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Solid-state NMR study on dealumination mechanism of H-MOR zeolite by high-temperature hydrothermal treatment



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ABSTRACT

The acidity of zeolites which plays an important role in various catalytic reactions is closely related to framework aluminum. After dealumination, not only the Si/Al ratio of zeolites increases, but also new aluminum species are generated. Furthermore, the pore structure and catalytic performance of zeolites are affected. High-temperature hydrothermal treatment, as a frequently-used method of dealumination, is widely concerned. However, the dealumination mechanism of zeolite during the hydrothermal treatment is not clear. In this work, the existence of different Al species in H-MOR during the process of high-temperature hydrothermal treatment was confirmed by ²⁷Al MQ MAS NMR. It was found that the second tetrahedrally coordinated framework aluminum (Al(IV)-2) species is the precursor of amorphous non-framework aluminum transformed from framework aluminum of H-MOR during high-temperature hydrothermal treatment. Besides, the ¹H-¹H DQ-SQ NMR was used to study spatial proximity between different hydroxyl species. Finally, the dealumination process of H-MOR zeolite is revealed: Al(IV)-1 species firstly transformed into Al(IV)-2 species, and then evolved into pentahedrally coordinated aluminum (Al(VI)) species.

1. Introduction

Zeolites, important industrial catalysts, are widely used in adsorption, separation, ion exchange and especially heterogeneous catalysis [1–5]. The hydrothermal stability of zeolite is an important factor restricting its industrial application due to many catalytic reactions are carried out under high temperature, high pressure and steam atmosphere. Hydrothermal treatment can cause irreversible damage to the framework of zeolites, such as framework collapse, desilication and dealumination [6–10]. Dealumination is the main factor for the loss of stability of zeolite under harsh heat and steam conditions due to Brönsted acid sites attract water molecules to tetrahedrally coordinated Al, promoting dealumination [11].

MOR zeolite has four nonequivalent tetrahedral T sites and the topology structure is characterized by parallel twelve membered-rings (12-MR, 6.5×7 Å) and eight membered-rings (8-MR, 2.6×5.7 Å) direct channels along the 001 direction which are connected by 8-MR side-pockets (SP, 3.4×4.8 Å) along the 010 direction [12]. In the

process of dealumination, the quantity and coordination state of Al species may change greatly although the topological structure of MOR zeolite remains unchanged. Studying dealumination mechanism at molecular scale not only has a profound understanding of the stability of framework Al, but also provides theoretical guidance for the preparation of highly stable zeolites. Abundant researches about the macro effect that dealumination of mordenites have on their structure, acidic properties and catalytic behaviours have been reported [13–18]. However, there are few studies on the mechanism of dealumination of mordenites in microscopic scale.

There are four kinds of framework Al sites in MOR zeolites. Among them, T1, T2 and T4 Al sites locate in 12-MR channels and T3 Al sites locate in 8-MR side pocket. Moreover, these sites can also be divided into 4-membered ring sites (T3 and T4) and 5-membered ring sites (T1 and T2). According to the literature, mordenite dealumination was performed to preferentially remove Al in 4-membered rings via a suggested coupled removal of (T3+T4) pairs. For example, Bodart [19] et al. studied aluminum siting in mordenite and dealumination mechanism by

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MAS NMR. It is demonstrated that aluminum atoms preferentially occupy tetrahedral positions in the four-membered rings of the mordenite. And a mechanism of dealumination that the aluminum atoms were removed two by two from the four-membered rings was inferred. Van Geem [20] et al. found that Al(IV) is randomly distributed over 4and 5-rings in the starting small-port mordenite but dealumination only removes framework Al from the 4-rings by IR and ²⁷Al NMR. For dealuminated H-MOR (Si/Al = 40), the temperature dependence of the 1 H spin-lattice relaxation time, t1, for adsorbed methane indicates that dealumination leads to an enlargement of the pore sizes of both the main channel and side-pocket and these effects are more pronounced in the side-pockets than in the main channels [21]. Thus, it can be concluded that T1 and T2 framework Al sites in 12-MR are more stable than T4 Al sites in 12-MR and T3 Al sites in 8-MR side pocket. Furthermore, T3 sites in 8-MR side pocket and T4 sites in 12-MR are usually preferentially removed in pairs in the process of dealumination.

Solid-state nuclear magnetic resonance (NMR) has unique advantages in the identification of Al species in the dealumination process and the research of dealumination mechanism [19,22,23]. Different coordination states of Al species can be identified by ²⁷Al MAS NMR and ²⁷Al MQ MAS NMR can further improve the resolution of ²⁷Al MAS NMR [24-26]. For example, Chen [27,28] et al. found the second tetrahedrally coordinated Al (Al(IV)-2), crosslinked tetrahedrally coordinated framework Al, in hydrothermally treated ZSM-5 by ²⁷Al MQ MAS NMR and ²⁷Al triple-quantum MAS NMR. Recently, Al(IV)-2 was also found in water-treated H-SSZ-13 by Fan [29] et al. via ²⁷Al MQ MAS NMR. $^{1}H^{-1}H$ homonuclear double-quantum (DQ) Moreover, and single-quantum (SQ) correlation techniques have been widely applied to probe the proton-proton proximities of various hydroxyl groups in zeolites. For example, Zheng [30] et al. clearly identified the spatial proximities and synergies between the Brönsted and various Lewis acid sites in dealuminated HY zeolite by ³¹P-³¹P DQ-SQ MAS NMR experiments using trimethylphosphine (TMP) as the probe molecule. They also studied acidic properties in different channels of H-MOR zeolite by ¹H-¹H DQ and SQ NMR correlation techniques using CH₃CN as probe molecule [31]. And the impact of acidic properties (e.g., detailed acidic distribution, pore confinement effect, and synergy effect of Brönsted acid pairs) of H-MOR zeolite on catalytic performance has been clarified.

In this work, we focused on the hydrothermal stability of framework Al of MOR zeolite. The dealumination processes of H-MOR zeolites by hydrothermal treatments at different temperature were studied by 1D and 2D solid-state NMR technology to understand the mechanism of dealumination at the micro level.

2. Experimental

2.1. Catalyst preparation

Raw powder Na-MOR (Si/Al = 7.3, containing template) was purchased from Catalyst Plant of Nankai University. The powder was calcined in static air atmosphere at 550 °C for 6 h in a muffle furnace to remove the template. Next, NH₄-MOR was prepared from Na-MOR by ion exchange with 1 M NH₄NO₃ at 80 °C for 2 h, 3 times. After ion exchange, the sample was washed by deionized water, filtered and dried at 120 °C overnight. NH₄-MOR zeolite was put in a tubular furnace and heated up to 500 °C from room temperature in flowing air for 4 h to obtain H-MOR. H-MOR samples were treated with steam at 400, 500, 600 and 700 °C respectively for 2 h by passing N₂ (100 mL/min) through saturation evaporator at 30 °C water bath. According to treatment temperatures from 400 to 700 °C, the samples obtained were named H-MOR-400, H-MOR-500, H-MOR-600 and H-MOR-700 respectively.

2.2. Catalyst preparation

The powder X-ray diffraction (XRD) patterns of H-MOR were recorded on a PANalytical X'Pert PRO X-ray diffractometer using Cu K_{α}

radiation ($\lambda = 1.5418$ Å) in a range of $2\theta = 5-60^{\circ}$ with a scan rate of $5^{\circ}/$ min (2 θ) to determine the crystallinity and purity of MOR. The morphology of crystals was obtained with a field emission scanning electron microscopy (SEM, Hitachi SU8020). The chemical compositions were determined by X-ray fluorescence (XRF) spectrometer (Philips Magix-601). Nitrogen adsorption-desorption experiments were carried at 77 K on Micromeritics ASAP 2020. The sample was dehydrated and pretreated under vacuum at 350 °C for 6 h. The surface area is calculated by BET (Brunauer-Emmett-Teller) method. The micropore surface area and pore volume were calculated by t-plot method. The infrared spectra of the samples were carried out on the IR spectrometer (Bruker TENSOR 27) to determine the effect of high temperature hydrothermal treatment on the Brönsted acid sites in the channels of H-MOR zeolites with scanning range of 4000-1000 cm⁻¹, scanning times of 32 and resolution of 4 cm⁻¹.

2.3. Solid state NMR experiments

 29 Si, 27 Al and 1 H MAS NMR experiments were performed on a 11.7 T Bruker Avance NEO spectrometer using a 3.2 mm HXY MAS NMR probe with resonance frequencies of 99.4, 130.3 and 500.1 MHz for 29 Si, 27 Al and 1 H, respectively. The 27 Al MAS NMR spectra were recorded using a single pulse sequence with the spinning rate of 12 kHz and a recycle delay of 2 s. The 29 Si MAS NMR spectra were recorded with a high-power proton decoupling sequence with a spinning rate of 8 kHz and a recycle delay of 10 s. Chemical shifts of 27 Al spectra were referenced to Al(NO₃)₃ solution at 0 ppm, and those of 29 Si spectra were referenced to kaolinite at -91.5 ppm. The Si/Al ratio of framework can be directly calculated according to the 29 Si MAS NMR spectrum after deconvolution peak fitting with Gaussian and Lorentz line type [32] in Dmfit software. The formula is as follows:

$$\left(Si_{Al}\right)_{NMR} = \frac{I_4 + I_3 + I_2 + I_1 + I_0}{I_4 + 0.75I_3 + 0.5I_2 + 0.25I_1}$$

Where I_n is the peak area of Si(nA1) signal.

¹H MAS NMR spectra were performed using a single pulse sequence with the spinning rate of 20 kHz and a recycle delay of 10 s. The background of the probe is deducted under the same acquisition conditions. Adamantane is chosen as the reference. Before ¹H MAS NMR experiments, all the samples were dehydrated at 420 °C for more than 12 h under vacuum conditions (<10⁻³ Pa) before testing. The Brönsted acid density of samples were calculated by deconvolution peak fitting of the spectrum with Gaussian and Lorentz linetype [32] in Dmfit software, using hexamethylbenzene as the external standard.

 27 Al multiple quantum (MQ, Fig. S1) MAS NMR experiments were performed on a Bruker Avance III 600 MHz (14.1T) spectrometer with a 3.2 mm H-X probe. Three pulses sequence filtered by Z-axis were used with the spinning rate of 20 kHz, and an excitation pulse p1 with the pulse width of 4.5 µs, a conversion pulse p2 with the pulse width of 1.5 µs and a selective pulse p3 with the pulse width of 13 µs. 600 scans were accumulated for each of the 64 points in t1 dimensions with an increment time of 50 µs and a recycle delay of 0.5 s.

¹H-¹H double quantum-single quantum (DQ-SQ, Fig. S2) correlation experiments were also conducted on a Bruker Avance III 600 MHz (14.1 T) spectrometer using a 3.2 mm H-X probe with the spinning rate of 20 kHz. The double-quantum coherence is excited and recoupled by BABA recoupling sequence. All the samples were dehydrated at 420 °C under vacuum conditions ($<10^{-3}$ Pa) before testing.

2.4. Evaluation of carbonylation activities

The catalyst evaluations were performed on the high-pressure fixed bed reactor with an 8 mm inner diameter. The loading amount of catalyst is 0.5 g, and the size is 20–40 meshes. The samples were pre-treated under N_2 purging (30 mL/min) for 2 h at 280 °C and cooled to

200 °C. Then N₂ was switched to the reaction mixture (DME: CO: N₂ = 5:35:60), and the reaction pressure was elevated to 2.0 MPa, with a gas hourly space velocity (GHSV) of 1800 mL/g/h. The effluent products were analyzed online by gas chromatography (Agilent GC 7890A) with a FID and TCD detector. The conversion of dimethyl ether and selectivity of methyl acetate were calculated based on the conservation of carbon atom mole number, as follows:

$$Con_{DME} = 1 - \frac{2c_{DME}}{2c_{DME} + 2c_{MAc} + 2c_{MeOH} + \sum_{i} ic_{i}}$$
$$Sel_{MAc} = \frac{2c_{MAc}}{2c_{MAc} + c_{MeOH} + \sum_{i} ic_{i}}$$

where c_{DME} , c_{MAc} and c_{MeOH} respectively represent the molar concentrations of dimethyl ether, methyl acetate and methanol in the outlet gas, c_i represents the molar concentrations of hydrocarbons in the outlet gas, and *i* refers to the number of carbon atoms contained in hydrocarbons.

3. Results and discussions

3.1. Structural characterization

Fig. 1 displays the XRD pattern of H-MOR zeolites and H-MOR zeolites after high-temperature hydrothermal treatment. It can be seen that characteristic diffraction peaks of MOR appeared on the XRD spectra of all the H-MOR zeolites, which means that the framework structures of H-MOR did not change after high-temperature hydrothermal treatments. In addition, the relative crystallinities of H-MOR zeolites increased after high-temperature hydrothermal treatment (see Table 1). The specific reason will be involved later.

The SEM images of H-MOR zeolites were shown in Fig. 2. Small, rodlike and clustered particles with a size range from 200 to 500 nm were observed from the image of original H-MOR. And the similar particles were observed in images of H-MOR zeolites hydrothermally treated at different temperatures. It indicates that the morphologies of H-MOR did not change obviously after high-temperature hydrothermal treatments.

Fig. S3 shows the N₂ physisorption isotherms of H-MOR and hydrothermally treated H-MOR. Table 1 shows values of physicochemical properties of all the above H-MOR zeolites. With the increase of steam



Fig. 1. XRD pattern of H-MOR zeolites with steam treatment at different temperatures.

treated temperature, the total specific surface area of H-MOR zeolites decreased from 459.0 m²/g to 393.1 m²/g and pore volume decreased from 0.24 cm³/g to 0.20 cm³/g, as well as the specific surface area of micropores decreased from 0.22 cm³/g to 378.7 m²/g and pore volume of micropores decreased from 0.22 cm³/g to 0.18 cm³/g, while the pore volume of mesopores generated by particle accumulation did not change significantly. It illustrated that the framework atoms of hydrothermally treated H-MOR zeolites might be removed or framework might become defective, which results in partial blockage of micropores and significant reduction in the specific surface area and pore volume of micropores, but no remarkable change in mesopores of H-MOR zeolites.

In order to determine the transformations of coordination state of framework T atoms (Si and Al), ²⁹Si and ²⁷Al MAS NMR experiments were carried out on above zeolites. The ²⁹Si MAS NMR spectra of untreated H-MOR and steam treated H- MOR zeolites at different temperatures are displayed in Fig. 3a. In the spectra, peaks at -99 ppm, -107 ppm and -103 ppm are assigned to Si(2Al), Si(1Al) and SiOH, respectively, and peaks at -112 to -114 ppm are allotted Si(0Al). It can be found that the signal intensity of Si(1Al) decreases as the increase of the temperature of hydrothermal treatment, which proves that a part of framework Al atoms have been removed. The framework Si/Al ratios calculated via fitting peaks in ²⁹Si MAS NMR spectra are shown in Table 1. It can be concluded that the higher temperature of hydrothermal treatment is, the higher degree of dealumination of H-MOR zeolite will be. Besides, more than half of the framework Al atoms of H-MOR have been removed when the temperature of hydrothermal treatment is 700 °C. When it comes to ²⁷Al, Fig. 3b shows ²⁷Al MAS NMR spectra of all the H-MOR zeolites. The peak at around 55 ppm is assigned to tetrahedrally coordinated framework aluminum (Al(IV)) and the peak at 0 ppm is ascribed to hexahedrally coordinated aluminum (Al(VI)). The peak at 55 ppm broadens toward the high field when the temperature of hydrothermal treatment rises to 600 °C, indicating that new Al species which different from the Al species in Brönsted acid sites, Al(IV)-1, have been generated. The new Al species can be attributed to twisted tetrahedrally coordinated aluminum (Al(IV)-2) and pentahedrally coordinated aluminum (Al(V)) [19,27,28]. According to the literature, it is identified as Al(IV)-2 which contains one or more Al-OH and partially bonds with framework [28,33]. It is reported that such Al(IV)-2 species also exists in USY and Beta zeolites [22,34]. Compared with H-MOR-600, the signals of Al(V) and Al(VI) species, which may be transformed from Al(IV)-2, are more obvious for H-MOR-700. With the increase of hydrothermal treatment temperature, the broadening of Al (IV) peak indicates the evolution of different Al species. Similar results can be found in acid zeolites modified by heat treatment [25]. Therefore, the temperature of hydrothermal treatment is the primary factor to influence the stability of zeolite framework.

3.2. Acidity characterization

Fig. 4a shows the ¹H MAS NMR spectrum of H-MOR zeolites. The ¹H peak at 3.9 ppm is assigned to the bridging Si(OH)Al, which also called Brönsted acid site. The signals of extra-framework Al-OH and nonacidic Si-OH appear at 2.6 ppm and 1.7 ppm, respectively [33]. The total amounts of Brönsted acid obtained from ¹H MAS NMR spectrum are shown in Table S1. It decreases from 1.86 mmol/g to 0.25 mmol/g with the increase of hydrothermal temperature, which means that H-MOR zeolites undergo different degrees of dealumination during hydrothermal treatments. Furthermore, the results of ¹H MAS NMR spectra are consistent with ²⁹Si MAS NMR and ²⁷Al MAS NMR spectra. The ratio of Al-OH/Brönsted acid concentration increases with the increase of hydrothermal treatment temperature, indicating that more Al-OH species are produced during dealumination by high-temperature hydrothermal treatment. In addition, the ratio of Al-OH/Brönsted acid decreases when the hydrothermal treatment temperature is higher than 600 °C, owning to the dehydration and condensation of polyhydroxy aluminum species. However, the ratio of Si-OH/Brönsted acid increases with increase of

Table 1

The physicochemica	l properties of H-MOF	zeolites with steam	n treatment at diff	erent temperatures.
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sample	C _{XRD}	Si/Al	Surface area	Surface area (m ² /g)			Pore volume (m ³ /g)		
	(%) ^a	ratio ^b	S _{BET}	Smicro	Sext	V _{total}	V _{micro}	V _{meso}	
H-MOR	100	9.7	459.0	443.8	15.2	0.24	0.22	0.02	
H-MOR-400	101.81	10.6	449.4	438.1	11.3	0.23	0.21	0.02	
H-MOR-500	101.79	11.2	452.0	417.9	35.1	0.22	0.19	0.03	
H-MOR-600	102.63	16.1	408.7	397.0	11.7	0.21	0.19	0.02	
H-MOR-700	103.5	34.7	393.1	378.7	14.4	0.20	0.18	0.02	

^a C_{XRD} represents relative crystallinity which was obtained from the ratio of the total areas of the sample's diffraction peaks (9.7°, 19.7°, 22.4°, 25.7° and 26.4°) to the areas of H-MOR (reference sample).

^b Framework Si/Al ratio obtained by²⁹Si MAS NMR spectra.



Fig. 2. SEM image of H-MOR zeolites with steam treatment at different temperatures.



Fig. 3. 29 Si (a) and 27 Al (b) MAS NMR spectra of H-MOR zeolites with steam treatment.



Fig. 4. ¹H (a) MAS NMR of H-MOR samples, FTIR (b) spectra and the deconvoluted results of signal at 3608 cm⁻¹ of H-MOR samples.

hydrothermal treatment temperature indicates that more defects of silicon species are produced during dealumination.

To further determine the influence of high-temperature hydrothermal treatment on Brönsted acids in the channels of acidic zeolites, FT-IR measurements of all H-MOR zeolites were conducted. The IR spectra of OH vibration region are shown in Fig. 4b. The strong signal near 3608 cm⁻¹ is assigned to Brönsted acid site, and the weak signals at 3660 cm^{-1} and 3740 cm^{-1} are attributed to extra-framework Al-OH and nonacidic Si-OH, respectively. The intensity of Brönsted acid decline with the increase of hydrothermal treatment temperature, which is consistent with ¹H MAS NMR results. In order to investigate the effect of high-temperature hydrothermal treatment on Brönsted acid sites in different channels of H-MOR, the absorption peaks at 3608 cm⁻¹ of above IR spectra were fitted. Combined with the total amounts of Brönsted acid given by ¹H MAS NMR, the amounts of Brönsted acid of 8-MR and 12-MR of H-MOR are obtained respectively and shown in Table S1. It can be seen that quantities of Brönsted acid in 8-MR and 12-MR of H-MOR decrease with the increase of hydrothermal treatment temperature (see Fig. 5).

3.3. Identification of aluminum species

The coordination state of aluminum changes obviously after hightemperature hydrothermal treatment. The amount of framework Al sites decreases while the non-framework Al species which are the source of Lewis acid sites are generated during dealumination process. Therefore, a detailed study of coordination state of aluminum is essential to know the influence of dealumination on acidity of zeolite. ²⁷Al MQ MAS NMR spectra of H-MOR and H-MOR-700 are shown in Fig. 6a and b, respectively. Two kinds of coordinated Al, Al(IV)-1 and Al(VI), was observed on H-MOR sample. While, there are two new signals assigned to Al(IV)-2 and Al(V) appeared in spectrum of H-MOR-700. It indicates that Al species underwent complex changes during dealumination of H-MOR. Based on relevant literatures, Al(IV)-2 partially bonds with the framework due to either the formation of crystal defects or the incomplete hydrolysis of framework Al [28]. Therefore, it can be speculated that the original Al(IV)-1 species suffered a lot of destruction and transformed into a large number of Al(IV)-2 species after high-temperature hydrothermal treatment, and then the Al(IV)-2 species further evolved into Al(V) and Al(VI) species. Furthermore, the Al(VI) species of high-temperature hydrothermally treated H-MOR zeolite are different from the Al(VI) species of original H-MOR zeolite due to the wider range of isotropic chemical shifts of hydrothermally treated H-MOR zeolite, which means that more complex changes have taken



Fig. 5. The variations of the different hydroxyl concentration with hydrothermal treatment temperature and the ratio change of Brönsted acid concentration in 8 MR and 12 MR.

place on Al (VI) species.

3.4. Study on spatial proximity of hydroxyl species

In order to further verify the rationality of the above mechanism, 2D ¹H-¹H double-quantum/single-quantum (DQ-SQ) correlation experiments were performed on H-MOR and H-MOR-700. 2D ¹H-¹H DQ/SQ NMR experiment is widely used to probe the proximity of two protons, where a spatially proximal spin pair induces a pair of peaks having the same chemical shift value in the DQ dimension, equal to the sum of the isotropic chemical shifts of these two spins in the SQ dimension. The presence of correlated peaks on the ¹H-¹H DQ-SQ spectrum means that two protons are spatially adjacent. Correlation strongly depends on the distance and number of the spin pair. It is generally believed only the space distance between nuclei is less than 5 Å can the correlated peak appear. Correlated peak (A, A) along diagonal line represent the existence of spatial proximity of protons with same isotropic chemical shift, and peaks (A, B) outside diagonal line indicate the correlation between two protons with different isotropic chemical shifts. Fig. 7a and b show ¹H-¹H DQ-SQ correlation spectra of H-MOR and H-MOR-700, respectively, where A is the signal of Brönsted acid site Si(OH)Al, signal B1, B2 as well as B3 are contributed by different Al-OH species and C stands for Si-OH. Thus, the strong correlated peak at (3.9, 7.8) ppm in Fig. 7a indicates that the Si(OH)Al in the H-MOR sample are not isolated but spatially adjacent. The peak at (1.7, 3.4) ppm evidences the spatial proximity between nonacidic Si-OH. The occurrence of a pair of peaks at (2.5, 4.7) ppm and (2.2, 4.7) ppm means that Al-OH species, B1 and B2, in the H-MOR are spatially adjacent. Besides, the correlation between Al-OH species, B1, and the bridged hydroxyl Si(OH)Al is verified by a pair of correlated peaks at (3.9, 6.4) ppm and (2.5, 6.4) ppm.

However, there are great differences for ¹H-¹H DQ-SQ spectra between H-MOR-700 and H-MOR. The correlation of self-correlated peaks at (3.9, 7.8) ppm extremely decreased, which indicates most of the framework Al at Brønsted acid sites were removed. A pair of correlated peaks at (2.8, 5.3) ppm and (2.5, 5.3) ppm confirmed the existence of two kinds of Al-OH, B3 and B1, with different chemical structures in the H-MOR-700. It illustrates that some framework Al species Si(OH)Al have evolved into B3 Al-OH during the dealumination process. In combination with ²⁷Al MQ MAS NMR results, B3 is considered as Al(IV)-2. The presence of new pair of cross peaks at (2.8, 6.7) ppm and (3.9, 6.7) ppm demonstrates the correlation between B3 Al-OH and Si(OH)Al in H-MOR-700 zeolite, which indicates that high-temperature hydrothermal treatment resulted in bond breaking near the spatially adjacent Si(OH)Al and further formation of Al(IV)-2 species with Al-OH. Here, the results of ¹H-¹H DQ-SQ NMR experiments reveal the spatial correlation between hydroxyl groups of H-MOR and H-MOR-700 zeolites in detail and once again confirm the mechanism of dealumination in Scheme 1: Al(IV)-1 first transformed into Al (IV)-2, and further evolved into Al(V) and Al (VI). And Al(OH)_n of Al(V) and Al(VI) will further transform into alumina species by hydrothermal treatment at higher temperature.

3.5. Carbonylation activity

Fig. 8 shows the conversion rates of DME versus time in the carbonylation reaction on H-MOR and H-MOR modified by high-temperature hydrothermal treatment. There are three periods in the process of DME carbonylation: induction period, highly efficient period and deactivation period. The conversion of DME gradually increases in the induction period of the carbonylation reaction (0–3 h). After 3 h of reaction, the conversion of DME increases to the maximum value of about 30%. Then the reaction goes through a highly efficient period of 2 h, and then the catalyst begins to be deactivated. It can be seen that the activity of carbonylation reaction is closely related to the hydrothermal treatment temperature, the conversion rate decreases. This is because the hydrothermal treatment temperature obviously affects the acid density of the



Fig. 6. ²⁷Al MQ MAS NMR spectra of H-MOR (a), H-MOR-700 (b).



Fig. 7. ¹H-¹H DQ-SQ NMR spectra of parent H-MOR (a) and H-MOR-700 (b), and the structural diagrams of different hydroxyl species are shown at the bottom.

catalyst, and then affects the reaction activity. The carbonylation activity of H-MOR-400 is of smaller difference with original H-MOR, indicating that hydrothermal treatment at 400 °C has less influence on the concentration of Brönsted acid. However, the catalytic activity of H-MOR-500 and H-MOR-600 has changed significantly and the highest conversion rate of DME is only 30% and 10%, respectively. Furthermore, there is almost no DME carbonylation activity on H-MOR-700 owing to the extremely few concentration of Brönsted acid in 8-MR.

4. Conclusions

In this work, the physical and chemical properties, performances of carbonylation, the stability of framework Al and the spatial proximity between different acid sites of untreated H-MOR zeolites and high-temperature hydrothermally treated H-MOR zeolites were studied, as well as the possible dealumination mechanism was proposed. With the increase of hydrothermal treatment temperature, the degree of dealumination of zeolites intensifies and the concentration of Brönsted acid decreases. Al(IV)-1 and Al(VI) were observed on original H-MOR by ²⁷Al MQ MAS NMR experiment. And new Al species, Al(IV)-2 and Al(V), appear in H-MOR-700. In addition, Al(IV)-2 is the intermediate species of non-framework Al species during high-temperature hydrothermal treatment. ¹H-¹H DQ-SQ NMR experiment explored the spatial correlation between hydroxyl groups in H-MOR zeolites in detail. Combined

with ²⁷Al MQ MAS NMR spectra, the dealumination mechanism is proposed as follows: Al(IV)-1 is first transformed into Al(IV)-2, and then into Al(V) and Al(VI) species. In addition, Al (V) and Al (VI) species with polyhydroxy group will further transform into alumina species at 700 $^{\circ}$ C.

CRediT authorship contribution statement

Xiu Bai: Writing – original draft, Visualization, Formal analysis, Data curation, Conceptualization. Jin Zhang: Validation, Software, Data curation. Chong Liu: Data curation. Shutao Xu: Writing – review & editing, Validation, Supervision. Yingxu Wei: Supervision, Project administration, Methodology. Zhongminn Liu: Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Scheme 1. Schematic diagram of dealuminization process.



Fig. 8. DME conversion and MAc selectivity as a function of time during DME carbonylation over H-MOR catalysts. Reaction conditions: 200 °C, 2 MPa, DME/CO/N₂ = 5/35/60, GHSV = 1800 mL/g/h.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.micromeso.2023.112555.

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