

# Catalysis for One-step Synthesis of Dimethyl Ether from Hydrogenation of CO<sup>†</sup>

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In this paper, a new catalyst system Cu-Mn-(M)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was developed for the directly synthesis dimethyl ether (DME) from synthesis gas in a fixed-bed reactor. The catalysts with different  $n(\text{Cu}) : n(\text{Mn})$  ratios, several promoter M (M is one of Zn, Cr, W, Mo, Fe, Co or Ni) were prepared and tested. The results showed the catalysts have a high conversion of CO and a high DME selectivity. The DME yield in tail gas reached 46.0% (at 63.27% conversion of CO) at 2.0 MPa, 275°C, 1500 h<sup>-1</sup> with the Cu<sub>2</sub>Mn<sub>4</sub>Zn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

**Keywords** Hydrogenation of carbon monoxide, dimethyl ether, copper, manganese, catalyst

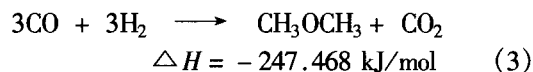
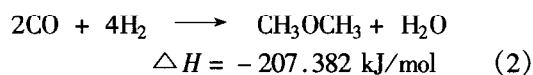
## Introduction

Dimethyl ether (DME) is an important chemical for the production of gasoline, ethylene, aromatics and other chemicals.<sup>1-4</sup> Its applications as a fuel or a fuel additive for vehicles and family cooking gas have been studied.<sup>5-7</sup> In view of the environmental protection, the substitution of DME for freons as an aerosol spray<sup>8</sup> and a refrigerant<sup>9</sup> is being considered.

At present time, almost all commercial dimethyl ether was produced by the dehydration of methanol using acidic porous materials such as zeolites, silica-alumina, alumina *etc.* as the catalyst<sup>10</sup>(Eq. 1), while methanol can be produced from synthesis gas.



It is reported that dimethyl ether can be synthesized from synthesis gas in a single step (Eqs. 2 and 3). It is much more favorable thermodynamically and economically.<sup>11-13</sup>



In early 1990's, most researches focused on dimethyl ether synthesis in a slurry reactor over the presence of dual catalyst system consisting of a methanol-synthesis catalyst (composed of CuO, ZnO, Al<sub>2</sub>O<sub>3</sub>) and a methanol dehydration catalyst ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or zeolites).<sup>1,11,14</sup> At the same time, there are quite a few patents describing the method of dimethyl ether synthesis directly from synthesis gas in a fixed-bed reactor.<sup>15-23</sup> The classical procedure in these patents is as follows: Synthesis gas passed over a hybrid catalyst consisted of a methanol synthesis catalyst and a dehydration catalyst at 240—300°C, 3.0—6.0 MPa, and GHSV = 500—5000 h<sup>-1</sup>. The catalysts employed in this process are MeOH synthesis catalysts (Cu-Zn, Zn-Cr, Cu-Zn-Al, Cu-Zn-Cr *etc.*) mixed with the dehydration catalyst ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or zeolites). Thus, the development of new catalyst or different preparation methods is highly desirable.

In this paper, we have developed a new catalyst

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system Cu-Mn-(M)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared by simple impregnation method. By using this catalyst, the reaction can be carried out at a lower pressure with high CO conversion and high selectivity of DME compared with the commercial dual catalysts.

## Experimental

The catalyst used in this paper can be described as Cu-Mn-(M)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The preparation method is follows: Cu(NO<sub>3</sub>)<sub>2</sub> was mixed with the corresponding amount of  $w = 50\%$  Mn(NO<sub>3</sub>)<sub>2</sub> solution, and deionized water was added to the mixture up to total volume of 35 mL. The nitrate of the third component was added to the solution, and the mixture was stirred until the components dissolved completely. The support such as 30 g  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (20–40 mesh) was added into the solution. The suspension was kept for 3 h at room temperature, then dried at 120°C for 18 h. The final stage of the calcination of the precursor was carried out at 350°C for 3 h in an atmosphere of air.

MRCS8004 (high pressure Microreactor-Chromatograph System, made in China) was employed for the activity test of the catalysts. The reactor is made of a stainless pipe with the inner diameter of 8 mm, the catalyst charged was 5.0 mL (about 5.5 g). Reaction conditions in the experiments were 2.0 MPa, 275°C, space velocity 1 500 h<sup>-1</sup> (STP), and the feed gas composed of  $n(\text{H}_2):n(\text{CO}) = 3:2$ . The feed was controlled by two sets of mass flow controllers (Brooks 5850E, made in USA) and the effluent was analyzed by on-line gas chromatography (HP 5890, Series II, made in USA).

## Results and discussion

### Effect of the catalyst component on catalytic character

#### Effect of $n(\text{Mn})/n(\text{Cu})$ ratio

Cu-Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with different  $n(\text{Mn})/n(\text{Cu})$  mole ratios were prepared and tested, the result is shown in Fig. 1.

With the ratio of  $n(\text{Mn})/n(\text{Cu})$  increasing from zero to 2, the conversion of CO increased quickly from 28% to 65% and the selectivity of DME increased from 16% to 69% with the highest yield of DME in tail gas being 44.4% at  $n(\text{Mn}):n(\text{Cu}) = 2:1$ . After this

point, the conversion of CO and selectivity of DME decreased slowly. The selectivity of CO<sub>2</sub> and methanol decrease slowly with the increasing of  $n(\text{Mn})/n(\text{Cu})$  ratio. On the other hand, the conversion of CO is lower than 10%, and the main product becomes CO<sub>2</sub> (>67%) on the Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. According to the DME yield and selectivity of DME in the organic products (>95% in this work), the result is better than that with hybrid catalysts of methanol synthesis catalyst and dehydration catalyst in the patent.<sup>22</sup> The conversion of CO and selectivity of DME on Cu-Mn/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are higher than that on Cu-Zn-M/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst prepared by the same method in the patent.<sup>23</sup>

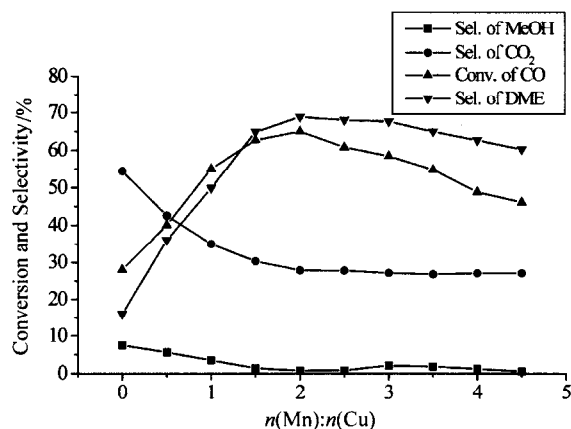
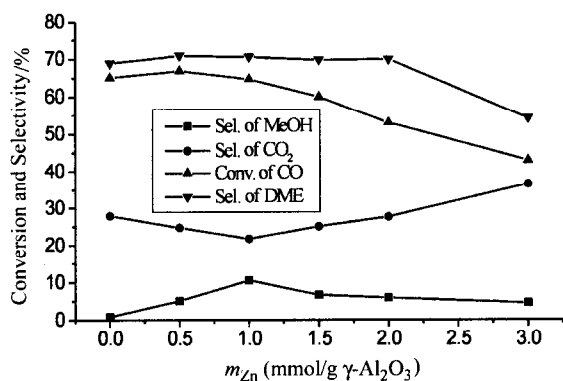


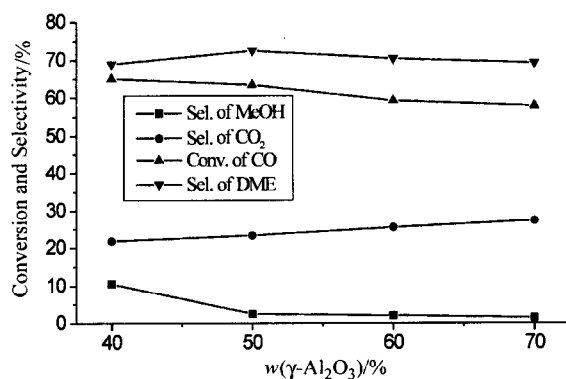
Fig. 1 Effect of  $n(\text{Mn})/n(\text{Cu})$  on the character of catalyst.  $m(\text{Cu}) = 2.0 \text{ mmol/g } \gamma\text{-Al}_2\text{O}_3$ ; Reaction conditions: 275°C, 2.0 MPa,  $n(\text{CO}):n(\text{H}_2) = 2:3$ , total flow = 125 mL/min(STP).

### Effect of Zn addition

It is well known that Cu-Zn is an excellent catalyst for methanol synthesis from syngas. So Zn was introduced as a promoter to improve the character of Cu<sub>2</sub>Mn<sub>4</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system for DME synthesis. The results of the modified catalysts are shown in Fig. 2. Addition of Zn to Cu<sub>2</sub>Mn<sub>4</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst improved the selectivity of methanol and DME. As compared with the Zn-free catalyst, the selectivity of methanol and DME increased from 0.80% and 68.8% to 10.5% and 70.5%, respectively (for the case  $m_{\text{Zn}} = 1.0 \text{ mmol/g } \gamma\text{-Al}_2\text{O}_3$ ). While Zn is excess (when  $m_{\text{Zn}} > 1.0 \text{ mmol/g } \gamma\text{-Al}_2\text{O}_3$ ), the activity of the catalyst and the selectivity of DME decreased (the conversion of CO dropped from 64.5% to



**Fig. 2** Effect of Zn addition to  $\text{Cu}_2\text{Mn}_4/\gamma\text{-Al}_2\text{O}_3$  on the character of catalyst.  $m(\text{Cu}) = 2.0$  mmol/g  $\gamma\text{-Al}_2\text{O}_3$ ,  $m(\text{Mn}) = 4.0$  mmol/g  $\gamma\text{-Al}_2\text{O}_3$ ; Reaction conditions:  $275^\circ\text{C}$ ,  $2.0$  MPa,  $n(\text{CO}):n(\text{H}_2) = 2:3$ , total flow =  $125$  mL/min (STP).

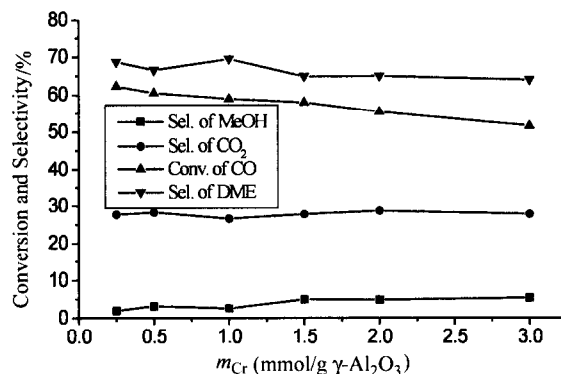


**Fig. 3** Effect of  $\gamma\text{-Al}_2\text{O}_3$  in  $\text{Cu}_2\text{Mn}_4\text{Zn}/\gamma\text{-Al}_2\text{O}_3$  on the character of catalyst.  $n(\text{Cu}):n(\text{Mn}):n(\text{Zn}) = 2:4:1$ , Reaction conditions:  $275^\circ\text{C}$ ,  $2.0$  MPa,  $n(\text{CO}):n(\text{H}_2) = 2:3$ , total flow =  $125$  mL/min (STP).

43.5%, the selectivity of DME dropped from 70.5% to 54.1%), and the selectivity of  $\text{CO}_2$  increased from 22.0% to 37.5% in the products.

#### Effect of amount of $\gamma\text{-Al}_2\text{O}_3$

As shown in Fig. 2, when the catalyst was modified with Zn, the selectivity of methanol raised to 10.50% on the  $\text{Cu}_2\text{Mn}_4\text{Zn}/\gamma\text{-Al}_2\text{O}_3$  catalyst. On the basis of the reaction mechanism,<sup>24,25</sup> the synthesis of methanol from hydrogenation of CO was catalyzed by Cu-Mn-Zn component, and then  $\gamma\text{-Al}_2\text{O}_3$  can dehydrate methanol to DME. So methanol is the intermediate pro-



**Fig. 4** Effect of Cr addition to  $\text{Cu}_2\text{Mn}_4/\gamma\text{-Al}_2\text{O}_3$  on the character of catalyst.  $m(\text{Cu}) = 2.0$  mmol/g  $\gamma\text{-Al}_2\text{O}_3$ ,  $m(\text{Mn}) = 4.0$  mmol/g  $\gamma\text{-Al}_2\text{O}_3$ ; Reaction conditions:  $275^\circ\text{C}$ ,  $2.0$  MPa,  $n(\text{CO}):n(\text{H}_2) = 2:3$ , total flow =  $125$  mL/min (STP).

duct in this reaction. If we increase the amount of  $\gamma\text{-Al}_2\text{O}_3$  in the bifunctional catalyst  $\text{Cu}_2\text{Mn}_4\text{Zn}/\gamma\text{-Al}_2\text{O}_3$ , the dehydration rate of methanol will be increased.

Fig. 3 shows the result of different amount of  $\gamma\text{-Al}_2\text{O}_3$ . The conversion of CO and selectivity of methanol decreased along with increasing amount of  $\gamma\text{-Al}_2\text{O}_3$ . The selectivity of DME reached 73.5% with the weight percentage of  $\gamma\text{-Al}_2\text{O}_3$  in the catalyst being 50%.

#### Effect of Cr addition

It is well known that Zn-Cr and Cu-Zn-Cr are the successful catalysts for methanol synthesis and direct synthesis of DME from synthesis gas, so we tested the Cr as a promoter to the  $\text{Cu}_2\text{Mn}_4/\gamma\text{-Al}_2\text{O}_3$  catalyst. The results are shown in Fig. 4. Except the conversion of CO decreased with the amount of Cr increasing in the catalyst, there is no other clear change in the reaction.

#### Effect of W, Mo, Fe, Co or Ni addition

In order to improve the reactivity of  $\text{Cu}_2\text{Mn}_4/\gamma\text{-Al}_2\text{O}_3$  system, W, Mo, Fe, Co or Ni have been used as promoters for the catalyst. The results are shown in Table 1.

Addition of W or Mo, the conversion of CO decreased and the selectivity of  $\text{CO}_2$  and  $\text{CH}_4$  increased. Fe added, the selectivity of methanol greatly enhanced

**Table 1** Effect of promoter M on the performance of catalyst <sup>a</sup>

M	$m^b$ (mmol/g)	Conv. of CO (mol%)	Selectivity (mol%)			
			DME	CO <sub>2</sub>	CH <sub>3</sub> OH	CH <sub>4</sub>
W	0.50	43.97	59.69	34.07	1.559	4.683
Mo	0.25	33.23	57.71	34.43	1.767	6.088
Fe	0.25	59.56	6.90	18.40	44.40	30.38
Co	0.25	98.36	2.06	14.40	20.30	63.24
Ni	0.50	94.56	7.98	13.84	3.18	75.00

<sup>a</sup> Catalyst: Cu<sub>2</sub>Mn<sub>4</sub>M/γ-Al<sub>2</sub>O<sub>3</sub>; Reaction conditions: 275°C, 2.0 MPa,  $n(\text{CO}):n(\text{H}_2) = 2:3$ , total flow = 125 mL/min(STP).

<sup>b</sup>  $m_M$ 's unit is mmol/g γ-Al<sub>2</sub>O<sub>3</sub>.

from 0.81% to 44.4%, and the selectivity of CH<sub>4</sub> increased from 0.57% to 30.4%, and selectivity of DME decreased to 6.90%. Co or Ni increased the conversion of CO to over 94%, but the product are CO<sub>2</sub> and CH<sub>4</sub> under the same reaction conditions.

It is concluded from the results of experiment that the Cu-Mn-Zn/γ-Al<sub>2</sub>O<sub>3</sub> is a good catalyst for dimethyl ether synthesis directly from synthesis gas in the fixed-bed reactor. The addition of Cr, W, Mo, Fe, Co or Ni can not improve the activity and selectivity of the catalyst.

#### Effects of reaction conditions on catalytic character

##### Effect of space velocity

It is found that the conversion of CO rises quickly from 21.39% to 75.83% with the decrease of space velocity from 7500 h<sup>-1</sup> to 350 h<sup>-1</sup> at 2.0 MPa, 275°C, and that the byproduct methanol decreases from 11.12% to 0.39% with the decreasing of space velocity. At the

**Table 2** Effect of space velocity on the catalytic character of Cu<sub>2</sub>Mn<sub>4</sub>Zn/γ-Al<sub>2</sub>O<sub>3</sub> Catalyst for CO hydrogenation to DME<sup>a</sup>

Space velocity h <sup>-1</sup>	Conversion of CO (mol%)	Selectivity (mol%) <sup>b</sup>				
		DME	CH <sub>3</sub> OH	CH <sub>4</sub>	CH <sub>2</sub> CH <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>
7500	21.39	68.05	11.12	0.00	0.00	0.00
6000	25.88	69.92	9.88	0.00	0.00	0.35
4500	31.92	71.13	7.92	0.00	0.00	0.33
3500	36.10	71.84	6.63	0.18	0.00	0.36
3000	43.46	72.17	4.87	0.44	0.33	0.48
1500	63.27	73.51	2.04	0.89	0.40	0.58
1000	64.99	72.91	1.71	1.28	0.34	0.64
750	69.88	73.13	0.96	1.40	0.41	0.78
350	75.83	71.79	0.39	1.80	0.63	1.10

<sup>a</sup> Reaction conditions:  $n(\text{CO}):n(\text{H}_2) = 2:3$ , 275°C, 2.0 MPa.

<sup>b</sup> Another product did not listed in the Table is CO<sub>2</sub>.

**Table 3** Effect of feeding gas on catalytic character of Cu<sub>2</sub>Mn<sub>4</sub>Zn/γ-Al<sub>2</sub>O<sub>3</sub> catalyst for CO hydrogenation to DME<sup>a</sup>

$n(\text{H}_2)/n(\text{CO})$	Conv. of CO (mol%)	Selectivity (mol%) <sup>b</sup>				
		DME	CH <sub>3</sub> OH	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>
15.0	74.39	67.62	7.25	4.53	1.63	1.24
10.0	73.03	70.21	6.81	3.32	0.96	1.10
5.60	71.63	70.88	4.99	2.18	0.93	0.94
4.00	68.97	70.65	4.39	1.76	0.69	0.88
2.25	66.09	73.17	3.62	1.27	0.63	0.62
2.00	60.57	72.25	3.49	1.15	0.59	0.56
1.75	60.01	73.54	2.64	1.02	0.49	0.55
1.50	63.27	73.51	2.04	0.89	0.40	0.58
1.25	59.81	73.45	2.12	0.88	0.27	0.51
1.00	55.30	74.90	1.70	0.11	0.09	0.10

<sup>a</sup> Reaction conditions: space velocity: 1500 h<sup>-1</sup>, 275°C, 2.0 MPa

<sup>b</sup> Another product did not listed in the Table is CO<sub>2</sub>.

**Table 4** Effect of pressure on catalytic character of  $\text{Cu}_2\text{Mn}_4\text{Zn}/\gamma\text{-Al}_2\text{O}_3$  catalyst for CO hydrogenation to DME<sup>a</sup>

Pressure (MPa)	Conv. of CO (mol%)	Selectivity (mol%) <sup>b</sup>				
		DME	CH <sub>3</sub> OH	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>
2.0	63.27	73.51	2.04	0.89	0.40	0.58
3.5	66.97	72.26	2.18	0.96	0.49	1.03
5.0	70.67	73.41	2.25	1.04	0.56	1.21
6.0	72.15	71.39	6.20	1.38	0.53	1.09
7.0	77.01	71.94	4.47	1.65	0.57	1.11
8.0	84.56	74.05	2.77	1.90	0.57	1.03

<sup>a</sup> Reaction conditions;  $n(\text{CO}):n(\text{H}_2) = 2:3$ ,  $1500 \text{ h}^{-1}(V/V)$ ,  $275^\circ\text{C}$ .

<sup>b</sup> Another product did not listed in The table is  $\text{CO}_2$ .

same time the hydrocarbons such as  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$  increased from zero to 1.80%, 0.63% and 1.10%, respectively.

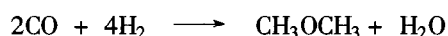
From the experiment of result shown in Table 2, CO hydrogenation for DME carried out *via* the following steps, i.e. first, hydrogenation of CO synthesized methanol, and then methanol dehydrated to DME. Hydrocarbons produced from further dehydration of DME, and  $\text{CO}_2$  produced from water gas shift reaction. This mechanism fits well with the literature.<sup>8</sup>

#### Effect of feeding gas

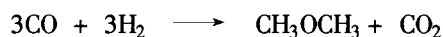
As shown in Table 3, with the increasing  $n(\text{H}_2):n(\text{CO})$  ratio in the feeding gas from 1.0 to 15.0, the conversion of CO increased slowly from 55.30% to 74.39% and the selectivity of DME decreased slowly from 74.90% to 67.62%, but the selectivity of byproduct  $\text{CH}_3\text{OH}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$  increased quickly. Another byproduct  $\text{CO}_2$  decreased slowly during this period. These results can also be explained with the above mentioned mechanism.

#### Effect of pressure

The overall reaction of production DME from CO hydrogenation is as follows:



or include the water gas shift reaction:



It can be seen that both of the above reactions are the

contraction processes of volume during the reaction. The effect of reaction pressure is shown in Table 4.

From the above table, we can see that the conversion of CO increased quickly with the increasing pressure, while the selectivity of DME changed little and that of hydrocarbons increased.

The process has been industrialized in Hubei Tianli Co. Ltd., P. R. China. This plant can produce 90 000-ton ammonia per year. DME is designed as a coproduct of ammonia. and the capability of the DME is 1 500-ton per year.

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