

Enhanced performance of methane dehydro-aromatization on Mo-based HZSM-5 zeolite pretreated by NH_4F

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Abstract

Enhanced performance of methane dehydro-aromatization reaction (MDA) were achieved on a Mo-based HZSM-5 zeolite catalyst in which HZSM-5 were pretreated by a proper amount of NH_4F (Mo/HZ(F)). The results of NH_3 -TPD and ^{27}Al MAS NMR demonstrated that the number of Brønsted acid sites decreased on the HZSM-5 zeolite and Mo/HZSM-5 catalyst after NH_4F treatment. TGA and TPO measurements showed that the Mo/HZ(F) catalysts were highly resistant to coke deposition, which resulted mainly from the elimination of the Brønsted acid sites after the pretreatment of the HZSM-5 zeolite with NH_4F .

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1. Introduction

Direct conversion of methane to useful and value-added industrial chemicals is a great challenge for the optimal utilization of natural gas resources. In 1993, Wang et al. reported that direct conversion of methane to aromatics and hydrogen could be realized on Mo/HZSM-5 catalysts in a flowing fixed bed reactor under non-oxidative conditions [1]. Since then, many research groups have paid great attention to the reaction of methane dehydro-aromatization (MDA). Efforts have been aimed to improve the catalytic performance of MDA over transition metal ion (TMI)-based zeolite catalysts, among which Mo-based catalysts were widely investigated. Several approaches, such as modifying the Mo/HZSM-5 catalysts with a second metal component (Mo–Ru/HZSM-5 and Mo–Fe/HZSM-5 etc.); evaluating other transition metals-based zeolite catalysts (W/HZSM-5 and Re/HZSM-5); developing other new zeo-

lites (Mo/HMCM-22 and Mo/HMCM-49, etc.) and transplanting of various methods to modify the acidity and pore structure of the zeolite (dealumination, silanation and alkali treatment), have been reported [2–6]. It is now well known that the Brønsted acid sites on the zeolites are a basic necessity for this reaction. However, the amounts and the distribution of the acid strength should be carefully controlled for obtaining an optimal MDA catalyst. Dealumination is a proper method for tuning the Brønsted acid sites of zeolite. Mo-based HZSM-5 and HMCM-22 in which HZSM-5 and/or HMCM-22 was pretreated by steam or by acid treatment have been reported to be more active and stable catalysts for the MDA reaction [4].

Modification of the zeolite acidity by F^- species has been known as a useful method. Treatment on the H-mordenite with aqueous HF will cause Al (under mild conditions) and Si (under more severe conditions) to be leached from the zeolite structure [7]. Kao and Chen have reported that the F^- species dissociated from $(\text{NH}_4)_2\text{SiF}_6$ (AHFS) could displace the hydroxide groups linked to silicon and aluminum of the H- β zeolite, and $\text{AlF}_x(\text{H}_2\text{O})_{6-x}$ were formed during the process [8]. Moreover, Van Mao et al. have

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reported that when a HZSM-5 zeolite was treated by an aqueous NH_4F solution with a low concentration, its acid sites and the acid strength were increased. The authors suggested that a kind of chemisorbed H^+F^- ion pair was formed on the zeolite surface and insertion of F atoms into the zeolite structure might happen [9]. However, no research work has been reported so far on the effect of HZSM-5 which was treated with NH_4F on the catalytic performance of MDA over Mo/HZSM-5 catalysts.

In this work, physico-chemical changes of HZSM-5 zeolites and corresponding molybdenum loaded samples after NH_4F treatment were characterized by using NH_3 -TPD and ^{27}Al MAS NMR techniques. The reaction performances of methane aromatization over Mo/HZSM-5 samples prepared with HZSM-5 pretreated by different amounts of NH_4F were evaluated in a flowing fixed bed reactor, and improved MDA activity and prolonged lifetime were observed for the Mo/HZSM-5 catalysts with HZSM-5 pretreated by a proper amount of NH_4F . The coked Mo/HZSM-5 samples with HZSM-5 pretreated by different amount of NH_4F were also characterized by the TGA and TPO techniques.

2. Experimental

2.1. Sample preparation

The HZSM-5 ($\text{Si}/\text{Al} = 25$) zeolite was supplied by Nankai University and denoted as HZ(P). It was treated with 1, 3.3 and 5.6 wt.% of NH_4F in aqueous solution, respectively. After drying at 393 K for 8 h, the samples were calcined at 623 K for 4 h and denoted as HZ(F1), HZ(F2) and HZ(F3), respectively. A series of Mo-based zeolite catalysts were prepared by the incipient wetness impregnation method with an ammonium heptamolybdate (AHM) solution to give a nominal Mo content of 6 wt.%. The samples were then dried at 393 K for 8 h and calcined at 773 K for 6 h. The catalysts thus prepared were denoted, hereafter, as Mo/HZ(P), Mo/HZ(F1), Mo/HZ(F2), and Mo/HZ(F3), respectively.

2.2. Catalytic evaluation

Reaction tests were carried out with a downflow fixed bed quartz reactor (8 mm i.d.) under atmosphere pressure. Mo/HZ catalysts (0.50 g, 20–40 mesh) were heated in a feed gas flow ($\text{CH}_4:\text{N}_2 = 9:1.25$ ml/min) from room temperature (r.t.) to 423 K, and then switched to a He flow till 973 K. Then feed gas was introduced again. The products were analyzed by an online gas chromatography (Varian cp-3800) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). By using N_2 as an internal standard (10% N_2) in the feed gas, the conversion of methane and the selectivity of the products, e.g., benzene, toluene, naphthalene and coke, were evaluated on the basis of carbon number balance, as suggested by Lunsford and his co-workers [10].

2.3. Catalyst characterization

NH_3 temperature programmed desorption (NH_3 -TPD) was carried out on a homemade setup equipped with a TCD detector. An amount of 0.10 g of the sample was charged, and then flushed with Ar (30 ml/min) at 873 K for 30 min, followed by cooling to 423 K. After the sample was saturated with NH_3 and the baseline of the integrator was stable, NH_3 -TPD was then promptly started from 423 K to 873 K at a heating rate of 10 K/min, and kept for 30 min at 873 K.

^{27}Al MAS NMR Spectra were obtained at 9.4 T on a Varian InfinityPlus 400 spectrometer. The sample was loaded in a 4 mm ZrO_2 rotor and spun at 10 KHz. The spectra were recorded at 104.3 MHz with a relaxation delay of 3 s and 400 scans. A 1% aqueous $\text{Al}(\text{H}_2\text{O})_6^{3+}$ solution was used as the reference of chemical shifts.

Cokes deposited on different Mo/HZSM-5 catalysts were analyzed by thermal gravity analysis (TGA) and temperature programmed oxidation (TPO) techniques. The TGA and TPO were carried out on a Perkin–Elmer TG S-II TG/DTA instrument and on an online quadruple mass spectrometer (Balzers, QMS 200), respectively, which were described elsewhere [11]. The TPO signal intensity of carbonaceous deposits was further correlated with the data measured by TGA.

3. Results and discussion

3.1. Reaction performance

The reaction performance of MDA over different Mo-based HZSM-5 catalysts prepared with the HZSM-5 zeolite without or with NH_4F pretreatment at 973 K are

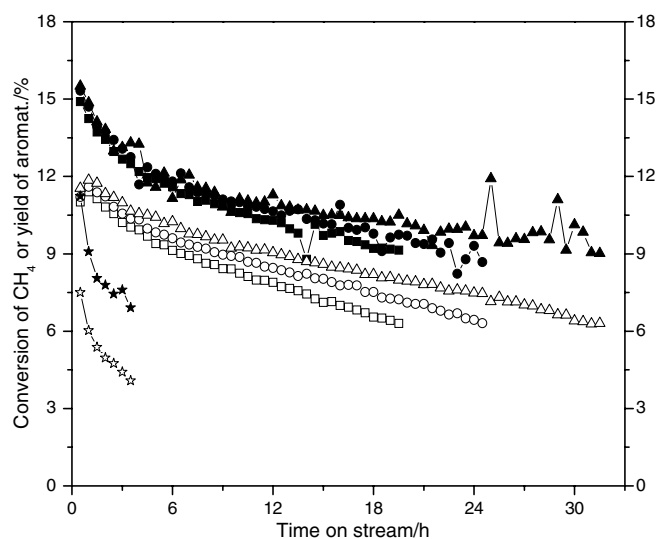


Fig. 1. Reaction performances over Mo/HZSM-5 catalysts in which HZSM-5 was pretreated with different amounts of NH_4F . ■, □ for Mo/HZ(P); □, ▲ for Mo/HZ(F1); ●, ○ for Mo/HZ(F2); and ★, □ for Mo/HZ(F3). Solid symbols: methane conversion; empty symbols: aromatics yield.

shown in Fig. 1. The best catalytic performance among the tested catalysts with improved activities and longer durations were obtained over Mo/HZ(F2) catalyst. On the Mo/HZ(P) catalysts, the aromatics yields were 11.4% and 7.0% at a methane conversion of 14.2% and 9.9% after running the reaction for 1 and 16 h, respectively. On the other hand, the aromatics yields are 11.9% and 8.5% at a methane conversion of 14.9% and 10.5% on the Mo/HZ(F2) catalysts. Moreover, it took about 20 h for the Mo/HZ(P) catalyst and about 32 h for the Mo/HZ(F2) catalyst to show a drop to the aromatics yield level of 6.0%. However, the aromatics yield fell from 6.1% at a methane conversion of 8.4% to 2.2% at a methane conversion 3.5% after running the reaction for 8 h on Mo/HZ(F3) catalyst.

3.2. NH_3 -TPD

NH_3 -TPD profiles of the HZSM-5 without or with NH_4F pretreatment are shown in Fig. 2a. The profile of the HZ(P) sample exhibits typical double-peak characteris-

tics of zeolite with the MFI-structure [12], and the corresponding peak temperatures are centered at ca. 549 and 750 K, respectively. Usually, the area of a specific peak is closely related to the amount of ammonia desorbed from the sample and can be taken as a quantitative measure of the amount of acid sites of the sample concerned [13]. All the NH_3 -TPD profiles of the HZ(F) samples were deconvoluted by the Gauss curve fitting method and the results are listed in Table 1. Peak I and II are assigned to the desorption peak of adsorbed ammonia on the weak acid site and/or to physically adsorbed ammonia. Peak III with a tem-

Table 1
Numerical results of NH_3 -TPD profiles by Gauss curve fitting method

Catalyst	Peak position/K			NH_3 adsorbed/ mmol g^{-1}		
	1	2	3	1	2	3
HZ(P)	549	–	750	0.82	–	1.21
HZ(F1)	545	603	752	0.62	0.13	1.20
HZ(F2)	539	593	727	0.26	0.12	0.79
HZ(F3)	540	600	730	0.39	0.30	0.32
Mo/HZ(P)	543	611	725	0.57	0.36	0.60
Mo/HZ(F2)	537	605	730	0.44	0.28	0.44

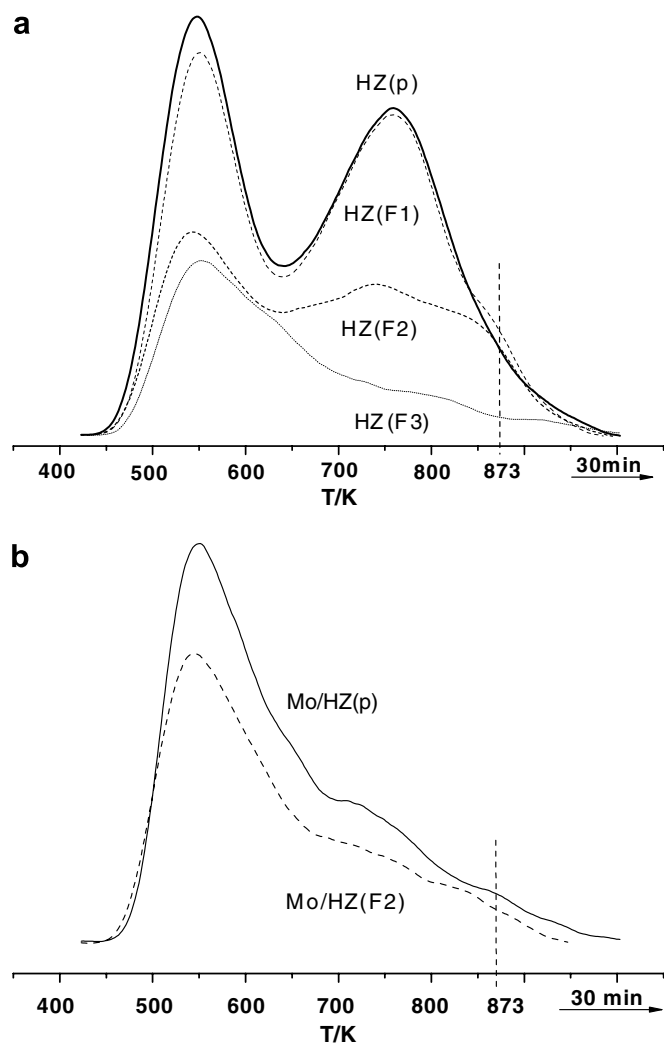


Fig. 2. NH_3 -TPD profiles of HZSM-5 samples pretreated with different amounts of NH_4F (a) and those after molybdenum supported (b).

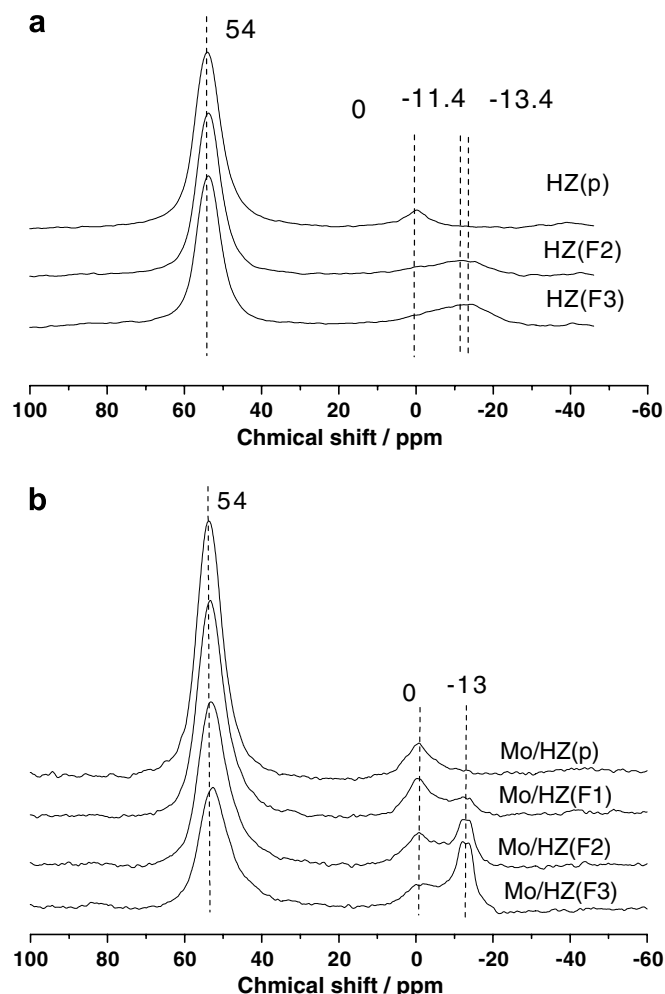


Fig. 3. ^{27}Al MAS NMR spectra of HZSM-5 samples pretreated with different amounts of NH_4F (a) and those after molybdenum supported (b).

perature ranging from 730 K to 750 K is attributed to strong Brönsted acid sites in nature, which are important for the MDA reaction [14]. By increasing the amount of NH_4F in the pretreatment process, the amount of ammonia desorbed (corresponding to peak III) from HZ(F1), HZ(F2) and HZ(F3) is ca. 99%, 65%, and 26% of the amount of ammonia desorbed from HZ(P).

NH_3 -TPD profiles of the Mo/HZ(P) and Mo/HZ(F2) are shown in Fig. 2b. The profiles were also deconvoluted by the Gauss curve fitting method and the corresponding numerical results are listed in Table 1. The amount of Brönsted acid sites falls from 1.21 mmol/gcat on the HZ(P) sample to 0.60 mmol/gcat on the Mo/HZ(P) sample when 6 wt.% molybdenum was loaded. These results clearly indicate that the Mo species interacted and replaced the Brönsted acid sites during the calcining procedure [15,16]. Similarly, the amount of Brönsted acid sites falls from 0.79 mmol/gcat on the HZ(F2) sample to 0.44 mmol/gcat on the Mo/HZ(F2) sample when 6 wt.% Mo was loaded.

3.3. ^{27}Al MAS NMR

^{27}Al MAS NMR profiles of the HZSM-5 samples are shown in Fig. 3a. The peak centering at $\delta = 54$ ppm is attributed to the four-coordinated framework Al, denoted as F_{Al} , from which the Brönsted acid sites arises; the small peak centering at $\delta = 0$ ppm is assigned to the six-coordinated extra-framework Al, denoted as E_{Al} . With increasing amount of NH_4F used for pretreatment, the intensity of the peak at $\delta = 54$ ppm decreases continuously, indicating the decrease in Brönsted acid sites of HZSM-5 samples with increasing amount of NH_4F , which is consistent with the NH_3 -TPD results. The variation of E_{Al} peaks is more complex. Comparing with the ^{27}Al MAS NMR profile of the HZ(P) sample, the intensity of the peak at $\delta = 0$ ppm decreases with increasing amount of NH_4F ; moreover, a new broad peak centering at around $\delta = -11.4$ ppm appears in the HZ(F2) and that at $\delta = -13.4$ ppm for the HZ(F3) sample. Chupas and Grey have reported that the resonance corresponding to six-coordinated Al species shifted to more negative values after the fluorination [17]. The authors suggested that there is an increase in the number of octahedral Al species in the form of oxyfluoride group, i.e., $\text{AlO}_{6-x}\text{F}_x$ ($0 < x < 1$). Similar shifts to more negative value were also reported for an H- β zeolite dealuminated by AHFS, which was deduced as an intermediate between those of AlO_6 and AlF_6 in local environments [8]. In this work, the broad peak is attributed to the overlapping of the signals of $\text{AlO}_{6-x}\text{F}_x$ with different x values, and it is also maybe associated with Al species which are affected by large quadrupole interaction. The results of ^{27}Al MAS NMR measurements on HZSM-5 before and after NH_4F treatment showed that F_{Al} is partly expelled under the influence of F^- , thus leading to the elimination of the Brönsted acid sites, and both the E_{Al} and the expelled F_{Al} can react with F^- species to form $\text{AlO}_{6-x}\text{F}_x$.

^{27}Al MAS NMR profiles of the Mo/HZSM-5 samples on HZSM-5 zeolite without or with NH_4F pretreatment are shown in Fig. 3b. After the Mo species was impregnated on the HZ(P), the intensity of the peak at $\delta = 54$ ppm decreased obviously and the intensity of the peak at $\delta = 0$ ppm increased, indicating that during the preparation of the Mo/HZSM-5 catalysts, the Mo species could extract some F_{Al} i.e., consume some Brönsted acid sites, accompanied with more E_{Al} produced, which is also accordance with NH_3 -TPD results. With an increase in the amount of the NH_4F used during the pretreatment of the HZSM-5, the decrease in the intensity of the peak at $\delta = 54$ ppm on all Mo/HZ(F) samples becomes more obvious, as compared with that on the Mo/HZ(P) sample, suggesting that NH_4F pretreatment can enhance the extraction effect of the Mo species on the F_{Al} . Moreover, the broad peak at $\delta = -11.4/-13.4$ ppm for the HZ(F) disappeared, and two new ones appeared at $\delta = 0$ ppm and $\delta = -13$ ppm, respectively. Here the signals at $\delta = -13$ ppm can be assigned to $\text{Al}_2(\text{MoO}_4)_3$ [18]. The sharp peak at ca. $\delta = -13$ ppm in Mo/HZ(F) implies that the $\text{AlO}_{6-x}\text{F}_x$ in the HZ(F) is also liable to react with the Mo species. The peak intensity at $\delta = -13$ ppm become stronger with the increasing in the amount of NH_4F used, and the peak split-

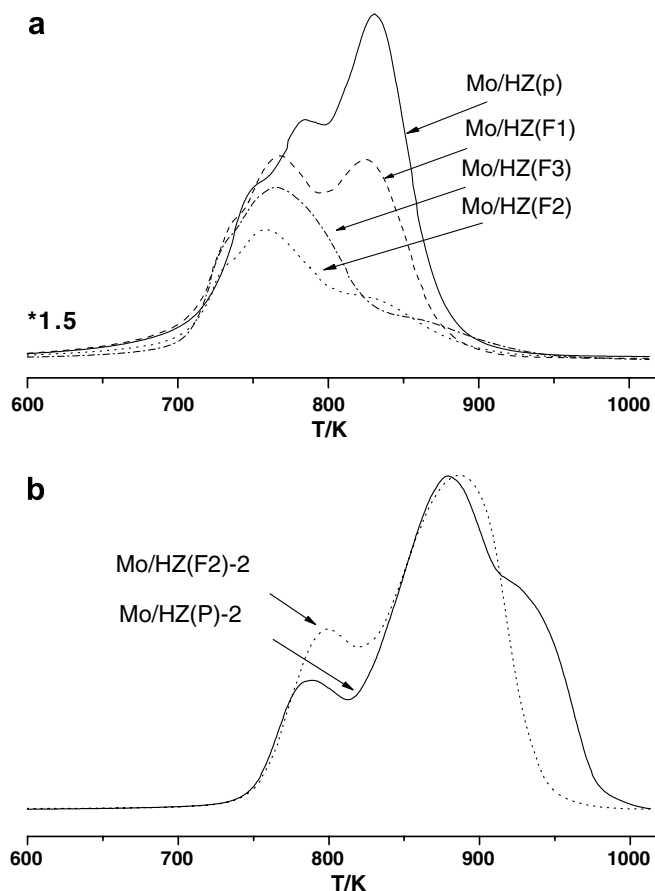


Fig. 4. TPO profiles of coked Mo/HZSM-5 pretreated with different amount of NH_4F after 12 h time on stream (a) and after aromatics yield decreased to 0.2% (b).

Table 2
Numerical results of TGA and TPO profiles by Gauss curve fitting method

Catalyst	TGA (mg/g)	TPO					
		T_1 (K)	C_1 (mg/g)	T_2 (K)	C_2 (mg/g)	T_3 (K)	C_3 (mg/g)
Mo/HZ(P) ^a	62.2	742	9.4	782	20.0	833	32.8
Mo/HZ(F1) ^a	45.9	737	9.2	768	16.9	827	19.7
Mo/HZ(F2) ^a	24.1	734	2.1	763	15.6	827	6.4
Mo/HZ(F3) ^a	26.5	737	2.6	773	20.1	867	3.8
Mo/HZ(p)-2 ^b	107.6	787	16.5	878	73.9	942	17.1
Mo/HZ(F2)-2 ^b	99.5	796	25.1	874	63.6	905	10.8

^a After 12 h time on stream.

^b After aromatics yield decreased to 0.2%.

ting even happened on the Mo/HZ(F3). After impregnation of the Mo species onto the HZ(F) zeolite, more $\text{Al}_2(\text{MoO}_4)_3$ was produced. Since $\text{Al}_2(\text{MoO}_4)_3$ is not the active species in the MDA reaction, the pretreatment by NH_4F will consumes part of the active Mo species for the MDA reaction on the Mo/HZ(F).

3.4. TGA and TPO measurements

TPO profiles of coked Mo/HZSM-5 pretreated with different amount of NH_4F after 12 h time on stream are shown in Fig. 4a, which were correlated with TGA results. The numerical results are listed in Table 2. Both Bao and Iglesia groups have reported TPO results on Mo/HZSM-5 and Mo/MCM-22 catalysts, and they attributed the first peak (530 K) to the carbidic carbon in the MoC_x , the second one (745 K) to carbonaceous species inside the channels and located near the Mo species, and the last one (820 K) to carbon deposits which were far away from the Mo species or on the Brønsted acid sites [14,16]. Ichikawa et al. attributed the high-temperature peak (>773 K) to irreversible or inert coke, whereas a kind of more reactive coke (lower than 673 K) was probably associated with Mo_2C [19]. In this work, the peaks centering around 735 K and 770 K in the TPO profiles are attributed to the carbonaceous deposits associated with the Mo species (C_M), and the peak centering around 835 K to cokes deposited on the Brønsted acid sites (C_H). The value of C_M is 29.4 mg/gcat for the Mo/HZ(P) catalysts, while it is 17.7 mg/gcat for the Mo/HZ(F2) and 22.7 mg/gcat for the Mo/HZ(F3). As demonstrated in the NH_3 -TPD results, the number of Brønsted acid sites decreased with the increasing of the NH_4F amount used on both of the HZ samples and the Mo/HZ catalysts. A consistent change can be found on the amount of coke deposited on the Brønsted acid sites, where the value of C_H is 32.8 mg/gcat on the Mo/HZ(P), 19.7 mg/gcat on the Mo/HZ(F1), 6.4 mg/gcat on the Mo/HZ(F2), and 3.8 mg/gcat (on Mo/HZ(F3)).

Mo/HZSM-5 catalysts without and with NH_4F pretreatment after aromatics yield decreased to 0.2%, denoted as Mo/HZSM-5(P)-2 and Mo/HZSM-5(F2)-2, were characterized by TGA–TPO techniques. The TPO profiles and corresponding numerical results are shown in Fig. 4b

and Table 2. Herein, the burning off peaks of coke around 790 K and 875 K are attributed to C_M and C_H , respectively. Their burning off temperatures all shift to higher values on Mo/HZ-2 s compared with Mo/HZ s, which can be induced by larger amount of coke and higher condensation degree of coke polymer for longer time on stream [20]. New peaks appear with temperature higher than 900 K on Mo/HZ-2 s and are assigned to the carbonaceous species with higher condensation degree deposit in channels of Mo/HZSM-5 (C_C). The value of C_M decrease from 25.1 mg/gcat (on Mo/HZ(F2)-2) to 16.5 mg/gcat (on Mo/HZ(P)-2), which maybe resulted from the longer reaction time on Mo/HZ(F2)-2 (60 h) than that on Mo/HZ(P)-2 (44 h), which is also supported by TPO results when comparing difference among Mo/HZ-2 s with that among Mo/HZ s. On the contrary, the value of C_H is higher on Mo/HZ(P)-2 (73.9 mg/gcat) than that on Mo/HZ(F2)-2 (63.6 mg/gcat), indicating that Mo/HZ(F2) shows stronger coke-resistance ability on Brønsted acid sites than Mo/HZ(P), again. On Mo/HZ(P)-2, the burning off temperature and the amount of C_C are all higher (943 K, 17.1 mg/gcat) than that (904 K, 10.8 mg/gcat) on Mo/HZ(F2)-2.

4. Conclusions

Improved performances of the MDA reaction were obtained on Mo/HZSM-5 catalysts in which the HZSM-5 was pretreated by proper amounts of NH_4F . After the treatment, the amount of Brønsted acid sites was reduced and this was the main reason for the enhanced activity and a prolonged lifetime of the catalyst. Mo/HZSM-5 catalysts with HZSM-5 pretreated by proper amount of NH_4F showed good resistance to coking, which was resulted mainly from depressing of the Brønsted acid sites.

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References

- [1] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang, Y. Xu, *Catal. Lett.* 21 (1993) 5.
- [2] Y. Xu, L. Lin, *Appl. Catal. A* 188 (1999) 53.
- [3] Y. Shu, M. Ichikawa, *Catal. Today* 71 (2001) 55.
- [4] Y. Xu, X. Bao, L. Lin, *J. Catal.* 216 (2003) 386.
- [5] L. Su, L. Liu, J. Zhuang, H. Wang, Y. Li, W. Shen, Y. Xu, X. Bao, *Catal. Lett.* 91 (2003) 155.
- [6] H. Wang, L. Su, J. Zhuang, D. Tan, Y. Xu, X. Bao, *J. Phys. Chem. B* 107 (2003) 12964.
- [7] A. Ghosh, R. Kydd, *J. Catal.* 103 (1987) 399.
- [8] H. Kao, Y. Chen, *J. Phys. Chem. B* 107 (2003) 3367.
- [9] R. Le Van Mao, T.S. Le, M. Fairbairn, A. Muntasar, S. Xiao, G. Denes, *Appl. Catal. A* 185 (1999) 41.
- [10] D. Wang, J. Lunsford, M. Rosynek, *Top. Catal.* 3 (1996) 289.
- [11] Y. Li, T. Wu, W. Shen, X. Bao, Y. Xu, *Catal. Lett.* 97 (2005) 185.
- [12] C. Hidago, H. Itoh, T. Hattori, M. Niwa, Y. Murakami, *J. Catal.* 85 (1984) 362.
- [13] N. Meshram, S. Hedge, S. Kukarni, *Zeolites* 6 (1986) 434.
- [14] D. Ma, Y. Lu, L. Su, Z. Xu, Z. Tian, Y. Xu, L. Lin, X. Bao, *J. Phys. Chem. B* 106 (2002) 8524.
- [15] Y. Xu, Y. Shu, S. Liu, J. Huang, X. Guo, *Catal. Lett.* 35 (1999) 233.
- [16] W. Ding, S. Li, G. Meitzner, E. Iglesia, *J. Phys. Chem. B* 105 (2001) 506.
- [17] P.J. Chupas, C.P. Grey, *J. Catal.* 224 (2004) 69.
- [18] W. Zhang, D. Ma, X. Han, X. Liu, X. Bao, X. Guo, X. Wang, *J. Catal.* 188 (1999) 393.
- [19] R. Onishi, S. Liu, Q. Dong, L. Wang, M. Ichikawa, *J. Catal.* 182 (1999) 92.
- [20] C. Querini, S. Fung, *Appl. Catal. A* 117 (1994) 53.