Catalysis Today 149 (2010) 207–211

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

An improved dealumination method for adjusting acidity of HZSM-5

Lijun Jin, Haoquan Hu *, Shengwei Zhu, Bin Ma

State Key Laboratory of Fine Chemicals, Institute of Coal Chemical Engineering, School of Chemical Engineering, Dalian University of Technology, 129 Street, Dalian 116012, People's Republic of China

ARTICLE INFO

Article history:
Available online 18 August 2009

Keywords:
Dealumination
HZSM-5
Acidity
HY
Hβ

ABSTRACT

An improved dealumination method for adjusting the acidity of HZSM-5 was developed by utilizing the self-adsorbed water in HZSM-5. The parent and treated HZSM-5 were characterized by XRD, FT-IR, ^{27}Al MAS NMR, N_2 adsorption, XRF and NH_3-TPD. The results showed that HZSM-5 can be dealuminated when treated at above 400 °C. About 80% acidic amount was removed from parent HZSM-5 with 8% adsorbed water and more Lewis acid sites were produced after treated at 500 °C. It is thought that the dealumination was mainly caused by its self-adsorbed water. The comparisons of the acidity in dealuminated HZSM-5 by traditionally steaming and improved methods indicated that the latter was more effective in decreasing the acidity and weakening acid strength, and more environmentally benign and timesaving. The method is also applicable to adjust acidity of other zeolites, such as HY, Hβ.

1. Introduction

Different catalytic reactions usually require catalysts with different acidic amount and strength. For example, weak acidic strength of HZSM-5 is preferable for synthesis of 2,6-dimethylnaphthalene, a preferred intermediate for high performance polymeric materials, by alkylation of 2-methylnaphthalene with methanol [1]. As known, the acid properties and catalytic activity of zeolite are closely related to the framework Si/Al ratio [2]. It is, therefore, of great importance to adjust Si/Al ratio by either *in situ* synthesis or post-treatment dealumination methods. However, some zeolites such as faujasite cannot be directly synthesized with a Si/Al ratio substantially higher than 2.5, at least not in economically reasonable crystallization times. The proposed dealumination methods by post-synthesis modification include $SiCl_4$ treatment, reaction with chelating agents like EDTA [3], $(NH_4)_2SiF_6$, leaching with HCl [4–6], steaming [7] and calcination [8]. Dealumination by steaming is the most common technique used to prepare industrially important catalysts of high activity, selectivity and stability [4]. Maijanen et al. [9] reported that the dealumination of ZSM-5 was a function of steam pressure and treatment time, and that the number of Brönsted acid sites decreased progressively as treatment time increased. Campbell et al. [10] studied hydrothermal treatment of HZSM-5 by changing treatment temperature, time and steam pressure and found that the zeolite with low aluminum content was more resistant to dealumination.

In the traditionally hydrothermal dealumination, steam is necessarily introduced into the system. To control the degree of dealumination, more attention has usually to be paid to changing steam pressure, treatment temperature and time. Therefore, the method is complicated and time-consuming. To overcome these drawbacks, in this contribution, we provide an improved dealumination method to remove the framework Al (FAl) by making full use of self-adsorbed water in HZSM-5 without other pretreatment, such as intentional addition or removal of water in the zeolite. Dealuminated HZSM-5 was characterized by X-ray diffraction (XRD), FT-IR, X-ray fluorescence (XRF), ^{27}Al MAS NMR, N_2 adsorption/desorption and temperature programmed desorption of NH_3 (NH_3-TPD) and compared with conventional steaming dealuminated sample.

2. Experimental

2.1. Dealumination of HZSM-5

HZSM-5 with a Si/Al ratio of 19 was purchased from Catalyst Plant of Nankai University in China. Different from traditional steaming dealumination method, the improved one, named as "dry steaming dealumination" (denoted as DSD), was performed by making full use of self-adsorbed water which is 8.1 wt.% in the parent HZSM-5. Typically, about 2.0 g pelletized HZSM-5 with a size of 20–40 mesh was placed in the middle of a stainless-steel reactor of 10 mm i.d. During the treatment process, the HZSM-5 sample was first heated from 25 to 400 °C with a heating rate of

---

* Corresponding author. Tel.: +86 411 39893966; fax: +86 411 39893966.
E-mail address: hhu@chem.dlut.edu.cn (H. Hu).

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.07.088

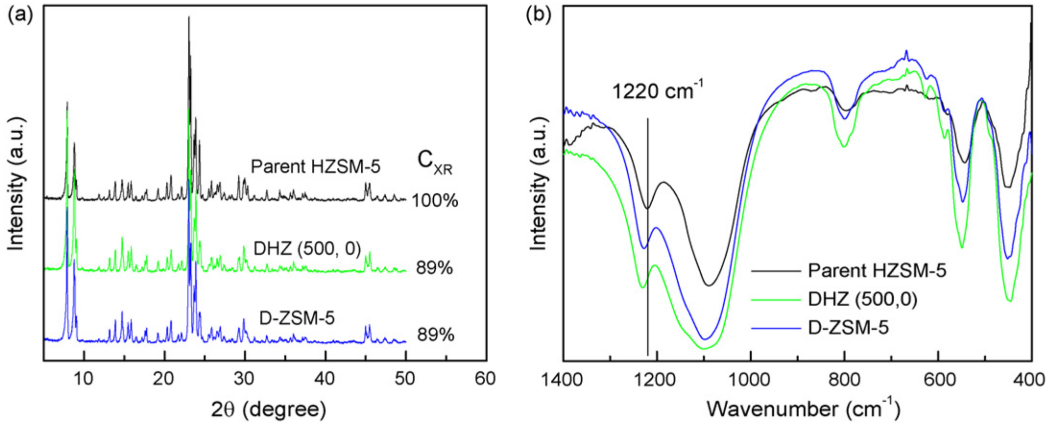

Fig. 1. XRD patterns (a) and FT-IR spectra (b) of parent HZSM-5, DHZ (500, 0) and D-ZSM-5 samples.

4 °C/min in N_2 flow of y ml/min at atmospheric pressure, then heated to x °C and kept for 2 h in the closed reactor, and finally cooled down to room temperature. The resultant HZSM-5 is abbreviated as DHZ (x, y). As to DHZ (200, 0) sample, HZSM-5 was first heated from 25 to 200 °C instead of 400 °C and kept at 200 °C for 2 h without N_2. For comparison, dealuminated HZSM-5 was prepared by traditionally hydrothermal method at 500 °C for 4 h in flowing 100% steam with a WHSV of 1 h^{-1} under atmospheric pressure, which is denoted as D-ZSM-5.

2.2. *Characterization*

XRD patterns of samples were recorded on a DMAX2400 diffractor with CuKα radiation. The relative crystallinity (C_{XR}) was determined by comparing the (0 5 1) peak intensities of modified samples with that of parent HZSM-5 which was considered to be 100% crystalline. FT-IR spectra of the structure band region (1400–400 cm^{-1}) were investigated on a FT-IR 460plus instrument using the KBr-pellet technique. For IR characterization of adsorbed pyridine (Py) molecules, spectra were recorded on an EQUINOX55 spectrometer at the desorption temperatures between 150 and 450 °C. The framework Si/Al ratio was determined by XRF spectroscopy on a SRS3400X instrument after the sample was washed with 1 M HCl at 90 °C for 3 h to remove the extra-framework aluminum. Specific surface area and pore volume were determined from N_2 adsorption/desorption isotherms at −196 °C on a Quantachrome AUTOSORB-1 adsorption analyzer. The samples were outgassed for 4 h at 300 °C prior to adsorption. ^{27}Al MAS NMR experiments were run on a Varian unity NOVA 300 MHz spectrometer. The resonance frequency was 78.157 MHz, and a spectral width of 54,682 Hz and an acquisition time of 0.02 s were used. The amount, strength and distribution of the acid sites were examined by NH_3-TPD on a conventional apparatus with a thermal conductivity detector. About 0.20 g sample was saturated with NH_3 at 120 °C, then flushed with helium to remove the physically adsorbed NH_3, finally the desorption of NH_3 was carried out from 100 to 600 °C at a heating rate of 10 °C/min in helium flow. The water content in the zeolite was measured by using thermogravimetry at 120 °C for 30 min in 60 ml/min N_2 flow on a TGA/SDTA851^e instrument.

3. Results and discussion

3.1. *XRD of dealuminated HZSM-5*

Fig. 1(a) gives the XRD patterns of parent and dealuminated HZSM-5 samples by DSD and steaming methods. Clearly, the DHZ (500, 0) exhibits similar XRD patterns as parent HZSM-5 and D-ZSM-5 samples, except for slight difference in the intensities of the peaks at 2θ being 7.90° and 8.82°, indicating no change in the basic structure of ZSM-5. Almost the same crystallinity (about 89%) was obtained when HZSM-5 treated at the same temperature of 500 °C as the steaming method. The unit cell parameters (a, b, c) and unit cell volume of parent HZSM-5 and DHZ (500, 0) are listed in Table 1. The unit cell parameters of DHZ (500, 0) decreased and the unit cell volume contracted, which was in agreement with the results by Hong and Fripiat [8] who also observed the changes in dealuminated ZSM-5 due to the extraction of the FAl by calcination.

3.2. *FT-IR analysis*

FT-IR spectra of dealuminated HZSM-5 by steaming and DSD methods are shown in Fig. 1(b). In the infrared skeletal vibration region of 1400–400 cm^{-1}, the existence of absorption bands around 542 and 450 cm^{-1} means that the dealuminated samples still keep the basic crystal structure of ZSM-5. When parent HZSM-5 was treated at 500 °C without N_2 flow, DHZ (500, 0) sample, the asymmetric stretching vibration frequencies of the Si–O–T linkages at 1220 and 1089 cm^{-1} shifted to higher wavenumbers. Szostak [11] ascribed it to lower mass of aluminum than that of silicon, i.e., the framework Si/Al ratio of HZSM-5 increased after

Table 1
Physicochemical properties of parent HZSM-5 and DHZ (500, 0).

Sample	Si/Al[a]	Unit cell parameter (Å)			V_{uc}[b] (Å^3)	S_{BET} (m^2/g)	V_{total}[c] (cm^3/g)	B/L[d]
		a	*b*	*c*				
Parent HZSM-5	19	20.05	19.93	13.44	5368	403	0.178	5.1
DHZ (500, 0)	42	20.09	19.90	13.30	5317	336	0.178	2.1

[a] Framework Si/Al ratio.
[b] Unit cell volume.
[c] Pore volume of HZSM-5.
[d] Ratio of Brönsted to Lewis acid sites.

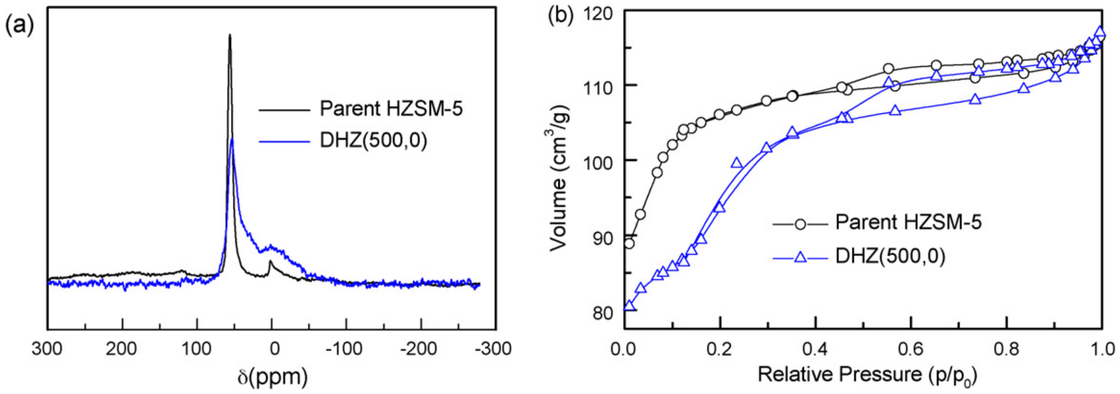

Fig. 2. ^{27}Al MAS NMR spectra (a) and nitrogen adsorption/desorption curves (b) of parent HZSM-5 and DHZ (500, 0) samples.

treatment, which was in agreement with the results by XRF analysis, shown in Table 1. The framework Si/Al ratio increased from 19 for parent HZSM-5 to 42 for DHZ (500, 0).

3.3. ^{27}Al MAS NMR spectra

^{27}Al MAS NMR spectra are usually used to determine the extra-framework Al (EFAl) or FAl contents of the zeolite as well as the coordination state of the EFAl species [12,13]. The ^{27}Al MAS NMR spectra of parent HZSM-5 and DHZ (500, 0) samples are illustrated in Fig. 2(a). Parent HZSM-5 shows a strong and narrow peak at about 56 ppm due to tetrahedrally coordinated FAl and a weak and narrow peak at about 0 ppm attributed to octahedrally coordinated EFAl. When HZSM-5 was treated at 500 °C by the DSD method, the intensity of tetrahedral ^{27}Al NMR signal decreased and the peak broadened. The chemical shift of this signal also reduced by about 2 ppm. However, the signal assigned to EFAl increased and became broad. All the changes suggest that more EFAl species were produced due to dealumination of zeolite framework when HZSM-5 was treated by the DSD method.

3.4. N_2 adsorption

The adsorption isotherms of parent HZSM-5 and DHZ (500, 0) samples are shown in Fig. 2(b) and the total surface area and pore volume are listed in Table 1. It is clear that the total specific surface area decreases and that the isotherms of DHZ (500, 0) exhibits a broader step in the adsorption branch and a more pronounced hysteresis loop between 0.1 and 0.4 of p/p^0 than parent HZSM-5. Triantafillidis et al. [14] also found the existence of hysteresis loop between 0.1 and 0.4 of p/p^0 in steaming dealuminated HZSM-5 and ascribed it to lower FAl content.

3.5. NH_3-TPD and Py-IR analysis

The acid properties of zeolite are known to be related to the Al content in the framework. Fig. 3(a) compares the changes in acid properties of parent and dealuminated HZSM-5. There are two ammonia desorption peaks on the NH_3-TPD curve of parent HZSM-5. The one, at about 230 °C, corresponds to weak acid sites, and another, at about 430 °C, corresponds to strong acid sites. It can be seen that the acidic amount, strength and temperature for peak II did not change markedly when HZSM-5 was treated at 400 °C or below. However, when treated at above 400 °C, the acidic amount gradually decreases and the acidic strength weakens with increasing the treatment temperature. For example, the temperatures corresponding to peaks I and II of DHZ (500, 0) decrease from 231 and 431 °C of parent HZSM-5 to 220 and 370 °C, respectively. About 80% acid sites were removed. From the Py-IR analyses shown in Fig. 3(b), DHZ (500, 0) has relatively less Brönsted acid sites, but more weak Lewis acid sites than parent HZSM-5. The ratio of Brönsted to Lewis acid sites decreases from 5.1 of parent HZSM-5 to 2.1 of DHZ (500, 0).

Based on the above mentioned results of XRD, FT-IR, Si/Al ratio, ^{27}Al MAS NMR and NH_3-TPD, it can be concluded that dealumination of parent HZSM-5 occurs during the DSD process. Hong and Fripiat [8] studied the dealumination of HZSM-5 by calcination method and found little change in acidity when

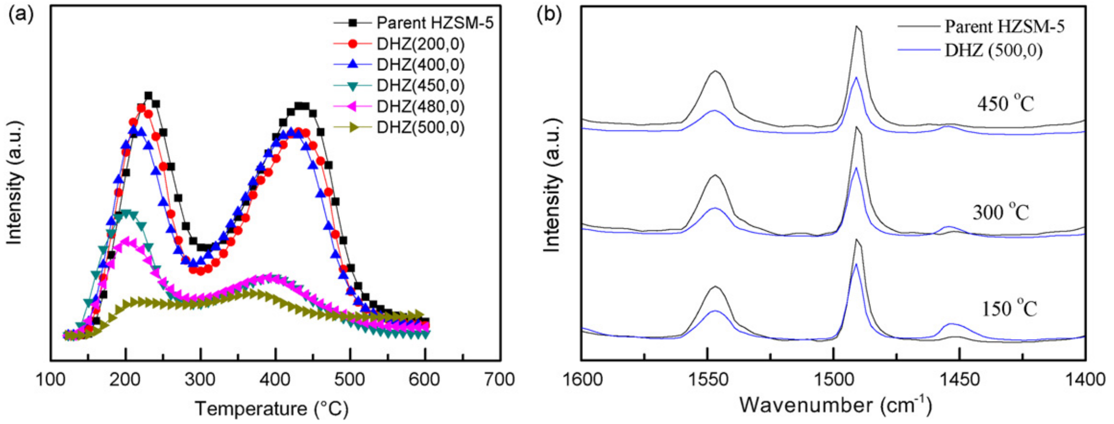

Fig. 3. NH_3-TPD profiles of dealuminated HZSM-5 by DSD method (a) and Py-IR spectra of parent HZSM-5 and DHZ (500, 0) (b).

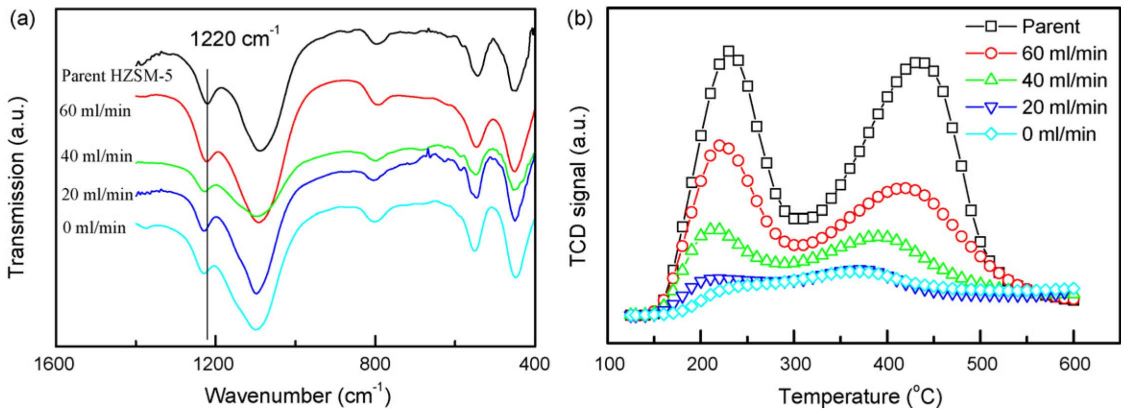

Fig. 4. Effect of N_2 flow rate (y, ml/min) during heating from 25 to 400 °C on FT-IR (a) and NH_3-TPD (b) spectra of DHZ (500, y) sample.

HZSM-5 was treated at 500 °C. Moreover, HZSM-5 is usually obtained by calcination of NH_4^+-ZSM-5 at 500 °C. Therefore, it can be inferred that the dealumination of HZSM-5 in our experiment was not caused by dry calcination. To explore the causes of dealumination by DSD, we examined the effect of adsorbed water in the zeolite. In the experiments, the water amount in zeolite was adjusted by increasing the flow rate of N_2 during heating up from 25 to 400 °C, i.e., less water content was obtained at higher N_2 flow rate. Because the IR absorption band around 1220 cm^{-1} is sensitive to the framework Si/Al ratio of ZSM-5, its shift was chosen to judge the variety of Si/Al ratio [15]. Fig. 4(a) shows that IR absorption band at 1220 cm^{-1} progressively shifted towards higher wavenumber with decreasing N_2 flow rate, suggesting that more FAl was removed to form EFAl. Moreover, the amount and strength of acid sites also changed with the flow rate, shown in Fig. 4(b). The amount of acid sites increases with the decrease of the adsorbed water content, i.e., increase of N_2 flow rate. When parent HZSM-5 was treated without removal of adsorbed water at 500 °C, about 80% acidity in parent HZSM-5 was removed. This means that dealumination of HZSM-5 is mainly caused by inherently adsorbed water. As to the dealumination mechanism, it is thought to be similar to that of the traditional steaming dealumination [7,16], i.e., siloxane bonds between the silicon and aluminum atoms are first hydrolyzed, and then the tetrahedral aluminum atoms are transformed into octahedrally coordinated ones. Therefore, when HZSM-5 contains high content of water or is treated at high temperature, the hydrolysis of siloxane bonds is accelerated to produce more EFAl, leading to the decrease in acidity.

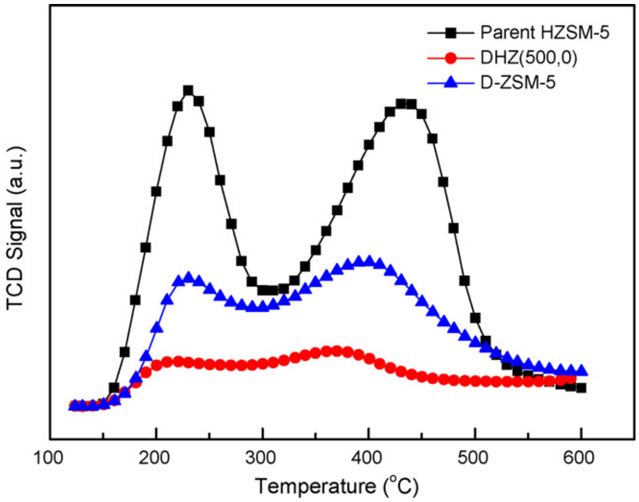

Fig. 5. NH_3-TPD spectra of parent HZSM-5, DHZ (500, 0) and D-ZSM-5 samples.

3.6. Comparison of acidic properties in dealuminated HZSM-5 by DSD and steaming methods

The effect of dealumination methods, by traditional steaming or DSD, on the acidity of HZSM-5 was compared and the results are shown in Fig. 5. Clearly, both methods can decrease the acidic amount and weaken the strength of acid sites. However, the DSD method is more effective than the traditional one in decreasing the

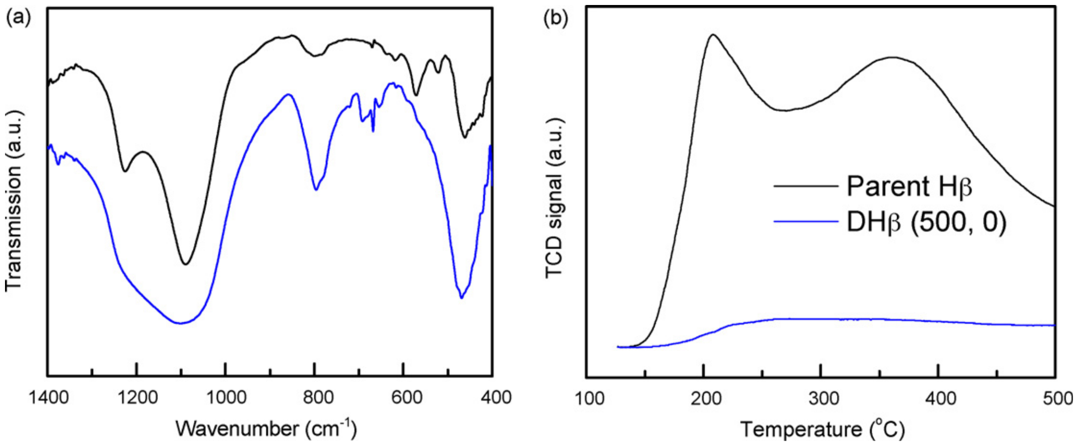

Fig. 6. FT-IR (a) and NH_3-TPD (b) spectra of parent Hβ and DHβ (500, 0).

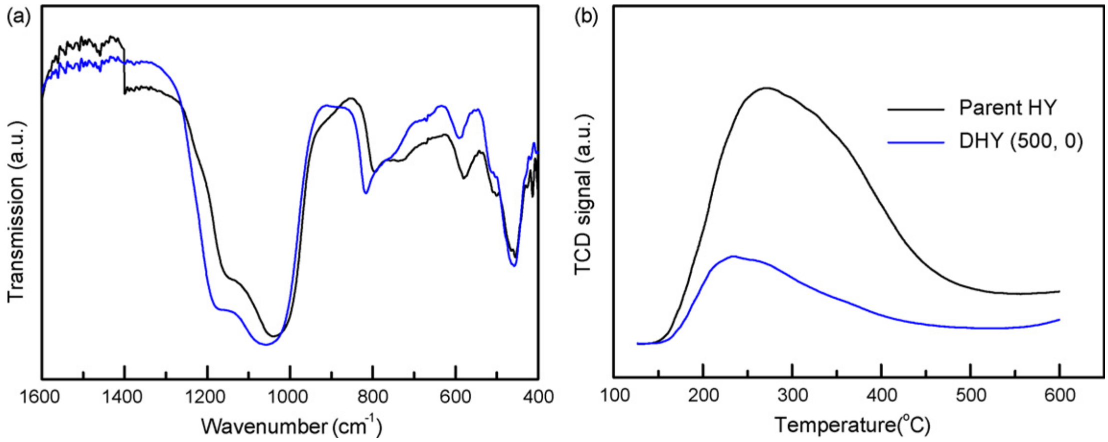

Fig. 7. FT-IR (a) and NH_3-TPD (b) spectra of parent HY and DHY (500, 0).

acidic amount and weakening the strength of acid sites at the same treatment temperature of 500 °C. Moreover, only 2 h treatment time is sufficient in DSD process rather than 4 h in traditional method.

Different from traditional steaming dealumination method in which steam is purposely introduced into the system and more attention is paid to the control of steam pressure, treatment temperature and time, in the proposed DSD method, the dealumination process can be accomplished at a certain temperature by making full use of self-adsorbed water in zeolite, without using other pretreatments like addition or removal of water. The dealumination degree can be conveniently adjusted by changing the treatment temperature and/or the amount of adsorbed water in HZSM-5 through changing N_2 flow rate during heating up to 400 °C. So the DSD method is very simple, convenient, efficient and controllable. Because of moderate temperature and no additional steam, the DSD method can be used to change the acidity of other zeolites, especially those with poor hydrothermal stability.

3.7. Dealumination of HY and Hβ by DSD method

To testify that the developed DSD method is also applicable to other zeolites, Hβ and HY from Catalyst Plant of Dalian University of Technology were chosen and treated at the same conditions as DHZ (500, 0). The resultant samples are named as DHβ (500, 0) and DHY (500, 0), respectively. Figs. 6 and 7 show the FT-IR and NH_3-TPD spectra of parent and modified Hβ and HY by DSD method, respectively. Compared with parent Hβ, the wavenumber of asymmetric vibration of T–O–T band at 1089 cm^{-1} of DHβ (500, 0) increases, see Fig. 6(a), indicating the framework dealumination, which is accordant with the result by Marques et al. [17]. The strength of acid sites also obviously weakens and the acidic amount decreases, see Fig. 6(b).

Fig. 7 shows the FT-IR and NH_3-TPD spectra of parent and modified HY by DSD. It can be seen that the absorption band attributed to asymmetric vibration of T–O–T band increases from 1029 to 1056 cm^{-1}, and the acidic strength obviously weakens. The peak temperature decreases from 271 °C for parent HY to 234 °C for DHY (500, 0). The acidic amount decreases remarkably. When the adsorbed water content in HY is 16.3 wt.%, about 70% acidity is removed. All the results suggest that the proposed DSD method is a useful and effective way to the dealumination of H-form zeolite.

4. Conclusion

In summary, the developed DSD method is an effective approach for dealumination of H-form zeolite by making use of inherently adsorbed water. About 80% acidity was removed from parent HZSM-5 with 8% adsorbed water and more Lewis acid sites were produced. Compared with the traditional steaming dealumination, the DSD method is more convenient, effective and timesaving. It is also applicable for other zeolites with poor hydrothermal stability.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (No. 20276011, 20376012) and Youth Teacher Training Foundation of Dalian University of Technology (No. 893240). Thank for Dr. Yanbin Wang providing the characterizations in ^{27}Al MAS NMR analysis.

References

[1] L.J. Jin, Y.M. Fang, H.Q. Hu, Catal. Commun. 7 (2006) 255.
[2] H.K. Beyer, Mol. Sieves 3 (2002) 204.
[3] P.J. Kooyman, P. van der Waal, H. van Bekkum, Zeolites 18 (1997) 50.
[4] S. Kumar, A.K. Sinha, S.G. Hegde, S. Sivasanker, J. Mol. Catal. A 154 (2000) 115.
[5] L.J. Jin, H.Q. Hu, X.Y. Wang, C. Liu, Ind. Eng. Chem. Res. 45 (2006) 3531.
[6] S. Han, D.S. Shihabi, C.D. Chang, J. Catal. 196 (2000) 375.
[7] T. Masuda, Y. Fujikata, S.R. Mukai, K. Hashimoto, Appl. Catal. A 172 (1998) 73.
[8] Y. Hong, J.J. Fripiat, Micropor. Mater. 4 (1995) 323.
[9] A. Maijanen, E.G. Derouane, J.B. Nagy, Appl. Surf. Sci. 75 (1994) 204.
[10] S.M. Campbell, D.M. Bibby, J.M. Coddington, R.F. Howe, R.H. Meinhold, J. Catal. 161 (1996) 338.
[11] R. Szostak, Principles of synthesis and identification, in: Molecular Sieves, Van Nostrand Rcinhold, New York, 1989, p. 17.
[12] E. Bourgeat-Lami, P. Massiani, F. Di Renzo, P. Esipiau, F. Fajula, Appl. Catal. A 72 (1991) 139.
[13] C.S. Triantafillidis, A.G. Vlessidis, N.P. Evmiridis, Ind. Eng. Chem. Res. 39 (2000) 307.
[14] C.S. Triantafillidis, A.G. Vlessidis, L. Nalbandian, N.P. Evmiridis, Micropor. Mesopor. Mater. 47 (2001) 369.
[15] Q. Xin, C.H. Liang, Petrochem. Technol. 30 (2001) 160.
[16] T. Sano, H. Ikeya, T. Kasuno, Z.B. Wang, Y. Kawakami, K. Soga, Zeolites 19 (1997) 80.
[17] J.P. Marques, I. Gener, P. Ayrault, J.C. Bordado, J.M. Lopes, F. Ramôa Ribeiro, M. Guisnet, Micropor. Mesopor. Mater. 60 (2003) 251.