Stepwise Dealumination of Zeolite Beta at Specific T-Sites Observed with ^{27}Al MAS and ^{27}Al MQ MAS NMR

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Abstract: Using ^{27}Al MAS and ^{27}Al MQ MAS NMR, dealumination of zeolite H-Beta has been observed at specific T-positions in the framework. ^{27}Al MQ MAS NMR is able to resolve aluminum in the T1 and T2 positions from the other (T3 − T9) positions in the framework. A quantitative analysis of the ^{27}Al MQ MAS NMR spectra shows that aluminum atoms in positions T1 and T2 resist dealumination and do not adopt an octahedral oxygen coordination. Moreover, it is shown that a heat treatment of 450 °C of NH_4-Beta gives a single type of fairly symmetric framework octahedral aluminum, which can be reconverted to framework tetrahedral aluminum by ammonia treatment. A more severe heat treatment (550 °C under steam) causes some of the tetrahedral framework aluminum atoms on positions T3−T9 to convert to at least two different types of *octahedral* aluminum that are connected to the framework. These sites are proposed to be different consecutive steps in the process of framework dealumination of zeolite Beta.

Introduction

Zeolites can be used in many catalytic applications due to their stability and activity combined with a high selectivity.[1] In general, the preparation of an active and stable catalyst involves the modification of the as-synthesized material. This is often done via a dealumination of the framework, either via steaming or acid leaching. Hydrolysis of the framework Si−O−Al linkages occurs, eventually resulting in the loss of aluminum from the framework. The final activity, selectivity, and stability depend strongly on the exact method of treatment. Understanding of the mechanism of dealumination is essential for optimization of the processes leading to stable, active, and selective catalysts.

The regular framework coordination of aluminum in the zeolite framework is tetrahedral. However, as pointed out by Fajula et al.,[2] octahedral aluminum can be present in the framework of zeolite Beta. More recently, the presence of octahedral aluminum in the zeolitic framework was indicated for zeolites ZSM-5[3] and Y.[4] Octahedral species have been associated with Lewis acid sites in the zeolites, either before[5] (as for zeolite Beta) or after the addition of water[3] (as for ZSM-5) to a tetrahedral aluminum site, which eventually creates the octahedral aluminum.

Wouters et al. showed that for zeolite Y [4] the creation of framework octahedral aluminum is associated with partial hydrolysis of the Si−O−Al bonds. It was suggested that a restoration of the original tetrahedral framework aluminum occurs after ammonia treatment at 388 K for zeolite ZSM (complete realumination), whereas in Y zeolite, no complete realumination was observed, and not all Si−O−Al bonds are restored.[6]

In ^{29}Si MAS NMR of silicates, a relation between the average Si−O−Si intertetrahedral angles and the isotropic chemical shift is well-established.[7] Indeed, experimental ^{29}Si MAS NMR spectra of highly siliceous zeolite Beta shows nine resonances according to the nine different T-positions in this zeolite.[8,9] Two resonances have a distinctly different chemical shift and are well-resolved in the ^{29}Si MAS NMR spectra. More recently, density functional theory calculations confirmed the relationship between the chemical shifts in ^{29}Si MAS and ^{27}Al MAS NMR spectra of respectively silicon and aluminum at different T-positions in zeolite Beta.[10] Empirically this relationship between the isotropic chemical shift in ^{27}Al MAS NMR spectra and the intertetrahedral Al−O−Si angle of the corresponding aluminum species in aluminosilicates was established by Lippmaa and co-workers.[11] This relationship proved to be valid for Si−O−Al angles up to 180°.[12]

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This study provides unique insight into the process of dealumination of zeolite Beta by a detailed investigation of the aluminum coordinations by means of ^{27}Al MQ MAS NMR.[13,14] ^{27}Al MAS NMR spectroscopy is a well-established tool to determine the aluminum coordinations in zeolites.[15−17] The presence of four-, five-, and six-coordinated aluminum in a sample can be determined. However, aluminum has a half-integer quadrupolar spin, complicating the interpretation of ^{27}Al MAS NMR spectra. The second-order quadrupolar interaction of the central transition causes resonances to move from their isotropic chemical shift (δ_{iso}), by the quadrupolar induced shift (δ_{QIS}), and broaden into specific powder line shapes, even under MAS conditions. The recently developed multiple quantum MQ MAS NMR technique[13,14] allows the detection of pure isotropic spectra, yielding a very significant increase in resolution. This permits an unambiguous assignment of the aluminum coordinations in the spectra. Moreover, the use of high spinning speeds (up to 30 kHz) and high external magnetic field strength (14.1 T) minimizes the chance that aluminum escapes detection.[18]

This study focuses on the aluminum coordinations as a function of treatment for zeolite (H)Beta. The isotropic chemical shifts of the aluminum resonances allow not only the determination of aluminum coordinations but also a further assignment of the lines on the basis of the Al−O−Si angles. The use of ^{27}Al MQ MAS NMR at a magnetic field strength of 600 MHz and spinning speeds up to 27 kHz provides a very high resolution that (partly) enables the distinction of aluminum in different T-positions in the framework. Previously, Sarv et al. found a framework T-site resolution in zeolite ZSM-5.[19] It will be shown that specific T-positions in the framework of zeolite Beta resist dealuminition although these sites are located in four-membered rings. Moreover, it is shown that two different *framework* octahedral aluminum species can be present in zeolite Beta, depending on the pretreatment conditions.

Experimental Section

Zeolite Synthesis. Macrocrystalline zeolite Beta (1∼2 μm) was prepared according to Kunkeler et al.[20] The as-synthesized Beta was carefully washed with water until pH 7. Debris, possibly formed during cooling of the synthesis mixture was removed by washing with a 0.025 M Na_2H_2EDTA solution at room temperature. The macrocrystalline Beta contained a tiny amount of mordenite as contamination (less than 1%).[20]

Calcination (Template Removal). The calcination was performed in a horizontal glass tube using 10 g of zeolite. First the obtained Beta was calcined under a pure ammonia atmosphere from ambient temperature to 400 °C (1 °C/min, 6 h, 400 °C). The resulting white material was sodium-exchanged overnight using a 1 M NaCl solution (100 mL/g of zeolite) under reflux. The thus obtained zeolite was calcined at 120 °C in oxygen containing ∼1% ozone, followed by a calcination step at 400 °C (1 °C/min, 6 h, 400 °C) in oxygen. Threefold ion exchange with a 0.1 M NH_4NO_3 solution at room temperature finally gave the parent sample (NH_4)Beta1. Nomenclature is according to the description given in a previous paper.[21]

Activation of Samples. Activation of small amounts of (NH_4)Beta1 (100−200 mg) was conducted in a small glass tube mounted horizontally in a tubular oven. To obtain a shallow calcination bed, the samples were spread out equally. Heating was performed at 1 °C/min for all activations.

Codes of the samples reflect their treatment. The charge-balancing cation is given in parentheses. The maximum temperature at which the sample has been treated is then given, together with the time the sample was kept at that temperature (h and d stand for hour and days, respectively). If the sample was heat-treated under a H_2O pressure of 30 Torr, it is denoted by w30, if dry nitrogen was applied, d is used. Addition of -NH_3 indicates the sample is treated with NH_3 for 1 day at 100 °C.

First, the parent sample (NH_4)Beta1 was heat-treated for 1 h at 450 °C under a stream of dry nitrogen. This sample is called (H)Beta1 450-(1h)d. Then, (H)Beta1 550(3d)w30 was formed by steam treatment of (NH_4)Beta1 at 550 °C during 3 days. Using a H_2O saturator operating at 30 °C, a small water pressure was maintained constant at 4.2 kPa. (H)Beta1 450(1h)-NH_3 and (H)Beta1 550(3d)w30-NH_3 were formed by treating (H)Beta1 450(1h)d and (H)Beta1 550(3d)w30 with NH_3 at 100 °C for 1 day.

All samples were checked with XRD, ^{27}Al MAS NMR, and N_2 physisorption. The samples were identified as "pure" zeolite Beta.

^{27}Al MAS NMR. Both ^{27}Al MAS NMR and MQ MAS experiments were carried out on a Chemagnetics Infinity 600 (14.1 T) operating at 156.3 MHz for aluminum using a Chemagnetics 2.5-mm HX MAS probe. Magic angle spinning was carried out at a rotation speed of 27 kHz. To allow quantitative evaluation of the single-pulse excitation (SPE) spectra, $\pi/18$ pulses using an rf field strength of 36 kHz were used. Chemical shifts were referenced relative to an aqueous $Al(NO_3)_3$ solution. The relaxation delays were 0.5 s, determined to be adequate for a quantitative analyses using saturation recovery experiments. ^{27}Al MQ MAS experiments were performed using the two-pulse *z*-filtered procedure.[22] The excitation pulse was a π pulse, and the conversion pulse was a $\pi/3$ pulse. The rf-field amounted to ∼170 kHz, and the relaxation delay was 0.5 s. The NMR parameters were determined from the ^{27}Al MQ MAS spectra. These parameters were then used to simulate the ^{27}Al MAS NMR spectra with the help of a program developed in MATLAB. Taking into account the distributions of NMR parameters, it was possible to yield quantitative results. The isotropic chemical shifts determined from the ^{27}Al MQ MAS and ^{27}Al MAS experiments agreed well within experimental accuracy.

^{27}Al MQ MAS NMR. The ^{27}Al MQ MAS NMR spectra are used to determine the coordinations of the aluminum species present in the zeolite Beta samples. In an MQ MAS experiment, the quadrupolar interaction is refocused and an isotropic direction, free of anisotropic quadrupolar interactions, is present in the spectra. In this paper, the spectra are sheared, so that the F1 axis is the isotropic dimension and the F2 axis contains the second-order quadrupolar line shape. Thus, the quadrupolar line shape is only reflected in the F2 direction and the quadrupolar-induced shift is visible in both directions. The line for which $\delta_{F1} = \delta_{F2}$ represents a hypothetical line where sites resonate that do not experience any anisotropic quadrupolar interaction. The position of the lines in the F1 projection, after scaling the sweep width in this dimension by a factor of 12/17 (for $I = {}^5/_2$), are given by

$$\delta_{F1} = \delta_{iso} - \frac{10}{17}\delta_{QIS} \quad (1)$$

where δ_{iso} the isotropic chemical shift and δ_{QIS} is the quadrupolar-induced shift.

Any broadening visible in the F1 projection is purely due to isotropic shift distributions, i.e., variations in Al−O−Si bond angle and/or Al−O bond lengths resulting in distributions in the quadrupolar couplings constant.[15] Resonances that correspond to aluminum experiencing a

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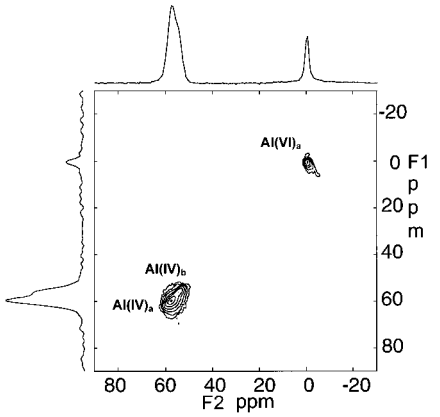

Figure 1. ^{27}Al MQ MAS NMR spectrum of calcined zeolite NH_4-Beta, (H)Beta1 450(1h)d. Two tetrahedral aluminums ($Al(IV)_a$ and $Al(IV)_b$) and one octahedral aluminum ($Al(VI)_a$) are visible. The corresponding ^{27}Al MAS NMR spectrum is given on top of the MQ MAS plot. The F1 projection shows a purely isotropic dimension, showing a clear resolution of the resonances corresponding to tetrahedral aluminum at different framework T-positions.

large quadrupolar interaction are reflected in the spectra by a ridge parallel to the axis in the F2 dimension. The center of gravity of a quadrupolar resonance is positioned in the F2 dimension at a chemical shift of

$$\delta_{F2} = \delta_{iso} + \delta_{QIS} \quad (2)$$

The aluminum coordinations can be determined from the isotropic chemical shift. This shift and the quadrupolar coupling constants (C_{QCC}) can be obtained from the MQ MAS spectra using the following relations

$$\delta_{iso} = (17\delta_{F1} + 10\delta_{F2})/27 \quad (3)$$

and, for $I = {}^5/_2$ spins,

$$P_Q = C_{QCC}\sqrt{1 + \frac{\eta^2}{3}} = \left(\frac{17}{162000}\nu_L{}^2((\delta_{F1} - \delta_{F2})\right)^{1/2} \quad (4)$$

where ν_L is the Larmor frequency. For detailed discussions on MQ MAS, we refer to the literature[15,23] Once the NMR parameters are known, the 1D ^{27}Al MAS NMR spectra can be simulated and a quantitative interpretation of the resonances in the ^{27}Al MAS NMR spectra of zeolite Beta can be made. In this paper, the ^{27}Al MAS NMR spectra are drawn on top of the MQ MAS spectra. These spectra are measured in a separate NMR experiment.

Results

Figure 1 shows the ^{27}Al MQ MAS NMR spectrum of (H)-Beta1 450(1h)d. All MQ MAS spectra are sheared and presented as a contour plot. The ^{27}Al MAS NMR spectra obtained from the same samples are given on top of the MQ MAS spectra. The spectrum shows resonances that can be directly attributed to octahedral and tetrahedral aluminum. The resonances corresponding to tetrahedral aluminum, visible in the region 50−60 ppm, consist of at least two contributions, which are assigned to aluminum at different T-sites in the zeolite, called $Al(IV)_a$ and $Al(IV)_b$, respectively. The intensity ratio of these peaks is 2.6 (vide infra).

At ∼0 ppm, a narrow resonance, called peak $Al(VI)_a$, is visible. This octahedral aluminum ($Al(VI)_a$) experiences a small quadrupolar interaction and has a small distribution in isotropic chemical shift.

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The peaks in the spectrum in Figure 1 are narrow in the F2-dimension and experience only a small induced shift indicating that the corresponding aluminums experience only a small quadrupolar interaction. The width of the lines in the F1 dimension is attributed to a distribution in isotropic chemical shift, caused by a variation in Al−O−Si angles. Using eqs 1−4, the isotropic chemical shifts and the C_{QCC} of the lines are determined and given in Table 1.

To obtain the relative intensities of the different resonances, the following procedure was followed: The F1 projections of the sheared MQ MAS spectra were deconvoluted using Gaussian line shapes. The intensities obtained from these deconvolutions were corrected for the MQ MAS excitation efficiencies.[14] The MAS spectra in Figures1 and 2 showing negligible quadrupolar broadenings were also deconvoluted using Gaussian line shapes, whereas the MAS spectra of Figures 3 and 4 were simulated using the quadrupolar parameters obtained from the MQ MAS experiments. The intensities obtained from the isotropic projections of the MQ MAS corresponded to those obtained from the analysis of the MAS spectra within experimental error, and their averaged values are given in Table 1. An important issue in this study is the relative intensity of peaks $Al(IV)_a$ and $Al(IV)_b$. Therefore, it is important to note that these sites experience small quadrupolar interactions, which are comparable in size and thus have a very similar MQ MAS efficiency.

The ^{27}Al MQ MAS and ^{27}Al MAS NMR spectra of (H)Beta1 450(1h)d-NH_3 (Figure 2) only show intensity in the range 50−60 ppm. From the MQ MAS spectrum, it is evident that this resonance consists of at least two contributions with identical isotropic chemical shifts, within the limits of accuracy, as the resonances in the spectra of (H)Beta1 450(1h)d (Table 1). The intensity ratio of $Al(IV)_a$ and $Al(IV)_b$ in (H)Beta1 450(1h)d-NH_3 is determined to be 3.3, whereas in the spectrum of (H)-Beta1 450(1h)d, this ratio is 2.6. The resonance corresponding to octahedral aluminum ($Al(VI)_a$) has completely disappeared from both the MQ MAS and the MAS spectra, indicating a complete disappearance of the corresponding 6-fold aluminum coordination after NH_3 treatment. It is noted here that the overall intensities in all the spectra are identical within limits of accuracy (±5% in total intensity), so all aluminum is accounted for in the spectra.

Figures 3 and 4 show the ^{27}Al MQ MAS NMR and ^{27}Al MAS NMR spectra of (H)Beta1 550(3d)w30 and (H)Beta1 550(3d)-w30-NH_3, respectively. The MQ MAS spectra indicate that three different tetrahedral aluminum sites are contributing to the intensity in the region 50−60 ppm. In addition to the two tetrahedral coordinations, $Al(IV)_a$ and $Al(IV)_b$ as observed in Figures 1 and 2, a third resonance, $Al(IV)_c$, corresponding to tetrahedral aluminum is observed. This tetrahedral aluminum is experiencing a large quadrupolar interaction, as seen from the broadening parallel to the F2 axis. This anisotropic quadrupolar broadening makes it difficult to identify it in the ^{27}Al MAS NMR spectra underneath the other two sites; however, in the isotropic F1 projection, it is clearly noticeable. The NMR parameters as given in Table 1 show the large quadrupolar interaction for this third tetrahedral aluminum. The MQ MAS efficiency of this third tetrahedral resonance differs from the other two tetrahedral resonances due its large quadrupolar interaction. It is noted that the ratio in intensity of the two tetrahedral aluminums that were already visible in Figures 1 and 2 has changed dramatically from 2.6 (for (H)Beta1 450-(1h)d) to $Al(IV)_a/Al(IV)_b = 0.4$. The MQ MAS spectrum of (H)Beta1 550(3d)w30 reveals that the intensity in the region −20 to 20 ppm consists of at least two resonances, $Al(VI)_a$ and

Table 1. NMR Parameters and Relative Intensity from the ^{27}Al(MQ)MAS NMR[a]

sample	$Al(IV)_a$	$Al(IV)_b$	$Al(IV)_c$	$Al(VI)_a$	$Al(VI)_b$
(H)Beta1 450(1h)d	59.1[b] (2.4)[c] [55][d]	55.8 (2.1) [21]	-	0.3 (1.6) [24]	
(H)Beta1 450(1h)d-NH_3	59.1 (2.2) [77]	55.7 (2.0) [23]			
(H)Beta1 550(3d)w30	58.9 (2.6) [8]	55.3 (2.4) [19]	~60.3 (5.5) [43]	0.7 (1.6) [4]	~1.2 (>5.5) [26]
(H)Beta1 550(3d)w30-NH_3	58.7 (2.2) [24]	55.2 (1.9) [17]	~59.4 (5.5) [59]		

[a] The total intensity in all spectra is identical. [b] δ_{IS} in ppm. [c] (Q_{QCC}) in MHz. [d] The relative intensity [rel int ±5%].

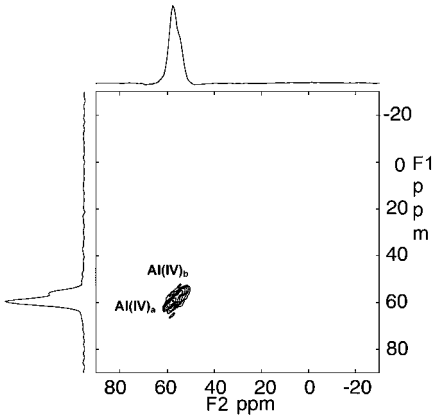

Figure 2. ^{27}Al MQ MAS NMR spectrum of calcined and subsequently ammonia-treated zeolite Beta, (H)Beta1 450(1h)d-NH_3. No octahedral aluminum is visible in the spectrum. The corresponding ^{27}Al MAS NMR spectrum is given on top of the MQ MAS plot.

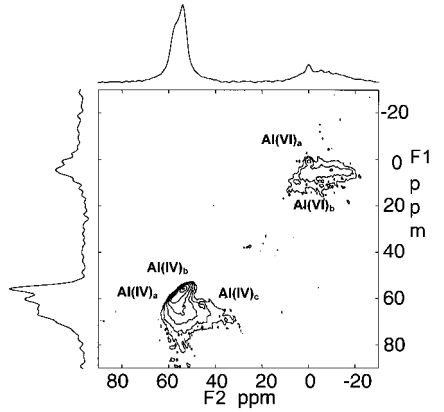

Figure 3. ^{27}Al MQ MAS NMR spectrum of steamed zeolite Beta, (H)Beta1 550(3d)w30. Three tetrahedral aluminums ($Al(IV)_a$, $Al(IV)_b$, $Al(IV)_c$) and two octahedral aluminums ($Al(VI)_a$, $Al(VI)_b$) are visible. The ^{27}Al MAS NMR spectrum is given on top of the MQ MAS plot.

$Al(VI)_b$, one being very similar to the resonance in the spectrum of (H)Beta1 450(d) ($Al(VI)_a$). The second resonance ($Al(VI)_b$) corresponds to distorted octahedral aluminum experiencing a large quadrupolar interaction. After the sample was treated with gaseous NH_3, (H)Beta1 550(3d)w30-NH_3, both the resonances corresponding to octahedral aluminum completely disappeared from the spectra without loss of signal in the ^{27}Al MAS NMR spectra. The resonances corresponding to tetrahedral aluminum are still present, although their relative intensities are altered from 0.4 to 1.4. Most of the intensity of the octahedral aluminum resonances is converted to $Al(IV)_a$ and $Al(IV)_c$ (Table 1).

Discussion

Resolution of Different T-Positions in ^{27}Al MQ MAS NMR. According to crystallographic data,[24] zeolite Beta contains nine different T-sites, of which the averaged T−O−T angles are given in Table 2. Two T-positions (viz. T1 and T2) have an averaged T−O−T angle that is significantly larger than the average angle for the other T-positions. In experimental ^{29}Si MAS NMR spectra of highly dealuminated zeolite Beta, nine resonances are observed attributed to the nine different T-positions.[8,9] The two T-positions that have a deviating T−O−T angle are well-resolved from the other resonances. This has been confirmed by density functional theory calculations.[10]

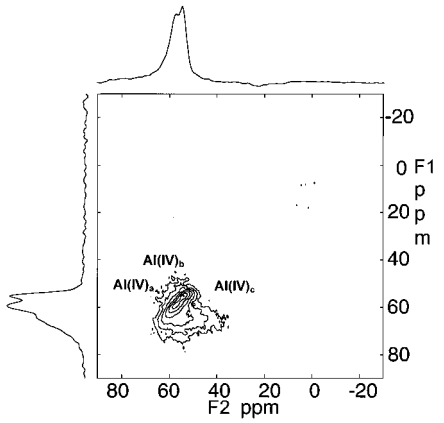

Figure 4. ^{27}Al MQ MAS NMR spectrum of steamed and subsequently ammonia-treated zeolite Beta, (H)Beta1 550(3d)w30-NH_3. Three tetrahedral aluminums ($Al(IV)_a$, $Al(IV)_b$, $Al(IV)_c$) are visible. No octahedral aluminum is visible in the spectrum. The ^{27}Al MAS NMR spectrum is given on top of the MQ MAS plot.

As mentioned in the Introduction, the isotropic chemical shift from ^{27}Al MAS NMR spectra can be used to determined the Al−O−Si angle of the corresponding aluminum atom[11,12] (or vice versa, the isotropic chemical shifts can be predicted from the T−O−T angles). Using the empirical formula obtained for the T−O−T angle,[11,12] the isotropic chemical shifts of the corresponding resonances in the ^{27}Al MAS NMR spectra can be estimated (fourth column in Table 2). The predicted isotropic chemical shifts for T1 and T2 are significantly lower than those of the other seven sites. The high magnetic field strength and spinning speeds used in the MQ MAS NMR allow the resolution of the two resonances corresponding to these two T-positions from the other seven (Figures 1−4, Table 1). Peak $Al(IV)_b$ is assigned to aluminum atoms on positions T1 and T2 in the framework of zeolite Beta, while peak $Al(IV)_a$ corresponds to aluminum positioned in T3−T9 sites.

Al Coordination as a Function of the Activation Treatments. In Table 3, the coordinations of aluminum as determined from ^{27}Al MQ MAS NMR are given. It is indicated whether these species are framework or not. As the total intensity in all NMR spectra is equal, an equal amount of aluminum is represented in all spectra. No aluminum in the samples becomes

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Table 2. The Nine Crystallographic T-Sites in Zeolite Beta with the Average <T−O−T> Angles (deg) and the Predicted Corresponding Isotropic Chemical Shifts in ^{27}Al MAS NMR Spectra

T-site	NNN	<T−O−T>	$\delta_{iso} = -0.5 \cdot \theta + 132$
T1	T2	155.3	54.4
	T3		
	T7		
	T8		
T2	T1	155.9	54.0
	T4		
	T8		
	T9		
T3	T1	148.0	58.0
	T4		
	T5		
	T8		
T4	T2	148.2	57.9
	T3		
	T6		
	T9		
T5	T3	151.8	56.1
	T5		
	T6		
	T7		
T6	T4	152.1	55.9
	T5		
	T6		
	T8		
T7	T1	152.8	55.6
	T1		
	T5		
	T5		
T8	T1	151.4	56.3
	T2		
	T3		
	T6		
T9	T2	149.7	57.2
	T2		
	T4		
	T4		

Table 3. Aluminum Coordinations from the ^{27}Al(MQ) MAS NMR Spectra

sample	tetrahedral Al	octahedral Al
(H)Beta1 450(1h)d	Framework	framework
(H)Beta1 450(1h)d-NH_3	Framework	none
(H)Beta1 550(3d)w30	Framework and nonframework	framework and nonframework?
(H)Beta1 550(3d)w30-NH_3	Framework and nonframework	none

broadened beyond detection in the spectra due to the sample treatments. On the basis of the identical isotropic chemical shifts and line widths, the ^{27}Al MAS NMR points unambiguously to the same tetrahedral coordination in samples (H)Beta1 450(1h)d and (H)Beta1 450(1h)d-NH_3. This shows that octahedral Al-$(VI)_a$ completely reverses back to a framework tetrahedral coordination after ammonia treatment. This has implications for the position of the octahedrally coordinated aluminum in the zeolite, since it is able to restore its original coordination. It has been proposed that this aluminum is connected to the framework via one or two oxygen atoms. Moreover, this species has been proposed to be an aluminum atom connected via four oxygen atoms to the framework and coordinated by one water molecule and one hydronium ion.[25−29] Our data confirm the connection of the octahedral aluminum with the framework in zeolite Beta.

Other alumina siliceous supports have shown an identical reversibility of coordination of the aluminum.[30] It has been reported that in zeolite NH_4^+-Y, which has been calcined at 673 K, framework octahedral aluminum is present. In ZSM-5, octahedral aluminum has been associated with framework Lewis acidity,[3] whereas in zeolite Beta it has been proposed that framework Lewis acidity results from tetrahedral framework aluminum that disappears after becoming octahedral.[5]

Framework Octahedral Aluminum on Specific T-Positions. The framework of zeolites does not contain so much freedom that it can accommodate easily octahedral-coordinated aluminum: building a framework structure containing octahedral aluminum is difficult. For zeolite Beta, several authors have tried to find T-positions that are able to convert to octahedral coordination.[31] From Table 1, it is clear that the amount of aluminum on crystallographic positions T1 and T2 (reflected by $Al(IV)_b$ in the spectra) is the same for all samples within the limits of accuracy. Hence, aluminum atoms in these positions in the framework do not convert to an octahedral coordination, nor do they dealuminate.

From this study and the recent literature, it can be concluded that octahedral aluminum can be present in the framework of many zeolites. The starting material is in the reported cases the NH_4^+-exchanged zeolite. A heat treatment removes gaseous ammonia, yielding the acidic zeolite. Only the presence of water can induce the creation of the framework octahedral aluminum.[2,4,32] Apparently, the Brønsted acidic zeolite attracts water molecules to stabilize the strong electric field induced by the proton and the cationic charge is delocalized. Throughout the framework, the zeolite is not able to accommodate too many of these strong electrical field centers; hence, water molecules are attracted and part of the framework tetrahedral aluminum may convert to octahedral aluminum, reducing the strong electrical fields in the framework. This could well be accompanied by hydrolysis of part of the Al−O−Si linkages, while each zeolite shows a unique tendency toward this process of hydrolysis. No other cations induce such an effect, which can be understood while realizing that protons are catalysts for hydrolysis reactions.

Once the proton is reexchanged for other cations, the framework octahedral aluminum is no longer detected.[25] Likewise, an ammonia treatment at 100 °C can revert the octahedral aluminum back to tetrahedral. An ammonia treatment at 100 °C has an effect very similar to ion exchange and it introduces NH_4^+ as the charge-compensating ion, thereby removing the water molecules, returning the coordination of aluminum back to tetrahedral. Our data suggest that the original structure of zeolite Beta after mild calcination can be completely restored by ammonia treatment, since no differences in isotropic chemical shifts or widths have been observed (Table 1).

Upon severe steaming, the situation is different. The high temperature and the water partial pressure causes complete hydrolysis of the framework tetrahedral aluminum, which is then extracted from the framework, in general becoming visible as tetrahedrally and octahedrally coordinated aluminum. In the

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spectrum of the severe steamed zeolite Beta (Figure 3), three tetrahedral and at least two octahedral coordinations are visible. Aluminum atoms corresponding to peak $Al(IV)_c$ are assigned to extraframework tetrahedral aluminum. One of the octahedral aluminum coordinations, $Al(VI)_a$, is identical to the octahedral aluminum in the at 450 °C activated zeolite Beta, showing identical resonances in the MQ MAS plots (Figures 1 and 3, Table 1). This octahedral aluminum was assigned to framework octahedral aluminum. It is clear from the MQ MAS spectra that no new resonances appear after ammonia treatment (Figure 4). However, after severe steaming, extraframework aluminum species have been formed.[21] The octahedral aluminum species corresponding to $Al(VI)_b$ are reversed to tetrahedral aluminum after the ammonia treatment, either to $Al(IV)_a$ or to (extraframework) $Al(IV)_c$. This strongly suggests that these extraframework species are not present in small alumina particles, since these particles are not expected to show such a reversal of coordination. Moreover, this implies that even some part of the octahedral aluminum represented by $Al(VI)_b$ is converted back into a *framework* tetrahedral position. Apparently, after the severe steaming treatment, some octahedrally coordinated aluminum species are present that are still connected to the framework. These octahedrally coordinated aluminum species are reflected in peak $Al(VI)_a$ and partly in $Al(VI)_b$. The amount of symmetrically octahedral aluminum, $Al(VI)_a$, in the severe steamed sample (Figure 3) is largely diminished compared to the amount of this aluminum species in (H)Beta1 450(1h)d (Figure 1, Table 1). The different octahedral framework aluminum species are proposed to represent different states of hydrolysis of the framework aluminum. First, after mild calcination, octahedral aluminum species represented by $Al(VI)_a$ are formed. Then, after severe steaming, a more hydrolyzed octahedral species represented in the spectra by $Al(VI)_b$ are produced. Both these octahedral aluminum species are able to revert back to a tetrahedral coordination. On the basis of the intensities in the ^{27}Al MAS NMR spectra (Table 1), it is shown that part of these tetrahedral sites is positioned in the framework.

Stepwise Dealumination. At certain conditions, extraframework aluminum is mobile and migrates to the surface of the crystallites. It is well known in the literature that dealumination causes an enrichment of aluminum at the surface of the crystallites.[33] Here, it can be concluded that the water partial pressure and temperature have a large influence on the extraction of aluminum from the framework and the migration inside the pores of zeolite Beta. First, at nonsevere conditions, framework octahedral aluminum is formed. This octahedral aluminum experiences a small quadrupolar interaction. More severe steaming causes the creation of distorted octahedral framework aluminum that eventually will lose all chemical bonds with any framework oxygen. The ruptured Al ion becomes mobile in the pores of the zeolite. This mobility causes part of the aluminum to lose connection to its original position in the framework. Ammonia treatment cannot cause this aluminum to be reinserted back into the framework, although the coordination is reverted to tetrahedral.

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Table 4. Ratio of Intensities of Tetrahedral Framework Aluminum Represented by Peaks $Al(IV)_a$ and $Al(IV)_b$

sample	ratio $Al(IV)_a/Al(IV)_b$
(H)Beta1 450(1h)d	2.6
(H)Beta1 450(1h)d-NH_3	3.3
(H)Beta1 550(3d)w30	0.4
(H)Beta1 550(3d)w30-NH_3	1.4

Specific T-Site Dealumination. Table 4 compares the ratios of the two resonances corresponding to framework tetrahedral aluminum $Al(IV)_a$ and $Al(IV)_b$ as determined from the spectra of the zeolite Beta samples. The ratio is altered after steaming to 0.4, whereas in the short activated samples it was 2.6. An ammonia treatment increases in both cases the intensity of peak $Al(IV)_a$, and the ratios are changed to 1.4 and 3.3, respectively. In all samples, the amount of $Al(IV)_b$ representing aluminum on T1 and T2 positions is very similar, and therefore, it is proposed that these sites resist dealumination by steam at even 550 °C. Moreover, the tetrahedral aluminum on sites T1 and T2 do not convert to framework octahedral aluminum (Figures 1 and 3). It is proposed here that, as these sites do not adopt an octahedral *framework* coordination, they are prevented from being dealuminated from the framework. This is a remarkable observation concerning the fact that both the T1 and T2 positions are positioned in a four-membered ring, which has the largest strain (biggest T−O−T angle, Table 2).

Conclusions

The use of ^{27}Al MQ MAS NMR using a high field strength of 14.1 T and high spinning speeds of 27 kHz resolves resonances in the ^{27}Al MQ MAS NMR spectra corresponding to aluminum atoms in the framework of zeolite Beta on crystallographic positions T1 and T2. It is shown that aluminum atoms in these framework positions are not able to adopt an octahedral coordination and that these sites resist dealumination during steaming at 550 °C.

After steaming at 550 °C, two types of octahedral aluminum atoms are positioned in or at least connected to the zeolite framework. These aluminum atoms are proposed to represent different steps in the process of hydrolysis of the tetrahedral framework aluminum during the dealumination of these sites. An increased hydrolysis of the corresponding aluminum is represented in the ^{27}Al MAS NMR spectra by a more distorted octahedral coordination.

This study shows that the process of zeolite activation by dealumination can be followed in great detail using ^{27}Al (MQ) MAS NMR performed at high magnetic field and high spinning speeds. This leads to a better understanding of the underlying processes occurring during activation and could eventually result in the development of better methods in zeolite activation.

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