

# Research on the acidity of the double-function catalyst for DME synthesis from syngas

Ligang Wang<sup>a,b</sup>, Yue Qi<sup>a</sup>, Yingxu Wei<sup>a</sup>, Deren Fang<sup>a</sup>, Shuanghe Meng<sup>a</sup>, and Zhongmin Liu<sup>a,\*</sup>

<sup>a</sup>Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China

<sup>b</sup>Graduate School of Chinese Academy of Sciences, Beijing 100039, P. R. China

Received 27 August 2005; accepted 6 October 2005

Two kinds of HZSM-5 zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50,300$ ) were introduced into the STD (syngas-to-DME) reaction and the double-function catalysts containing  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  and HZSM-5 were investigated by activity evaluation and  $\text{NH}_3$ -TPD. It was found that the acidity of HZSM-5 played a critical role in the performance of STD catalyst, and an appropriate acidic amount was required to obtain the best activity of STD catalyst; more and less acidic amount were both unfavorable for DME yield.

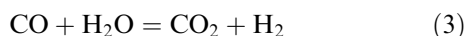
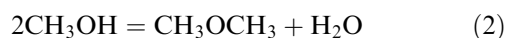
**KEY WORDS:** syngas; dimethyl ether (DME); methanol;  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio; dehydration.

## 1. Introduction

It is well known that dimethyl ether (DME) as an important chemical is widely used in producing gasoline, ethylene, aromatic and other chemicals [1,2]. Recently, it has received much attention as an alternative diesel fuel due to its low NOx emission, near zero smoke and less engine noise [3].

Traditionally, DME is produced by methanol dehydration over solid-acid catalysts, while methanol is produced from synthesis gas ( $\text{CO}/\text{H}_2/\text{CO}_2$ ). Recently, a direct route called STD process (synthesis gas-to-dimethyl ether) has received much attention [4]. It was reported that STD process was more thermodynamically and economically favorable than the traditional route.

There are three major reactions in STD process [5]:



It can be seen that methanol produced by reaction (1) is consumed by dehydration reaction (2), while water formed by reaction (2) can be react with CO through water gas shift reaction (3). Therefore, CO conversion can be remarkably increased. Typically, a mixed double-function catalyst was used in STD process, which composed of a methanol synthesis catalyst ( $\text{Cu}/\text{Zn}/\text{Al}$ ,  $\text{Cu}/\text{Zn}/\text{Cr}$ ,  $\text{Cu}/\text{Zn}/\text{Zr}$ , etc) and a methanol dehydration catalyst (zeolite [6,7] or  $\gamma$ -alumina [8,9]).

The acidity of the methanol dehydration catalyst is very important to influence the rate of reaction (2) [10–

12]. Kim *et al.* [13] investigated NaZSM-5 and HZSM-5 with three Si/Al ratios (30,50,100) and concluded that the acid strength of ZSM-5 increased with a decrease in the Si/Al ratios and the methanol dehydration rate was dependent on the acid strength of the ZSM-5, the difference of acid strength would change the optimal ratio of the two components, because the relative rate of intrinsic methanol synthesis and methanol dehydration was changed. Ramos *et al.* [14] compared with HZSM-5, alumina, tungsten–zirconia and sulfated-zirconia and concluded that the determining rate of DME direct synthesis was determined by the acid properties of the dehydrating catalyst, i.e., its acid strength and number of acid sites. Recently, Mao *et al.* [15] postulated that if the solid acid catalyst was so active, the acidity of the solid acid catalyst affected only the selectivity for DME; in reverse, if the acidity of the solid acid catalyst was not strong enough to convert effectively the methanol to DME, the acidity of the solid acid catalyst greatly affected both the CO conversion and the selectivity for DME. In this work, we introduced two kinds of HZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50,300$ ), and fixed the amount of methanol synthesis component ( $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ ) in all catalysts, the effect of acidity, especially the acidic amount, on the performance of the double-function catalyst was investigated in detail.

## 2. Experimental

### 2.1. Catalyst preparation

The catalyst for Methanol synthesis is  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  (Xinan Institute of Chemical Engineering, China).

The catalyst for methanol dehydration is HZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50,300$ ). NaZSM-5 was obtained from Fuxu chemical company (Shanghai China), which was

\* To whom correspondence should be addressed.

E-mail: zml@dicp.ac.cn

calcined in flowing air at 550 °C for 5 h to remove the template. The calcined sample was converted into  $\text{NH}_4$ -form by exchanging with a 1.0 M ammonium nitrate solution for three times at 80 °C. Subsequently, the exchanged sample was washed thoroughly with deionized water to remove the  $\text{NO}_3^-$  ion and dried 120 °C for 3 h. Finally, the ZSM-5 in  $\text{NH}_4$ -form was calcined at 500 °C for 6 h to convert into HZSM-5.

$\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ , HZSM-5, and quartz sand (over 200 mesh) were mixed mechanically, then, the powder was molded under pressure into tablets, which were crushed and sieved to particles of 20–40 meshes. In all the catalysts, the weight percentage of  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  is 30% and the weight ratio of  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  to HZSM-5 are 4:1, 2:1, and 1:2.

For convenience, the catalysts will be designated by a abbreviation: CZAHS(X, Y), where ‘CZA’ denotes  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ , ‘H’ denotes HZSM-5, ‘S’ denotes quartz sand ‘X’ denotes  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio so  $X=50$  or 300, and ‘Y’ denotes the weight ratio of  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  to HZSM-5, so  $Y=4,2$ , or 0.5.

## 2.2. Catalytic evaluation

The STD catalysts were evaluated for activity in a tubular fixed-bed stainless reactor system. Before evaluation, the catalysts had been reduced with pure hydrogen under the following heating program: heat up from room temperature to 200 °C in 4 h and then stay at 200 °C for 2 h, heat up to 250 °C in 1 h and stay at 250 °C for 1 h, at last, drop to room temperature. After reduction, the synthesis gas ( $\text{H}_2/\text{CO}=2$ ,  $\text{CH}_4$  0.22%  $\text{CO}_2\approx 1\%$ ) was fed into the reactor. Program-heating reactions were employed, at every temperature pot, samples were analyzed after 1 h stabilization. The products were warmed and analyzed by on-line HP 6890 chromatograph with TCD detector, hydrogen as a carrier gas.

## 2.3. $\text{NH}_3$ -Temperature-programmed desorption ( $\text{NH}_3$ -TPD)

The sample (0.14 g) was loaded into a stainless U-shaped reactor and pretreated at 600 °C for 0.5 h in flowing He. After the pretreatment, the sample was cooled to 150 °C and saturated with  $\text{NH}_3$  gas. As soon as the baseline in gas chromatograph was stable, the  $\text{NH}_3$ -TPD was carried out under a constant flow of He (20 ml/min) from 150 to 600 °C at a heating rate of 18 °C/min. The concentration of ammonia in the exit gas was monitored continuously by a gas chromatograph with a TCD detector.

## 3. Results and discussion

### 3.1. Catalyst characterization by $\text{NH}_3$ -TPD

Figure 1 shows the  $\text{NH}_3$ -TPD results of the two kinds HZSM-5. For both of the two samples, two peaks of

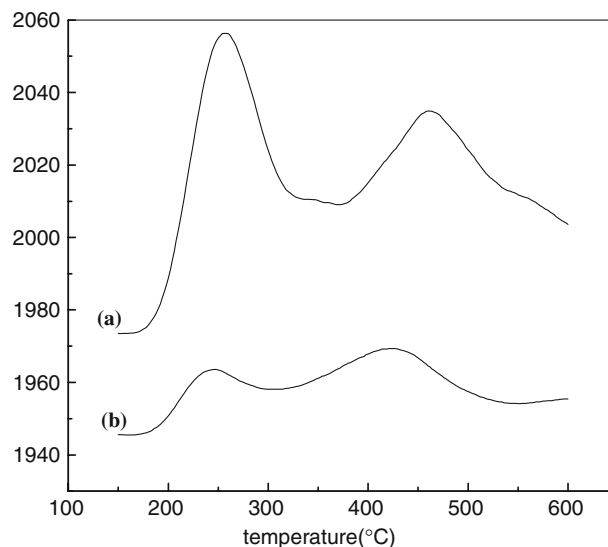


Figure 1.  $\text{NH}_3$ -TPD profile of the two HZSM-5 (a) HZSM-5 (50); (b) HZSM-5 (300).

$\text{NH}_3$  desorption can be observed. The peak at lower temperature can be attributed to  $\text{NH}_3$  eluted from the weak acid sites of HZSM-5, while the higher one is related to the strong acid sites. More detailed data are shown in table 1. It can be seen that the number of acid site of HZSM-5 (50) are much larger than that of HZSM-5 (300), whether the number of weak sites or strong acid sites. Furthermore, the temperature of  $\text{NH}_3$  desorption on HZSM-5 (50) is higher than that on HZSM-5 (300), suggesting that the acid strength of the former is much higher than that of the latter. The  $\text{NH}_3$ -TPD results shows that the largest distinction of the two kinds HZSM-5 is on acidic amount, as comparison, the difference of acid strength is smaller.

### 3.2. Catalytic activity evaluation test

#### 3.2.1. The influence of acidity on product distribution

It is on solid acid catalyst that the methanol is dehydrated (equation (2)), resulting in the equilibrium conversion of CO hydrogenation reaction (equation (1)) shifting rightwards. Therefore, the acidity of solid acid is important to affect the rate for methanol dehydration and indirectly influence the rate for CO hydrogenation. Table 2 shows the effect of acidity on the product distribution of syngas-to-DME reaction, under the condition of 3 MPa, 260 °C. It can be seen that, in all the catalysts, the amounts of CZA are almost the same (0.27 g). The activity of catalysts containing HZSM-5 (50 or 300) was much higher than that of catalyst without zeolite (CZAS), showing on the significant increase of CO conversion, DME selectivity, as well as DME yield. This result suggested that the introduction of HZSM-5 were valid to enhance DME yield, significantly promoting CO hydrogenation, but there was obvious difference on the capability of the two HZSM-5

Table 1  
NH<sub>3</sub>-TPD data of the two kinds HZSM-5 zeolite

HZSM-5	Weak acid site		Strong acid site		Total acid site
	Temperature of NH <sub>3</sub> desorption (°C)	Amount of NH <sub>3</sub> desorption (mmol NH <sub>3</sub> /g)	Temperature of NH <sub>3</sub> desorption (°C)	Amount of NH <sub>3</sub> desorption (mmol NH <sub>3</sub> /g)	Amount of NH <sub>3</sub> desorption (mmol NH <sub>3</sub> /g)
50	258	0.367	464	0.493	0.860
300	242	0.092	426	0.172	0.264

zeolite, due to their different acidity, especially the acidic amount.

As the catalysts containing HZSM-5 (50) is concerned, with decreasing the ratio of CZA to HZSM-5 (50), the acidic amount increased, but the activity declined clearly. When the ratio of CZA to HZSM-5 was 4:1, the CO conversion on CZAHS (50,4) was as high as 69%, the DME selectivity also reached 65%, and there was only a trace amount of methanol remained, indicating that almost all the methanol formed by CO hydrogenation had been converted to DME. As to the catalyst of CZAHS (50,2), in which the acidic amount was over twice than that of CZAHS (50,4), the selectivity of DME was not decreased significantly, but the CO conversion declined to 60%, suggesting that under this ratio, the amount of acid was still enough to convert almost all the methanol to DME, but the activity of CZA was decreased. These results were quite different from the previous works of Mao *et al.* [15], as they had postulated that if the solid acid catalyst was so active, only the selectivity for DME would be affected by the acidity of the solid acid catalyst, but the conversion of CO would not. Considering that, if the acidity of solid acid was so active, the CO hydrogenation on CZA was the rate-determining step [13, 15], and the amount of CZA was the same in CZAHS (50,4) and CZAHS (50,2), it was reasonable to conclude that the activity of CZA had been influenced by HZSM-5, possibly, due to the interaction between CZA and HZSM-5. When the ratio further lowered to 0.5, the activity of CZAHS (50,0.5) decreased markedly, compared with CZAHS (50,4) and CZAHS (50,2),

implying again that the activity of CZA was heavily influenced by HZSM-5, and more acidic amount were, more influence occurred. In addition, it should be pointed that the DME selectivity of CZAHS (50,0.5) declined clearly, while the selectivity of C<sub>2</sub> increased obviously, suggesting that with the increase of strong acid sites, wherein the dehydration reaction of DME to hydrocarbon became significant [16].

In contrast to the performance of catalysts containing HZSM-5 (50), the catalysts containing HZSM-5 (300) exhibited quite different activity, the acidic amount increased as the ratio of CZA to HZSM-5 decreased, so did the catalytic activity. The activity of CZAHS (300,4) was only slightly higher than CZAS, with CO conversion was 16.6% and methanol was the major product, showing that, under this ratio, the acidic amount was not enough to convert all the methanol to DME, so that the dehydration rate was much lower than the rate for methanol synthesis, causing no efficient promoting of the CO hydrogenation reaction. When the ratio of the two components was 2, the activity of catalyst was enhanced remarkably, compared to CZAHS (300,4), with the DME selectivity increased remarkably to 55%, while the methanol selectivity decreased to 9.8%. This result indicated that the methanol dehydration rate was enhanced greatly due to the increase of acidic amount in catalyst CZAHS (300,2). When the ratio declined to 0.5, differing from CZAHS (50,0.5), the DME selectivity on CZAHS (300,0.5) was as high as 63%, while there was no obvious increase of C<sub>2</sub> selectivity. This can be assigned to that there were fewer number of

Table 2  
Product distribution of DME synthesis from synthesis on catalysts with different acidity

Catalyst	The total weight of catalyst (g)	CZA(g)	Total acid number (mmol NH <sub>3</sub> )	CO conversion (%)	DME yield (mol/mol CO)	Product selectivity (%)				
						CH <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub>	DME	CH <sub>3</sub> OH
CZAHS(50,4)	0.91	0.27	0.059	69.20	0.45	1.12	32.84	0.87	64.82	0.35
CZAHS(300,4)	1.02	0.30	0.020	16.60	0.027	5.91	23.33	3.19	16.29	51.28
CZAHS(50,2)	0.90	0.27	0.12	60.00	0.38	1.2	33.34	1.32	64.05	0.097
CZAHS(300,2)	0.88	0.26	0.035	43.33	0.24	2.05	31.71	1.18	55.26	9.80
CZAHS(50,0.5)	0.90	0.27	0.47	36.68	0.21	1.80	35.77	4.19	58.25	n.d
CZAHS(300,0.5)	0.90	0.27	0.14	41.32	0.26	1.44	33.69	1.734	63.14	n.d
CZAS	0.98	0.29	n.d	15.62	0.015	6.44	20.98	3.50	9.29	59.79

Reaction conditions: 3 MPa, 260 °C, C<sub>2</sub>=ethene and ethane.

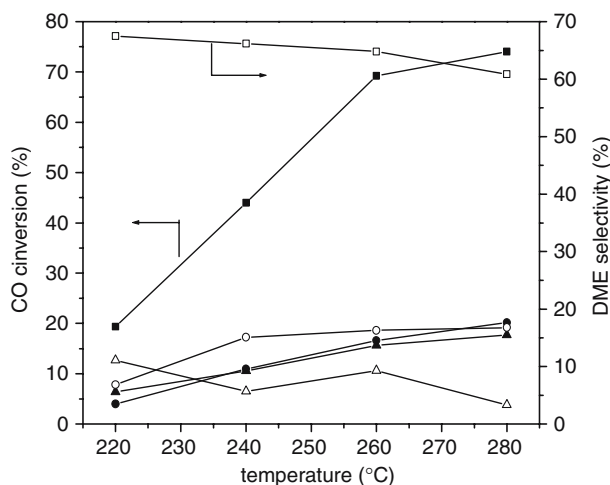


Figure 2. Conversion of CO and selectivity for DME as the function of temperature, under the mixing ratio of 4:1. Conversion of CO: (■) CZAHS (50,4); (●) CZAHS (300,4); (▲) CZAS. Selectivity for DME: (□) CZAHS (50,4); (○) CZAHS (300,4); (△) CZAS.

strong acid sites on HZSM-5 (300) than those of HZSM-5 (50), under the same ratio of CZA to HZSM-5.

### 3.2.2. The influence of acidity on catalytic activity under different temperature

The STD catalytic performance heavily depends on reaction temperature, and more significant difference of catalyst performance, caused by different acidity, can be obtained by varying reaction temperature.

Figure 2 shows the catalyst performance under mixing ratio of 4:1. Within all the temperature region, the activity of CZAHS (50,4) was much higher than that of CZAHS (300,4) and CZAS, with CO conversion increasing rapidly with temperature until 280 °C, due to the restriction of thermodynamics equilibrium, and the selectivity of DME maintaining over 60%. It is clear that under the mixing ratio of 4:1, only on CZAHS (50,4), the rate for methanol dehydration was greatly enhanced, matching with the methanol formation rate, resulting in the CO conversion and DME selectivity were both greatly promoted, on the contrary, the methanol dehydration rate was very low on CZAHS (300,4).

The catalyst performance under mixing ratio of 2:1 is different, as shown in figure 3. The CO conversion on CZAHS (50,2) and CZAHS (300,2) were both rapidly increased with raising of temperature, and the selectivity for DME of them were higher than 60% in all the temperature region, indicating that the activity of CZAHS (50,2) and CZAHS (300,2) were much higher than CZAS, due to the increase of acidic amount, nevertheless, it required more acidic amount for CZAHS (300,2) to make all the methanol dehydrated as that exhibited on CZAHS (50,2).

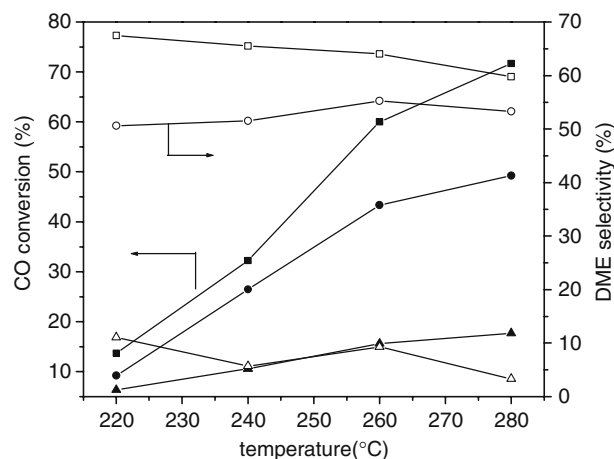


Figure 3. Conversion of CO and selectivity for DME as the function of temperature, under the mixing ratio of 2:1. Conversion of CO: (■) CZAHS (50,2); (●) CZAHS (300,2); (▲) CZAS. Selectivity for DME: (□) CZAHS (50,2); (○) CZAHS (300,2); (△) CZAS.

Figure 4 shows the catalyst performance under mixing ratio of 1:2. it can be seen that the activity of CZAHS(50,0.5) and CZAHS(300,0.5) were both declined to a large extent, as contrasting to those under other ratios. On CZAHS (50, 0.5), the decline trend of DME selectivity with temperature was very distinct, but there was only slightly decline on CZAHS (300,0.5), suggesting that higher temperature was more beneficial for the dehydration of DME, which occurred on strong acid sites, and was more serious on CZAHS (50,0.5).

### 3.2.3. Correlation of catalyst acidity with activity

In order to demonstrate the effect of acidity on catalytic activity more clearly, the acidic amount (stand by  $\text{NH}_3$  desorption amount) and catalytic activity were correlated, as shown in figures 5, 6.

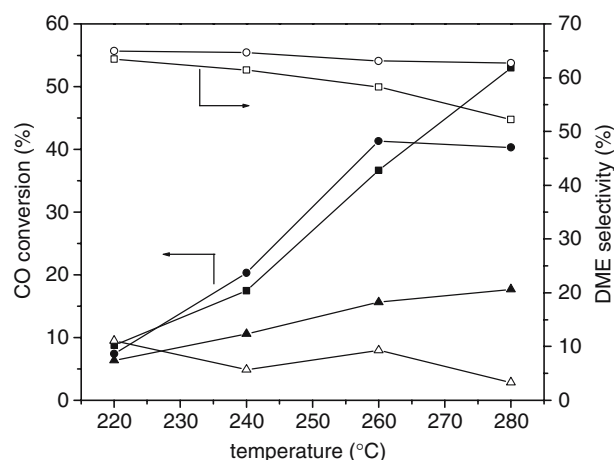


Figure 4. Conversion of CO and selectivity for DME as the function of temperature, under the mixing ratio of 1:2. Conversion of CO: (■) CZAHS (50,0.5); (●) CZAHS (300,0.5); (▲) CZAS. Selectivity for DME: (□) CZAHS (50,0.5); (○) CZAHS (300,0.5); (△) CZAS.

Figure 5 shows that the activity of catalysts containing HZSM-5 (50) decreased rapidly with increasing acidic amount, whether on weak or strong acidic sites, suggesting that the total acidic amount of 0.06 mmol  $\text{NH}_3$  was enough to make all the methanol be dehydrated, and more acidic amount caused bad influence on DME yield; but as to catalysts containing HZSM-5 (300), the trend was in reverse (figure 6), that is, the activity of catalysts containing HZSM-5 (300) increased remarkably as acidic amount increased, indicating that the acidic amount of HZSM-5 (300) was far less than that needed to convert all the methanol to DME. Although we can not clarify whether the dehydration active center is on weak acid sites as Ge [17] have suggested or on strong acid sites as Liu *et al.* [18] have postulated, the correlation of acidic amount with catalytic activity clearly shows that the number of dehydration active sites is crucial for DME yield.

Furthermore, within all the catalyst tested, the total acidic amount and catalytic activity corresponding to 1 g CZA were also correlated, as shown in figure 7. It is obvious that acidic amount with an optimized range was needed for 1 g CZA to get the best DME yield. Below that range, for example, the acidic amount of 0.066 mmol  $\text{NH}_3$  was too little to make all the methanol produced by 1 g CZA dehydrated, as the dehydration rate was much lower than the rate for methanol formation; on the contrary, over that range, for example, at acidic amount of 1.74 mmol  $\text{NH}_3$ , a rapid decline of DME yield can be observed, due to the reasons have mentioned above.

However, it should be mentioned that the optimized acidic amount required for 1 g CZA to gain the best catalyst performance is not identical for the two kind HZSM-5, suggesting that there are also other factors (for example, the acid strength, the ratio of weak to

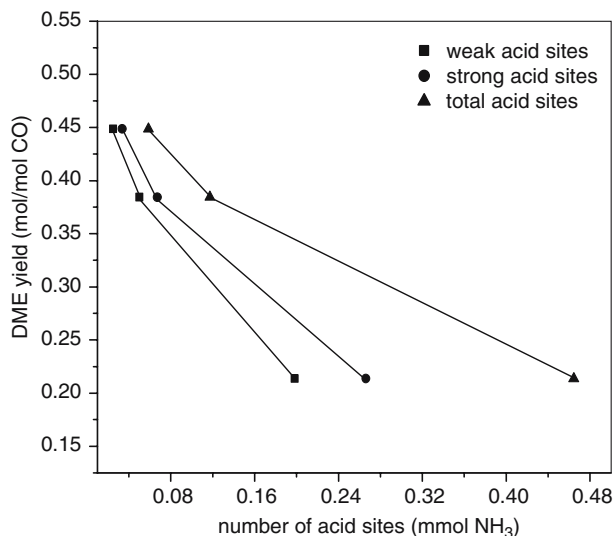


Figure 5. The correlation of acidic amount with activity on the catalyst of CZAHS (50) series. Reaction conditions are same as that in table. 2.

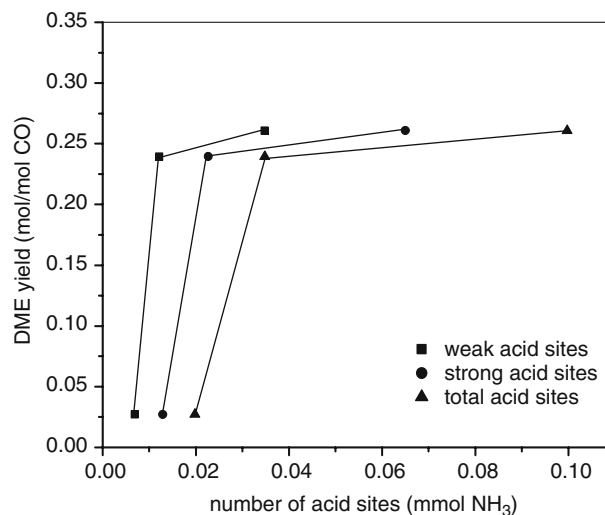


Figure 6. The correlation of acidic amount with activity on the catalyst of CZAHS (300) series. Reaction conditions are same as that in table 2.

strong acid sites, and the distance of acid centers etc) influencing the catalyst performance.

#### 4. Conclusion

The acidity of zeolite exerted important influence on the performance of STD catalyst. Under the condition of fixing the amount of methanol synthesis catalyst, an appropriate acidic amount was required to gain the best catalytic activity, less acidic amount would cause only part of methanol formed be dehydrated; while more acidic amount would be unfavorable for the activity of methanol synthesis catalyst, due to the interaction of  $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$  with zeolite, and, furthermore, the

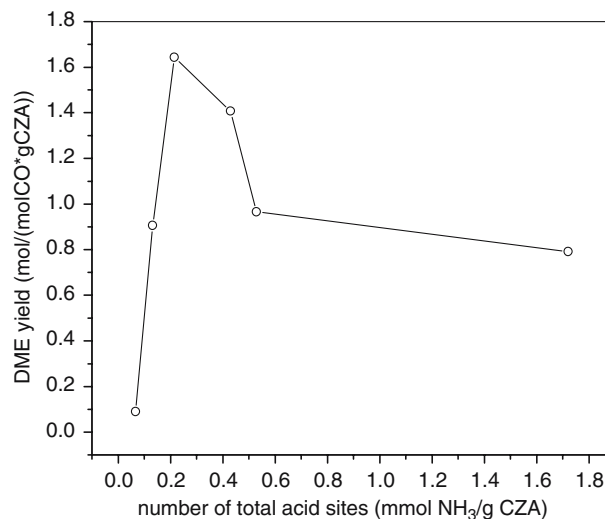


Figure 7. The correlation of total acidic amount with catalytic activity corresponding to 1 g CZA, the reaction conditions are same as that in table 2.

dehydration reaction of DME to hydrocarbons would be increased.

## References

- [1] T. Shikada, K. Fujimoto, M. Niyauchi and H. Tominaga, *Appl. Catal. A: General* 7 (1983) 361.
- [2] G. Cai, Z. Liu, R. Shi, C. He, L. Yang and C. Sun, *Appl. Catal. A: General* 125 (1995) 29.
- [3] J.B. Hansen and T. Oishi, *Petrotech.* 20 (1997) 823.
- [4] Q. Ge, Y. Huang and F. Qiu, *React. Kinet. Catal. Lett.* 63 (1998) 137.
- [5] K. Fujimoto, K. Asami, T. Shikada, H. Tominaga, *Chem. Lett.* (1984) 2051.
- [6] M. Jia, W. Li, H. Xu, S. Hou, C. Yu and Q. Ge, *Catal. Lett.* 84 (2002) 31.
- [7] W.K. Bell and C.D. Chang, US Patent 4423155 (1983).
- [8] J.L. Li, X.G. Zhang and T. Inui, *Appl. Catal. A: general* 147 (1996) 23.
- [9] G. Qi, X. Zheng, J.H. Fei and Z. Hou, *J. Mol. Catal. A: Chemical* 176 (2001) 195.
- [10] Y. Fu, T. Hong, J. Chen, A. Auroux and J. Shen, *Thermochimica Acta* 434 (2005) 22.
- [11] M.B. Sayed, R.A. Kydd and R.P. Cooney, *J. Catal.* 88 (1984) 137.
- [12] E.S. Priboczki, N. Kumar, T. Salmi, Z. Kovacs and D.Y. Murzin, *Catal. Lett.* 93 (2004) 101.
- [13] J.H. Kim, M.J. Park, S.J. Kim, O.S. Joo and K.D. Jung, *Appl. Catal. A:General* 264 (2004) 37.
- [14] F.S. Ramos, A.M.D. de Farias, L.E.P. Borges, J.L. Monterio, M.A. Fraga, E.F. Sousa-Aguiar and L.G. Appel, *Catal. Today* 101 (2005) 39.
- [15] D. Mao, W. Yang and J. Xia, *J. Catal.* 230 (2005) 140.
- [16] T. Takeguchi, K. Yanagisawa and T. Inui, *Appl. Catal. A: General* 192 (2000) 201.
- [17] Q. Ge, Y. Huang and F. Qiu, *Appl. Catal. A: General* 167 (1998) 23.
- [18] Z. Liu, J. Liao, J. Tan, D. Li and S. Huagong(China) 28 (1999) 236.