The effect of additives on Cu/HZSM-5 catalyst for DME synthesis

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Received 18 March 2002; accepted 17 July 2002

The addition of ZnO or ZrO_2 into CuO/HZSM-5 was investigated for DME synthesis from syngas by using the reactive frontal chromatography method, TPR and *in situ* TPR. These promoters enhanced the catalytic activity of Cu/HZSM-5 and promotion with ZnO and ZrO_2 produced a maximum activity, which could be explained by the improvement of the dispersion of Cu and the promotion of CuO reduction. The Cu^+ species existing during the reaction have been detected, based on which a $Cu^0 \leftrightarrow Cu^{+1}$ redox cycle model was put forward.

KEY WORDS: CuO : HZSM-5; Cu-ZnO-ZrO_2 : HZSM-5; syngas; dimethyl ether synthesis; methanol synthesis.

1. Introduction

It is well known that dimethyl ether (DME) has many advantageous properties and DME could be a proper substitute for diesel or liquefied petroleum gas (LPG) in the next decades. The single-step DME synthesis from syngas involves methanol synthesis, methanol dehydration and water-gas shift reactions, in which a bifunctional catalyst, usually including methanol synthesis and methanol dehydration components, is used [1–3]. It is generally considered that the methanol synthesis reaction is a key reaction step, and although numerous investigations of the methanol synthesis reaction have been carried out, there are still controversies concerning the active states of copper and the effect of additives [4–8]. Waugh [4] *et al.* suggested that it is merely metallic Cu that carries the catalytic activity and ZnO is only stabilizing a specific higher Cu surface area. Hence, in their opinion, ZnO acts only as an inert support. Nonneman and Ponec [9] have reported that a pure Cu catalyst is inactive for methanol synthesis from CO and H_2. R.G. Herman [10] obtained the same results. They found that in the methanol synthesis, the activity of pure ZnO and pure Cu were zero within detection limits. Burch [11] proposed that activity was enhanced by spillover of hydrogen from ZnO, which acts as a reservoir of adsorbed hydrogen. Klier [12] proposed that the methanol synthesis activity could be attributed to the concentration of Cu^{+1} dissolved in ZnO. Fujitani [13] suggested that the active component was not only Cu^+ but also Cu^0. In this paper, we used HZSM-5 as a dehydration component and an attempt was made to reveal the active state of the copper and the effect of the additives in single-step DME synthesis by using the "reactive frontal chromatography" technique, TPR and *in situ* TPR.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by the coprecipitation sedimentation method [14], wherein a nitrate solution of copper, zinc and zirconium and a solution of sodium carbonate are coprecipitated when added to H_2O simultaneously and dropwise at a pH of 8.0 and temperature of 70 °C under vigorous stirring. The nominal mole ratio of Cu : Zn : Zr was 70 : 30 : 7. Then the precipitates were filtered, washed and added to the suspended liquid including water and HZSM-5. After that, the mixtures were stirred, filtered, dried and calcined in air at 360 °C for 6 h. Lastly, the resultant powder was molded under pressure into tablets. The catalysts used in this paper included Cu : HZSM-5, Cu-ZnO : HZSM-5 (Cu : Zn = 70 : 30) and a systematic series Cu-ZnO-ZrO_2 : HZSM-5 with varying Cu : Zn ratio. The weight ratio of HZSM-5 was 0.5 in all catalysts.

2.2. Measurement of activity for DME synthesis

The DME synthesis was carried out in a conventional tubular fixed-bed stainless reactor. The catalyst was reduced in pure H_2 applying a heating ramp of 0.5 °C to 210 °C and a holding time at 210 °C of 6 h. Then the syngas was fed into the reactor and the reaction conditions were: 3.0 MPa, 1500 h^{-1}. The syngas contained 63.7% H_2, 31.8% CO and 4.35% N_2. The products were analyzed by on-line chromatography with TCD detector, helium as a carrier gas and with the FID detector, N_2, as the carrier gas.

2.3. Reactive frontal chromatography

The copper surface area (S_{Cu}) was determined by the technique of "reactive frontal chromatography" as

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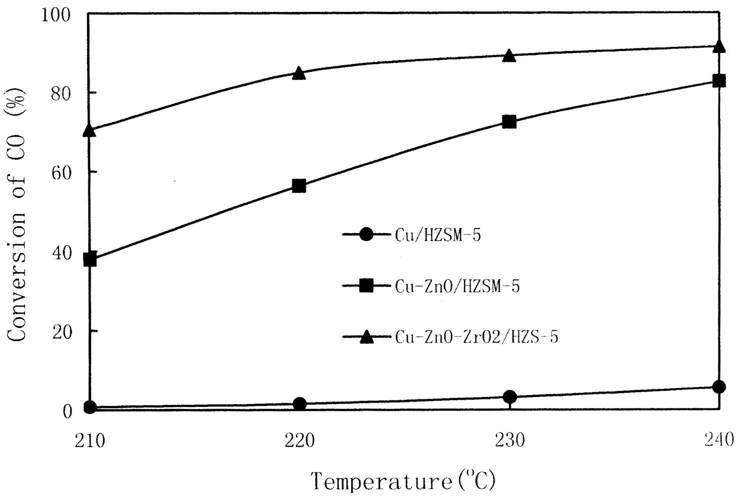

Figure 1. The influence of temperature on the CO conversion.

described by Chinchen [15]. Under this condition, ZnO and copper oxide could not decompose N_2O [15,16]. A catalyst sample (about 0.2 g) was placed in a quartz tube reactor and reduced in flowing hydrogen (20 ml/min) at 210 °C for 2 h. After reduction, the gas flow was switched to purified helium (10 ml/min) and the temperature was lowered to 45 °C. Then, the gas was changed from He to a mixture of 1% N_2O in He and the products were analyzed on-line by a mass spectrometer detector. The N_2O reacts quantitatively only with the Cu surface atoms forming gas-phase N_2: $N_2O(g) + 2Cu_s = N_2(g) + Cu_s\text{-}O\text{-}Cu_s$. The formed amount of N_2 has been determined by the mole flow of N_2O and the time interval between the start of N_2 production and N_2O breakthrough. The specific Cu surface area has been calculated by using a value of 1.47×10^{19} atoms per m^2 for the mean Cu surface atom density.

2.4. Temperature-programmed reduction

Temperature-programmed reduction (TPR) was carried out in a quartz–glass reactor. Firstly, the sample was pretreated at 350 °C for 1 h in a 20 ml min^{-1} stream of pure Ar. Secondly, the temperature was lowered to 30 °C. Then the catalyst was reduced by 5% H_2–Ar with a heating-rate of 5 °C/min and the amount of H_2 uptake during the reaction was measured by a thermal conductivity detector.

2.5. In situ TPR

The *in situ* temperature-programmed reduction was done as follows: (1) The catalyst was reduced in pure H_2 at 210 °C for 4 h; (2) the syngas was then fed into the DME reactor at 2.0 MPa, 220 °C for 3 h; (3) the reactor was cooled rapidly to room temperature, depressurized and the syngas was swept out by Ar in order to keep the real valence state of Cu formed during the reaction. Then a second TPR run was carried out to estimate Cu^{+1} content.

3. Results and discussion

3.1. The influence of ZnO and ZrO_2 on the activity

The influence of temperature on the CO conversion over these catalysts was showed in figure 1 and table 1. These results showed that Cu/HZSM-5 was not active for the DME synthesis and the activity of the catalyst was improved greatly with the addition of ZnO. The second component, ZrO_2, further improved the activity.

Table 1
The activity of catalysts.

Catalyst	S_{Cu} (m^2/g)	220 °C		240 °C						
		Conv. CO (%)	Conv. CO (m^2Cu)	Conv. CO (%)	Conv. CO (m^2Cu)	The selectivity of the products (%)				
						CH_3OH	DME	C_2	CO_2	CH_4
Cu : HZSM-5	5.9	1.56	1	5.61	1.0	18.73	54.11	0.0	27.16	0.11
Cu-ZnO : HZSM-5	11.6	56.31	18	82.50	7.5	6.17	60.56	1.23	32.04	0.01
Cu-ZnO-ZrO_2 : HZSM-5	18.5	84.90	17	91.35	5.0	2.65	75.99	0.55	20.81	0.01

Reaction condition: 1500 h^{-1}, 3.0 MPa. Feed gas: $H_2 : CO = 2 : 1$, 4.35% N_2.

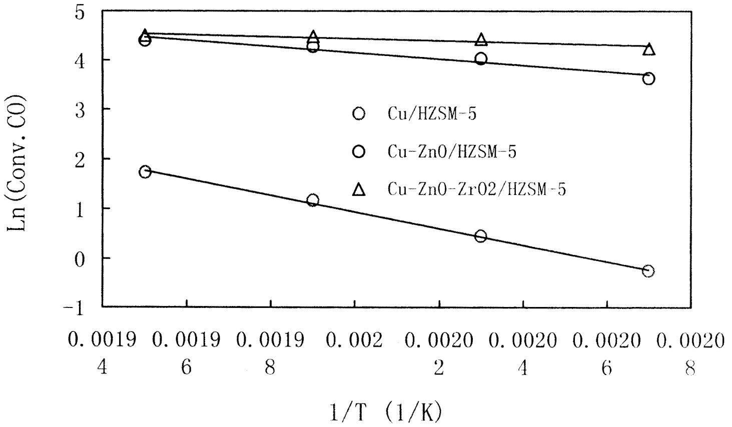

Figure 2. The Arrhenius plot over different catalysts.

The ratio of apparent activation energy, E_a, on Cu:HZSM-5, Cu-ZnO:HZSM-5 and Cu-ZnO-ZrO_2:HZSM-5 was calculated to be about 17:4.5:1 from the Arrhenius plot shown in figure 2, assuming the reaction as a pseudo-first-order reaction. The results indicated that the effect exerted by ZnO and ZrO_2, especially ZnO, was great for Cu:HZSM-5 in DME synthesis. The addition of ZnO and ZrO_2 decreased the activation energy. From the data of the copper surface area (table 1), it could be seen that the ratio of copper surface area for all three catalysts was about 1:2:3, by which we could conclude that the increase of activity was related to the increase of Cu active surface. The specific activity (the CO conversion on m^2 Cu), however, was not the same. It clearly indicated that the increase in copper surface area was not the only reason for the activity improvement. Other factors, such as the active center or the copper valence state induced by the adding of the additives, might play a role.

3.2. The TPR measurement

Figure 3 shows the TPR profile of catalysts. The experiment of TPR conducted on pure ZnO under the same condition shows no hydrogen consumption. So only CuO could be reduced under the condition. The data, including the CuO content, the temperature of the peak and the ratio of two reduction peaks, is listed in table 2. There were two obvious reduction peaks over both CuO-ZnO:HZSM-5 and CuO-ZnO-ZrO_2:HZSM-5 while only one broad peak was found over the CuO:HZSM-5 with a minor shoulder at 480 K. In the presence of ZnO, the temperature of the first reduction peak of CuO was about 40 K lower than that of CuO:HZSM-5. With ZrO_2 addition, two peaks remained, but the temperature of the first reduction peak increased slightly. It should be noticed that the ratio of the two peaks changed from 1.9 with Cu-ZnO:HZSM-5 to 1.3 with Cu-ZnO-ZrO_2:HZSM-5. Combined with the specific activity data, it was concluded that the ratio of the two peaks appeared to show a correlation with the specific activity of the catalyst.

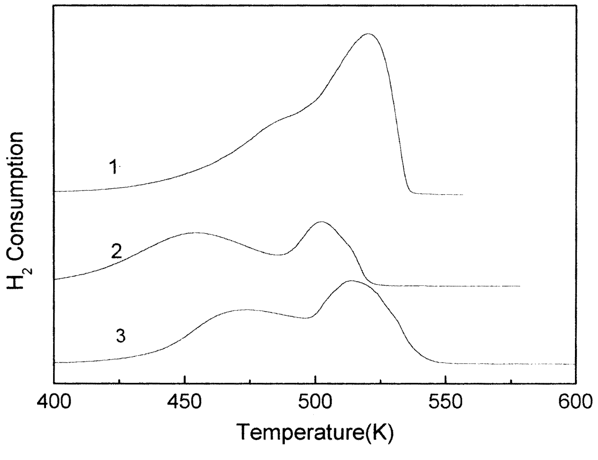

Figure 3. TPR profile. (1) CuO:HZSM-5, (2) CuO-ZnO:HZSM-5, (3) CuO-ZnO-ZrO_2:HZSM-5.

From figure 4, it could be found that in CuO-ZnO-ZrO_2:HZSM-5 varying the ZnO content affected the performance of the catalyst and the 30:70 ratio of Zn:Cu had the highest activity in the DME synthesis system. M.M. Günter [17] considered that the 20:80 ratio of Zn:Cu exhibited the highest activity in the methanol synthesis.

The TPR of CuO-ZnO-ZrO_2:HZSM-5 with different Zn:Cu ratio was studied in figure 5. The results showed that with variation of the ZnO content, the shape of TPR profile changed gradually. Varying the Zn:Cu ratio from 10:90 to 20:80 lowered the temperature of the reduction peak slightly. When the content increased to 30:70, two peaks were detected and the first peak appeared at the

Table 2
The TPR results.

Catalyst	The temperature of peaks (K)		The total peak area (area/g CuO)	The ratio of two peaks
CuO:HZSM-5	480	521	2.15×10^{10}	–
CuO-ZnO:HZSM-5	445	490	2.14×10^{10}	1.9
CuO-ZnO-ZrO_2:HZSM-5	481	520	2.15×10^{10}	1.3

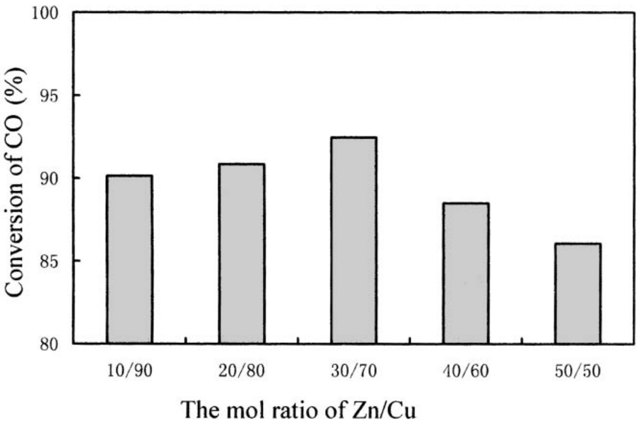

Figure 4. The influence of the ZnO content varying in Cu-ZnO-ZrO_2 : HZSM-5.

lower temperature. A further increase in the ratio of Zn : Cu induced little change of profile shape.

3.3. *In situ TPR measurement*

In order to investigate the Cu valence state during the reaction, an *in situ* TPR test was designed. The sample was first treated by a TPR procedure up to 210 °C for 4 h, after which we concluded that oxide states of Cu no longer existed since no further hydrogen consumption was found. Then, the reduced catalyst was fed with syngas at 2.0 MPa, 220 °C for 3 h reaction. After that, the system was cooled rapidly and depressurized to 0.1 MPa, under which condition we supposed the catalyst should keep any *in situ* formed Cu-species with different oxidation states. Then a second TPR measurement was carried out to estimate the content of Cu^+ species formed during reaction. Figure 6 shows that in all cases hydrogen consumption could be observed. The actual amount of Cu^{+1} species in all catalysts might be a little greater than that detected due to the catalyst quenched in the presence of reducing gas mixture.

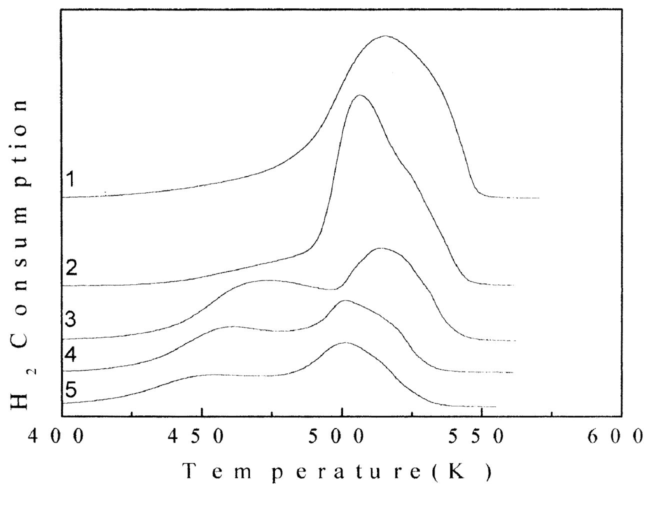

Figure 5. TPR profile with various ZnO contents in Cu-ZnO-ZrO_2 : HZSM-5. The ratio of Zn : Cu: (1) 10 : 90; (2) 20 : 80; (3) 30 : 70; (4) 40 : 60; (5) 50 : 50.

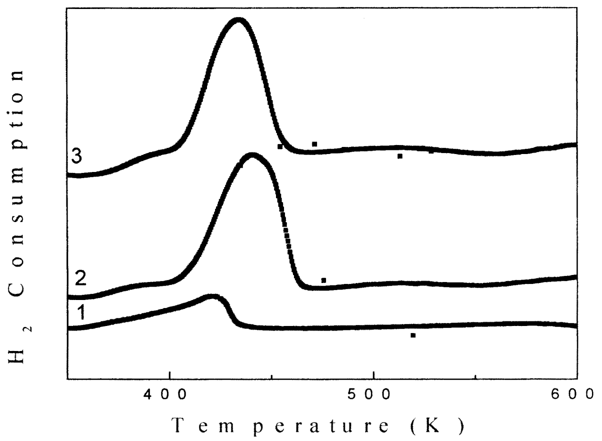

Figure 6. *In situ* TPR profile. (1) Cu : HZSM-5, (2) Cu-ZnO : HZSM-5, (3) Cu-ZnO-ZrO_2 : HZSM-5.

The peak area of Cu : HZSM-5 catalyst was much smaller than that of Cu-ZnO:HZSM-5 and Cu-ZnO-ZrO_2: HZSM-5 catalyst. It seems likely that the Cu oxide state (Cu^{+1}) in the reaction is related to the activity of the catalyst, despite the ratio of Cu^{+1} with Cu^0 only being about 0.03. Thus, there should be a $Cu^0 \leftrightarrow Cu^{+1}$ redox cycle during the catalytic reaction.

The redox cycle may be formed according to the following model: Cu^0 was oxidized by the oxygenate intermediate, while Cu^+ was reduced to Cu^0 by H_2 and CO during the reaction. On the one hand, reactant gas could be absorbed and activated on Cu^0; on the other hand, the presence of Cu^+ could promote the formation of surface formate, which is a pivotal intermediate for methanol synthesis, and the hydrogenation of copper formate is suggested as the rate-determining step [18,19]. Hence, DME activity may have a similar dependence on both Cu^0 and Cu^+ in the reaction.

4. Conclusions

1. The activity of Cu:HZSM-5 was very low in the DME synthesis. The addition of ZnO and ZrO_2 could enhance the activity of Cu:HZSM-5 for DME synthesis.
2. The introduction of ZnO and ZrO_2 enhanced the dispersion of Cu particles and promoted reduction of CuO.
3. The interaction between Cu, ZnO and ZrO_2 promoted the formation of a Cu^+ oxide state. There exists a Cu^0:Cu^{+1} redox pair on the catalyst, which may play a role in the methanol (and DME) synthesis.

Acknowledgments

The authors are grateful to the Ministry of Science and Technology of China for its financial support (G1999022401).

References

[1] K. Fujimoto, K. Asami, T. Shikada and H. Tominaga, Chem. Lett. (1984) 2051.

[2] A.C. Sofianos and M.S. Scurrel, Ind. Eng. Chem. Res. 30 (1991) 2372.

[3] X.D. Peng, A.W. Wang, B.A. Toseland and P.J.A. Tijm, Ind. Eng. Chem. Res. 38 (1999) 4381.

[4] G.C. Chinchen, K.C. Waugh and D.A. Whan, Appl. Catal. 25 (1986) 101.

[5] G.C. Chinchen and K.C. Waugh, J. Catal. 97 (1986) 280.

[6] G.R. Sheffer and T.S. King, J. Catal. 115 (1989) 376.

[7] K. Klier, Appl. Surf. Sci. 19 (1984) 267.

[8] T. Fujitani, I. Nakamura, T. Watanabe, T. Uchijima and J. Nakamura, Catal. Lett. 35 (1995) 297.

[9] L.E.Y. Nonneman and V. Ponec, Catal. Lett. 7 (1990) 213.

[10] R.G. Herman, K. Klier, G.W. Simmons, B.P. Finn and J.B. Bulko, J. Catal. 56 (1979) 407.

[11] R. Burch, S.E. Golunski and M.S. Spencer, Catal. Lett. 5 (1990) 55.

[12] J.G. Nunan, K. Klier, C.W. Young, P.B. Himelfarb and R.G. Herman, J. Chem. Soc. Chem. Commun. 193 (1986).

[13] Y. Kanai, T. Watanabe, T. Fujitani, M. Saito, J. Nakamura and T. Uchijima, Catal. Lett. 27 (1994) 67.

[14] Q. Ge, Y. Huang, F. Qiu and S. Li, Appl. Catal. 167 (1998) 23.

[15] G.C. Chinchen, C.M. Hay, H.D. Vandervell and K.C. Waugh, J. Catal. 103 (1987) 79.

[16] J.W. Evans, M.S. Wainwright, A.J. Bridgewater and D.J. Young, Appl. Catal. 7 (1983) 75.

[17] M.M Günter, T. Ressler, B. Bems, C. Büscher, T. Genger, O. Hinrichsen, M. Muhler and R. Schlögl, Catal. Lett. 71 (2001) 37.

[18] G.J. Millar, C.H. Rochester and K.C. Waugh, Catal. Lett. 14 (1992) 289.

[19] G.J. Miller, C.H. Rochester and K.C. Waugh, J. Chem. Soc., Faraday Trans. 87 (1991) 1491.