during the reaction).

As DME and CO<sub>2</sub> are the main products, if the selectivity for CO<sub>2</sub> is increased, the selectivity for DME is decreased accordingly. Therefore, the parameter of DME/CO<sub>2</sub> reflects the relative changes of methanol synthesis and WGS reaction with reaction conditions. It is noteworthy that the production of C<sub>2</sub> should exert influence on the DME/CO<sub>2</sub> ratio, but we found that the changes of the C<sub>2</sub> yield was very small in all the catalysts we tested; therefore, we considered that the formation rate of C<sub>2</sub> is almost the same and the influence of it can be omitted in our analysis on catalysts and other reaction conditions.

### 3.3.2 Catalyst performance CuO-ZnO/HZSM-5 under various feed gas

#### 3.3.2.1 Influence of Cu/Zn ratio and feed gas on CO conversion

Figure 3 shows the changing of CO conversion



**Figure 3. CO conversion as a function of Cu/Zn molar ratio and feed gas**

Reaction conditions: 2 MPa, 533 K, 3000 h<sup>-1</sup>

with Cu/Zn molar ratio and feed gas. With increasing the Cu/Zn ratio, the conversion of CO increased rapidly, reached the maximum at Cu/Zn=1, and subsequently declined quickly. The sequence of the catalytic activity was as follows: CZH(1)>CZH(0.5)>CZH(4)>CZH(2)>CZH(0.25).

The highest catalytic activity was obtained on the sample of Cu/Zn=1. Considering that the reaction of methanol formation is the key step in the STD process, as analyzed above, there should be more active sites for methanol synthesis over the catalyst with Cu/Zn=1. Related with the XRD and TPR results, the interaction between CuO(Cu) and ZnO, during the course of catalyst preparation and reduction, was strengthened by the intimate contact of the copper species with ZnO and should be responsible for the appearance of the active phase. More active phases could be obtained by the rather close contact at Cu/Zn=1. Many researches have been made to elucidate the nature of the active phase in methanol synthesis reaction, such as the model of Cu/Zn alloy, Cu<sup>+</sup>/ZnO solid solution model, and the spillover model etc [19–21].

The feed gas also influenced CO conversion significantly. Over all the five catalysts, increasing the amount of CO<sub>2</sub> in feed gas gradually declined CO conversion. It could also be due to the decline of CO partial pressure.

### 3.3.2.2 Influence of Cu/Zn molar ratio and feed gas on DME/CO<sub>2</sub>

Table 3 shows that over all the catalysts, the concentration of CO<sub>2</sub> in out-let gas is always larger than that in feed gas, meaning that the rate for WGS reaction (equation (4)) is much greater than that of CO<sub>2</sub> hydrogenation (equation (2)), where CO<sub>2</sub> acted mainly as a product. With increasing the CO<sub>2</sub> content in feed gas, the  $\Delta$ CO<sub>2</sub> (%) and DME% in out-let gas were both decreased, meaning that both methanol synthesis and WGS reaction were restrained.

When CO<sub>2</sub> content of the feed gas was increased from 1.2% to 9.2% (feed gas A replaced by feed gas B), the ratio of DME/CO<sub>2</sub> decreased slightly (Figure 4). This result might be discussed as follows. Dynamic tests [22] on methanol synthesis from CO/CO<sub>2</sub>/H<sub>2</sub> system have proven that the optimum concentration of CO<sub>2</sub> to promote CO hydrogenation is 2%–8%. Above this content, the increased amount of CO<sub>2</sub> might have restricted CO hydrogenation by its competing adsorption with CO on the

active sites. But CO<sub>2</sub> hydrogenation and the WGS reaction were not substantially affected. Hence, the selectivity for CO<sub>2</sub> increased, causing DME/CO<sub>2</sub> to decline. With the content of CO<sub>2</sub> amounting to 23.5% in the feed gas (feed gas C), the DME/CO<sub>2</sub> ratio increased significantly, suggesting that the CO<sub>2</sub> selectivity declined greatly. Compared to feed gas A and B, the concentration of CO and CO<sub>2</sub> was greatly changed in feed gas C. Therefore, the relative role of CO and CO<sub>2</sub> in methanol synthesis might also be substantially altered. Although CO<sub>2</sub> hydrogenation was promoted, WGS reaction and CO hydrogenation were heavily suppressed. The end result was that a significant decline on the selectivity for CO<sub>2</sub> occurred.

Table 3. Changes of CO<sub>2</sub> with feed gas

Feed gas	$n(\text{Cu})/n(\text{Zn})$	CO <sub>2</sub> (v%) (Feed gas)	CO <sub>2</sub> (v%) (Out-let gas)	$\Delta$ CO <sub>2</sub> (v%)
A	1/4	1.2	7.2	6.0
	1/2	1.2	10.1	8.9
	1/1	1.2	11.3	10.1
	2/1	1.2	8.9	7.7
	4/1	1.2	9.2	8.0
B	1/4	9.2	13.7	4.5
	1/2	9.2	16.4	7.2
	1/1	9.2	17.7	8.5
	2/1	9.2	15.7	6.5
	4/1	9.2	16.0	6.8
C	1/4	23.5	26.5	3.0
	1/2	23.5	28.2	4.7
	1/1	23.5	29.4	5.9
	2/1	23.5	27.6	4.1
	4/1	23.5	28.1	4.6

Reaction conditions: 2 MPa, 533 K, 3000 h<sup>-1</sup>, 1 ml catalyst

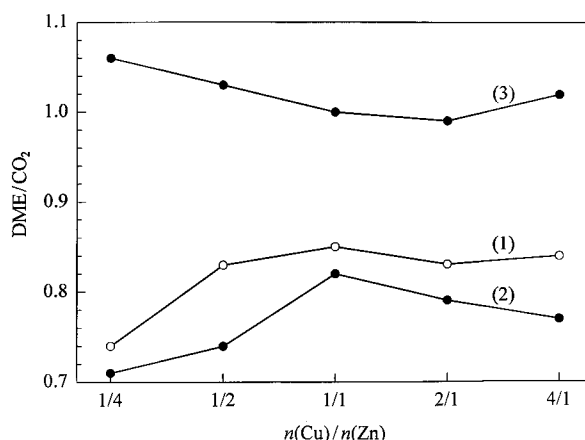


Figure 4. Changes of DME/CO<sub>2</sub> with Cu/Zn molar ratio and feed gas

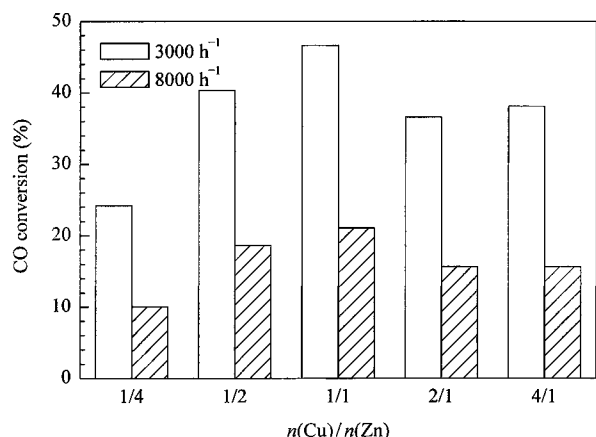
(1) Feed A, (2) Feed B, (3) Feed C

Reaction conditions are the same as those in Figure 3

Compared to the feed gas, the influence of Cu/Zn ratio on DME/CO<sub>2</sub> was much smaller. When feed gas A or B was used, the DME/CO<sub>2</sub> ratio was lower on low Cu/Zn catalysts (1/4, 1/2), compared to high Cu/Zn catalysts (1/1, 2/1, 4/1). The lower DME/CO<sub>2</sub> may be ascribed to the increase of CO<sub>2</sub> production. This result possibly suggests that low Cu/Zn ratio is more beneficial for WGS reaction, as Uchida *et al.* [23] have proposed that with Cu/Zn atom ratio increasing, the apparent activation energy of WGS reaction declined significantly and reached minimum at Cu/Zn=0.4. The catalyst (Cu/Zn=1) exhibited the highest DME/CO<sub>2</sub> value under feed gas A and B, suggesting that there might be more active sites for methanol formation, in agreement with the result of CO conversion. From these results, we considered that the number of active sites for the two reactions varied with Cu/Zn ratio and the active sites for them might be not the same.

### 3.3.3. Catalyst performance under different space velocity

The space velocity is a crucial factor to influence catalyst performance. Figure 5 shows that the conversion of CO dramatically decreased with increasing space velocity from 3000 to 8000 h<sup>-1</sup>, but no changes of the sequence of catalytic activity with Cu/Zn ratio appeared.

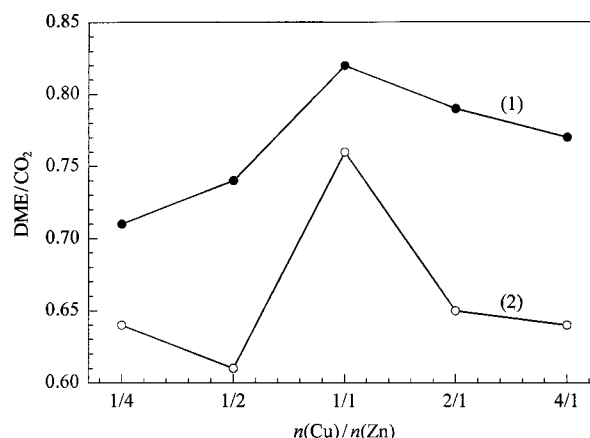


**Figure 5. CO conversion as a function of Cu/Zn molar ratio and space velocity**

Reaction conditions: feed gas B, 2 MPa, 533 K

Figure 6 shows that over all the five catalysts, as increasing the space velocity, the DME/CO<sub>2</sub> ratio decreased dramatically, meaning that selectivity for CO<sub>2</sub> increased significantly at the expense of the selectivity for DME. We did not detect any methanol

remaining in the products, which should have been converted to DME. The increasing of selectivity for CO<sub>2</sub> shows that under increased space velocity, the rate for methanol synthesis was heavily restrained, while that for WGS reaction was less affected. This might be due to the fact that the rate of the CO<sub>2</sub> hydrogenation reaction was much slower than that of WGS reaction. Therefore, under increased space velocity, the amount of CO<sub>2</sub> that took part in the CO<sub>2</sub> hydrogenation reaction was decreased greatly.



**Figure 6. Changes of DME/CO<sub>2</sub> with Cu/Zn molar ratio and space velocity**

Space velocity: (1) 3000 h<sup>-1</sup>, (2) 8000 h<sup>-1</sup>

Reaction conditions are the same as those in Figure 5

Under the enhanced space velocity, the activity order of the five catalysts is not greatly changed and it is interesting that much higher DME/CO<sub>2</sub> ratio can be obtained over the catalyst with Cu/Zn=1 than other catalysts. This result might indicate again that there should be more methanol synthesis active sites over the sample with Cu/Zn=1.

## 4. Conclusions

Both methanol synthesis and WGS reaction rely on the reaction conditions of the STD process, including the factor of catalysts. Under our experimental conditions, the main results can be summarized as follows:

(1) Methanol synthesis and WGS reaction in the syngas to DME process were both affected by Cu/Zn ratio. Low Cu/Zn ratio (*e.g.* 1/4, 1/2) was more beneficial to the WGS reaction, as more WGS active centers might be represented at those ratios; however, catalysts with high Cu/Zn ratios (*e.g.* 1/1, 2/1, 4/1) exhibited greater activity for methanol synthesis, more so at Cu/Zn=1, the catalyst represented the

highest catalytic activity and DME selectivity, which might be ascribed to the atomic dispersion between CuO and ZnO, and a stronger interaction of CuO with ZnO.

(2) Increasing the concentration of CO<sub>2</sub> in feed gas would be unfavorable to both methanol formation and WGS reaction, and at a higher CO<sub>2</sub> concentration, a greater inhibition to WGS reaction would occur.

(3) By increasing reaction space velocity, lower catalytic activity and DME selectivity could be obtained, but the selectivity for CO<sub>2</sub> was increased.

(4) WGS reaction occurred more easily on thermodynamics than the methanol synthesis reaction, and the latter is the key step of the STD process.

(5) To enhance the yield of DME, it can be realized in a way, by adding appropriated amount of CO<sub>2</sub> to the syngas (CO/H<sub>2</sub>), using a catalyst with Cu/Zn ratio about 1, and employing low reaction space velocity.

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