

Dealumination process of zeolite omega monitored by ^{27}Al 3QMAS NMR spectroscopy

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Abstract

From the ^{27}Al MAS NMR and 2D 3QMAS NMR experiments, it can be concluded that during the steaming process of zeolite omega, some part of the framework tetrahedral Al species are gradually distorted. The 30 ppm broad hump in the 1D ^{27}Al spectra is mainly due to appearance of the distorted tetrahedral Al. With the dealumination process going on, penta-coordinated Al species are formed and contribute also to the 30 ppm broad hump. There exists the trend that the formation of penta-coordinated Al occurs with the consumption of the distorted tetrahedral Al species. Because the same phenomenon of the ^{27}Al NMR signals has also been observed in other zeolites, such as mordenite, ZSM-5 and Y, it could be regarded as a general procedure in the process of dealumination of acidic zeolites.

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1. Introduction

The catalytic potential of zeolite omega had attracted much attention based on its structure and acidic properties [1]. Zeolite omega, a large pore (0.75 nm) zeolite with a silica–alumina ratio in the range of 5–10, was the synthetic isotype of mineral mazzite (topological code MAZ [2]). In its unit cell, 36 tetrahedral atoms bridged by oxygen atoms form gmelinite cages and 12-membered cylindrical channels along the crystallographic c-axis. The lattice contains two kinds of crystallographically non-equivalent tetrahedral sites denoted as T1 and T2 (Fig. 1). The T1 sites (24 per unit cell) are located in the four-membered rings (4-MRs) of the gmelinite cages while the T2 sites (12 per unit cell) are located in the six-membered rings (6-MRs). In addition to its large pore system, secondary mesoporous structure could be created by mild dealumination [3–5], which may facilitate the transport of reactant and reduce the deposition of coke.

The strong acidity of zeolite omega is also accounted for its catalytic properties. It has been shown that zeolite mazzite possesses acid sites superior in strength to other zeolites commonly used as catalysts, such as mordenite, faujasite or zeolite beta [1,7]. It is well known that the

strong acid sites present in dealuminated mazzite are associated with the framework aluminum atoms, whereas nonframework species contribute essentially to the weaker acidity. McQueen et al. [8] studied the acidity of dealuminated mazzite and reported the three families of acid sites: (i) very strong Lewis sites, whose assignment to framework species was supported by the photoelectron and infrared data, (ii) structural Brønsted sites, associated with bridging hydroxyl groups, which exhibited an acid strength higher than those of mordenite and faujasite, and (iii) Lewis and Brønsted sites with weak or medium strength, originating from nonframework aluminum-containing species formed by high-temperature hydrolysis of structural Al–OH–Si groups.

Nowadays, ^{27}Al MAS NMR is widely applied in the research of zeolite structure and properties [9,10], but there still remain some questions about the interpretations of the NMR spectrum due to the quadrupolar broadening of ^{27}Al [11]. In the ^{27}Al MAS NMR spectra of zeolites, signals centered at around 55–60, 30–40 and ~0 ppm can be easily observed. Usually, the signal at around 60 ppm was attributed to framework tetrahedrally coordinated Al species and that at 0 ppm was assigned to octahedrally coordinated species. The assignment of the broad signal at around 30 ppm, however, had raised many disputations. In literature reports on the ultrastable Y zeolite (USY) several assignments were reported for the latter signal: four-coordinated Al species

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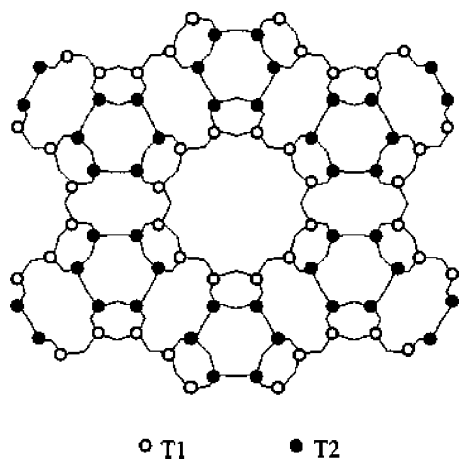


Fig. 1. Projection of the MAZ topology along the [001] axis indicating the two crystallographically non-equivalent tetrahedral sites denoted as T1 and T2 [6].

shifted upfield due to the quadrupolar induced chemical shift [12,13], pentacoordinated Al [14,15] or an overlap of both four- and five-coordinated Al species [16].

With the development of two-dimensional multiple quantum MAS NMR spectroscopy, a powerful tool for the study of quadrupolar nuclei is available [17,18]. Now, ^{27}Al 3Q MAS NMR was not only used to determine the real line shape of aluminium signals in ^{27}Al MAS NMR, which was applied by Wouters et al. to determine the AIT1/AIT2 Ratio in MAZ Zeolites [19], but also used to study the coordinations of aluminium associated with the dealumination process of zeolite [20].

In present study, dealumination of zeolite omega was characterized by ^{27}Al MAS NMR and ^{27}Al 3Q MAS NMR spectroscopy. The signal at around 30 ppm in the spectrum of the dealuminated zeolite omega was clearly distinguished in the ^{27}Al 3Q MAS NMR spectrum, and the source and the coordination state of the Al species giving rise to this signal was discussed.

2. Experimental

The hydrothermal synthesis was carried out as follows: sodium metalluminate, silica gel, tetra-methyl ammonium hydroxide and sodium hydroxide were mixed and stirred at room temperature for 10 h. The molar composition of the gel was (4.5–5) $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:14 \text{SiO}_2:2.2 \text{TMAOH}:220 \text{H}_2\text{O}$. The gel was aged at 323 K for 10 days and then was crystallized at 413 K for 8 h in an autoclave. The product was washed and then calcined at 723 K for 4–5 h to remove the organic compounds. The Na^+ -omega was exchanged with 0.5 M NH_4Cl at 363 K for four times, and then was calcined at 723 K for 4 h to get H-omega, which was then treated by high temperature water steam (hydrothermal treatment). The samples were heated to 723, 773 or 823 K in a quartz boat within a quartz cannulation inhaled with water steam for 2 h.

XRD was carried out on a Rigaku D/Max 2500 X-ray diffractometer at 40 kV and 100 mA with $\text{Cu K}\alpha$ radiation.

A BRUKER DRX400 spectrometer (9.4 T) was used to record the ^{27}Al MAS NMR and 3QMAS spectra. For the 1D ^{27}Al MAS NMR experiments, a $0.3 \mu\text{s}$ pulse length with a radio frequency field of around 120 kHz was applied. The repetition time was set to 0.1 s and 3000 scans were accumulated. An aqueous solution of $\text{Al}(\text{NO}_3)_3$ was used as reference. The MAS frequency was 20 kHz for all the aluminium measurements. The 2D 3Q MAS NMR spectra were obtained using the three-pulse, amplitude-modulated split- t_1 sequence described by Brown and Wimperis [21]. After each increment of t_1 , the phase of the first pulse was increased 30° and TPPI was applied in the 2D Fourier transformation. This pulse sequence provides directly a sheared spectrum that contains isotropic resolution along the F1 dimension. For the 3Q measurements 128 spectra were acquired in the F1 dimension. An increment of $5 \mu\text{s}$ between two successive spectra was used.

3. Results and discussion

Fig. 2 displayed the ^{27}Al MAS NMR spectra of parent and steamed H-omega samples. The two signals at around 50 ppm in the spectrum of parent H-omega (Fig. 2a) could be assigned to the framework tetrahedrally coordinated Al atoms T1 (left) and T2 (right), while the signal at 0 ppm was attributed to extra-framework Al atoms in an octahedral environment [22]. It was also reported that some framework-related octahedrally coordinated Al in zeolite HY may appear at 0 ppm [23], and this phenomenon might also be expected in other kinds of zeolites.

The two signals, which were assigned to T1 and T2 sites, decreased with the increase of steaming temperature,

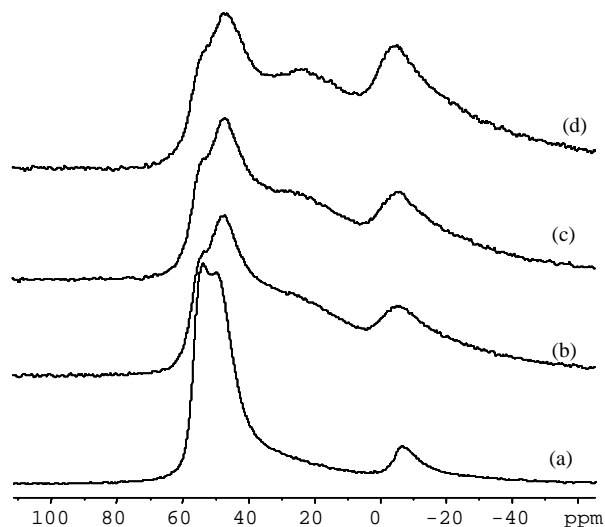


Fig. 2. ^{27}Al MAS NMR spectra of zeolite omega: (a) parent (673 K calcined to get rid of the organic template); (b) 723 K, (c) 773 K, (d) 823 K steamed for 2 h.

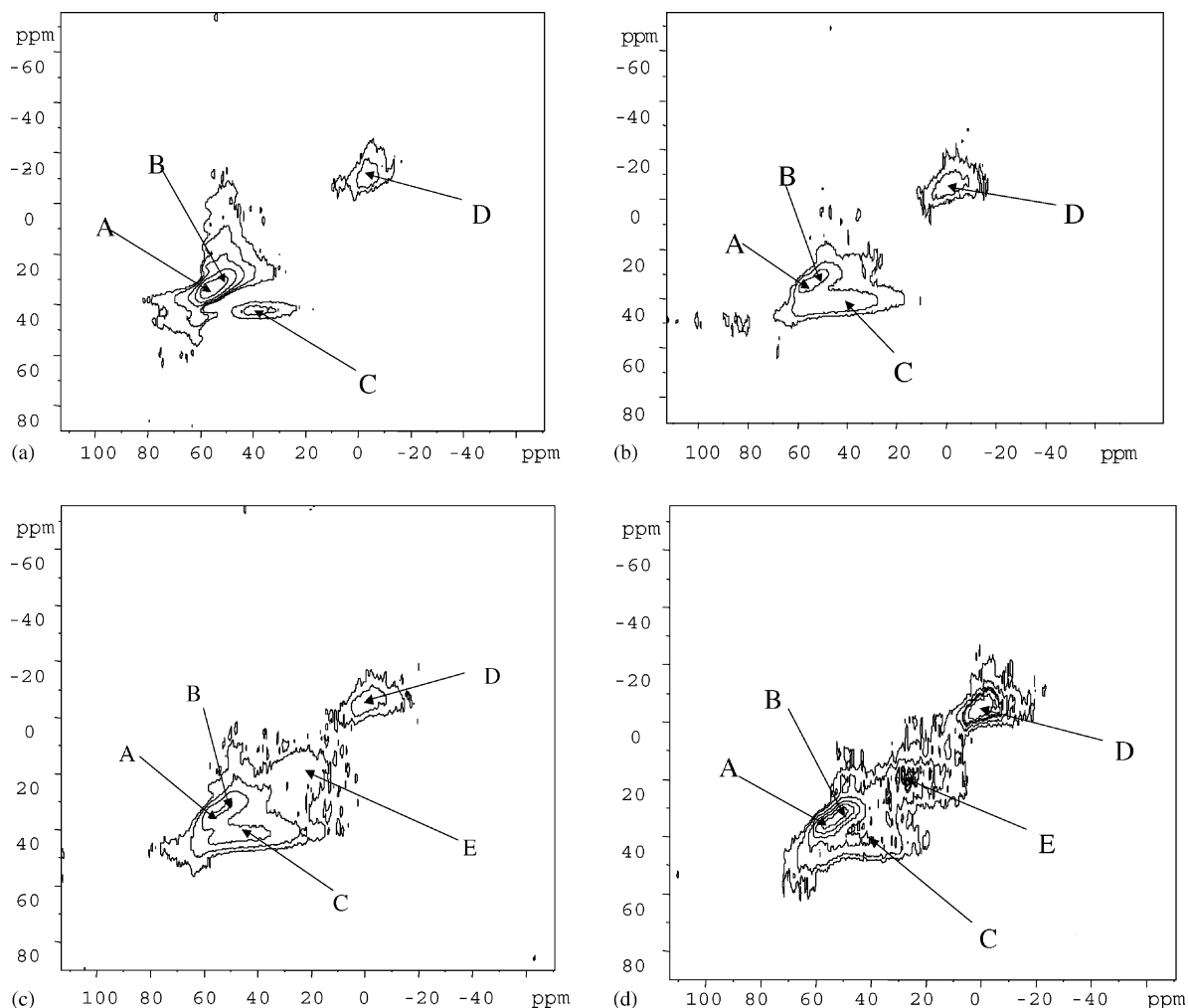


Fig. 3. 2D $3Q$ ^{27}Al MAS NMR spectra of zeolite omega parent and after 723, 773, 823 K steamed for 2 h.

suggesting dealumination of the framework aluminium atoms. In the spectra of the steam-treated samples (Fig. 2b–d), besides the three peaks at 55, 50 and 0 ppm, a broad line gradually emerges at around 30 ppm with the increasing of steaming temperature. This signal revealed the source of extra-framework aluminum species and was worthy of further care.

By application of the 2D ^{27}Al 3Q MAS NMR technique, the resolution of the ^{27}Al MAS NMR spectra of the steam treated samples was enhanced, as shown in Fig. 3. In these spectra the position of the lines in the MAS-dimension corresponded to the conventional ^{27}Al MAS NMR measurements, while isotropic resolution was obtained in the F1 dimension. In the spectrum of the H-omega (Fig. 3a), two strong signals A and B originating from the framework aluminium and a signal D due to the octahedrally coordinated aluminium were observed. Furthermore a small signal C appeared near the four-coordinated Al (signals A and B). This signal could be correlated with the small signal at 30 ppm in the 1D ^{27}Al MAS NMR (Fig. 2a).

After steam treated at 723 K (Fig. 3b), signals A, B, C and D were still present, while the intensity of C and D increased with the steaming temperatures (Fig. 3c and d). From the position in the isotropic-dimension of the 3Q MAS NMR spectrum, signal C should be regarded as four-coordinated aluminium species. When the steaming temperature was raised to 773 K, a new signal E (Fig. 3c) emerged which was not clear in the 1D NMR spectra. So the signal at around 30 ppm in the 1D NMR was made up of two broad signals. With the rise of the steaming temperature, signal E was also strengthened. The NMR spectra of the series of steamed samples were similar to those of the calcined mordenite samples [20].

NMR signal of five-coordinated species were expected to appear between four-coordinated and six-coordinated aluminium. As signal C and E were concerned, signal E should be penta-coordinated, and signal C should be distorted tetra-coordinated. Four-coordinated aluminium species first transformed to distorted four-coordinated and then some distorted four-coordinated aluminium in the structure was further transformed to five-coordinated species by thermal or hydrothermal treatment.

4. Conclusion

From the ^{27}Al MAS NMR and 2D 3QMAS NMR experiments, it can be concluded that the process of dealumination of zeolite omega was supposed to begin from the formation of distorted four-coordinated Al in MAZ during the steaming treatment. The 30 ppm broad hump in the 1D ^{27}Al NMR spectra were due to the distorted tetrahedral Al. With the dealumination going on, penta-coordinated Al species were formed and contributed also to the 30 ppm broad hump. There exists the trend that the formation of penta-coordinated Al occurred with the consumption of the distorted tetrahedral Al species. Because the same phenomenon has also been observed in other zeolites, such as mordenite and Y, it could be regarded as a general procedure in the dealumination process of acidic zeolites.

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