

State of Aluminum in Dealuminated, Nonhydrated Zeolites Y Investigated by Multinuclear Solid-State NMR Spectroscopy[†]

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Received: January 28, 2004; In Final Form: March 18, 2004

A series of dealuminated zeolites Y with framework $n_{\text{Si}}/n_{\text{Al}}$ ratios of 2.8–6.0 was prepared by steaming and characterized by atomic emission spectroscopy and ^1H , ^{27}Al , and ^{29}Si NMR spectroscopy. The steaming of zeolite H-Y was performed under water vapor pressures of 3.4–81.5 kPa and at a temperature of 748 K. To exclude an additional modification of the dealuminated zeolites Y, the samples were investigated in the nonhydrated state, i.e., without hydration after the dealumination. By ^{29}Si magic-angle spinning (MAS) NMR spectroscopy, a strong high-field shift of the signals of Si(3Al) and Si(2Al) sites in the spectra of nonhydrated zeolites Y in comparison with those of the hydrated samples was observed. This finding is explained by a change of the Si–O–T bond angles of Si(n Al) sites in the local structure of nonhydrated framework AlO_4 tetrahedra. With increasing water vapor pressure during the dealumination, a systematic decrease of the total amounts of framework aluminum atoms in nonhydrated zeolites Y was found by ^{27}Al spin–echo NMR and ^{29}Si MAS NMR spectroscopies. The amounts of disturbed framework aluminum atoms, probably 3-fold-coordinated species in nonhydrated zeolites Y, were determined by the increase of the concentrations of bridging OH groups after an ammonia adsorption/desorption treatment and by application of ^1H MAS NMR spectroscopy. By a quantitative comparison of the amounts of tetrahedrally coordinated framework aluminum atoms, responsible for the occurrence of negative framework charges, and the amounts of charge-compensating residual sodium cations and bridging hydroxyl protons, the mean cationic charge of extraframework aluminum atoms was estimated. This mean cationic charge per extraframework aluminum atom was found to vary from ca. +2 for weakly dealuminated zeolites Y to ca. +0.5 for strongly dealuminated samples.

Introduction

For more than two decades, solid-state NMR spectroscopy has been one of the most applied methods for the investigation of dealuminated zeolites.^{1–15} In most of these studies, the nature of framework and extraframework aluminum species was investigated in the hydrated state of samples. Recently introduced techniques, however, have shown that strong changes of aluminum species occur upon hydration of zeolites. By application of X-ray absorption near-edge spectroscopy, e.g., van Bokhoven et al. observed the formation of 3-fold-coordinated framework aluminum after steaming of zeolite H- β at temperatures above 675 K.¹⁶ These 3-fold-coordinated aluminum species were found to be unstable; i.e., they convert back into tetrahedrally coordinated aluminum atoms in the presence of water. Wouters et al. have shown that hydration of weakly steamed zeolites Y leads to a local destruction of the zeolite framework.^{17,18} A sharp ^{27}Al magic-angle spinning (MAS) NMR signal in the chemical shift range of octahedrally coordinated aluminum species at ca. 0 ppm was explained by the formation of framework-related AlOH groups. Ammonia adsorption on dehydrated samples was found to convert the coordination of these aluminum species back to a tetrahedral coordination.^{17,19,20} Very recently, we were able to show that this ammonia-induced coordination change of framework aluminum species is accompanied by an increase of the amount of bridging OH groups as observed by ^1H MAS NMR spectroscopy.²¹

In the ^{27}Al MAS NMR spectra of hydrated samples, penta-coordinated and octahedrally coordinated extraframework aluminum species are indicated by signals at ca. 30 and 0 ppm, respectively.^{19,22} According to Scherzer, extraframework aluminum species in steamed zeolites can be cationic compounds, such as Al^{3+} , AlO^+ , $\text{Al}(\text{OH})^{2+}$, and $\text{Al}(\text{OH})_2^+$, or neutral and polymerized compounds, such as $\text{AlO}(\text{OH})$, $\text{Al}(\text{OH})_3$, and Al_2O_3 .²³ Since the nature of extraframework aluminum species is strongly influenced by the presence of water, the present NMR investigation of the state of these aluminum species is performed using samples which were not hydrated after the dealumination by steaming. For this purpose, the equipment used for the dealumination of zeolites H-Y was combined with an air-lock, allowing the nonhydrated samples to be placed in tight glass containers without contact with air.

^{27}Al NMR investigations of aluminum atoms in nonhydrated zeolites are limited by the strong line broadening due to quadrupolar interactions of the spin 5/2 nuclei. As shown by Kentgens et al., ^{27}Al DFS-enhanced 3QMAS spectroscopy (DFS = double-frequency sweep) allows the separation of signals caused by different aluminum species in a dehydrated zeolite H-ZSM-5.²⁴ The most widely applied technique for investigating aluminum atoms in nonhydrated zeolites, however, is the application of an ^{27}Al spin–echo NMR experiment, which allows the determination of the quadrupole coupling constants and the relative amounts of the corresponding species.^{25–27} The quadrupole coupling constant $C_{\text{QCC}} = e^2qQ/h$ (Q = nuclear quadrupole moment; h = Planck constant) depends on the z -component of the electric field gradient, $V_{zz} = eq$, at the

[†] Part of the special issue “Gerhard Ertl Festschrift”.

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position of the resonating nuclei.²⁸ By application of an ²⁷Al spin-echo NMR experiment, quadrupole coupling constants of $C_{\text{QCC}} = 13\text{--}16$ MHz were obtained for tetrahedrally coordinated framework aluminum atoms in the local structure of bridging OH groups (SiOHAl) in nonhydrated zeolites H-Y and H-ZSM-5.^{26,27} Tetrahedrally coordinated framework aluminum atoms compensated by sodium or ammonium cations such as in nonhydrated zeolites Y and ZSM-5 are characterized by C_{QCC} values of ca. 5 MHz.^{26,27} For extraframework aluminum species in dealuminated and dehydrated zeolites H-ZSM-5, quadrupole coupling constants of ca. 9 MHz were determined.²⁶

A further approach to study the state of aluminum atoms in nonhydrated zeolites is the NMR spectroscopic investigation of nuclei contributing to the local structure of these species. ²⁹Si MAS NMR spectroscopy, e.g., allows determination of the relative amounts of framework silicon atoms bound to 0–4 framework aluminum atoms in the first coordination sphere of T atoms (Si(0Al) to Si(4Al)) and calculation of the framework $n_{\text{Si}}/n_{\text{Al}}$ ratios.²⁹ Via quantitative ¹H MAS NMR spectroscopy, the coverage of nonhydrated zeolites by bridging OH groups, defect SiOH groups, and AlOH groups is obtained.³⁰ Hence, this method gives the amount of framework aluminum atoms which are compensated in their framework charges by bridging hydroxyl protons.

In the present work, multinuclear solid-state NMR spectroscopy is utilized in combination with bulk chemical analysis to study the state of framework and extraframework aluminum in dealuminated, nonhydrated zeolites Y.

Experimental Section

Zeolite Na-Y ($n_{\text{Si}}/n_{\text{Al}} = 2.7$) of Degussa AG, Hanau, Germany, was 6-fold-exchanged in a 1.0 M aqueous solution of NH_4NO_3 at 353 K for 12 h. The obtained zeolite $\text{NH}_4\text{-Y}$ was washed with demineralized water until no nitrate ions were detected any more. Subsequently, the powder material was dried in air at 353 K for 12 h. After this treatment, a cation-exchange degree of 93.3% was reached as determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Perkin-Elmer Plasma 400). X-ray diffraction (Siemens D5000, Cu K α radiation) and solid-state NMR spectroscopy were applied to exclude framework defects and extraframework aluminum in the obtained zeolite $\text{NH}_4\text{-Y}$. For the dealumination, ca. 2 g of zeolite $\text{NH}_4\text{-Y}$ was placed in a horizontal quartz glass tube under flowing nitrogen (200 cm³/min). Subsequently, the material was heated with a rate of 1.6 K/min to 748 K, followed by a calcination at 748 K for 10 h. The steaming of the zeolite materials was performed at 748 K for 2 h after switching from a flow of dry nitrogen to a flow of nitrogen loaded with water vapor. The water vapor pressure was varied from 3.4 to 81.5 kPa. This was achieved by routing the flow of nitrogen through a water bath at temperatures of 299–367 K. The dealuminated zeolites Y obtained by steaming were denoted as deH-Y/ p , where p is the water vapor pressure. To exclude an uncontrolled modification of the resulting materials by hydration of the dealuminated zeolites Y, these materials were put into glass containers under dry nitrogen in an air-lock. Prior to the NMR investigations of nonhydrated samples, an additional evacuation was performed at a pressure of $p \leq 1.5$ Pa for 12 h at 723 K. Some of the nonhydrated samples were loaded with ammonia at a pressure of 20 kPa for 4 h at 373 K. Subsequently, these samples were evacuated in a vacuum ($p \leq 1.5$ Pa) for 10 h at 723 K. The nonhydrated powder materials were put into MAS NMR rotors under dry nitrogen using a glovebox.

¹H, ²⁷Al, and ²⁹Si NMR studies were carried out on a Bruker MSL 400 spectrometer at resonance frequencies of 400.13,

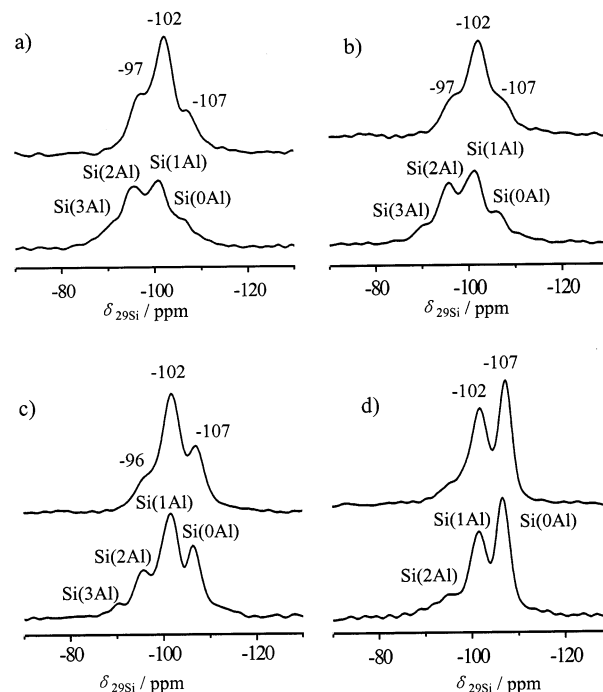


Figure 1. ²⁹Si MAS NMR spectra of nonhydrated (top spectra) and hydrated (bottom spectra) zeolites H-Y (a), deH-Y/7.4 (b), deH-Y/31.1 (c), and deH-Y/81.5 (d).

104.26, and 79.49 MHz, respectively. ²⁹Si MAS NMR spectra were recorded with a 7 mm MAS rotor system and a sample spinning rate of 3.5 kHz and after a $\pi/2$ single-pulse excitation of 6.0 μs . Repetition times of 50 s for nonhydrated samples and 30 s for rehydrated samples were used. To decrease the longitudinal relaxation time of silicon atoms in nonhydrated zeolites Y, these samples were loaded with synthetic air ($p = 100$ kPa) consisting of 20 vol % oxygen and 80 vol % nitrogen. By comparison of the ²⁹Si MAS NMR spectra of loaded and unloaded samples, it was ensured that the gaseous oxygen has no influence on the shapes of the spectra. ²⁷Al spin-echo NMR experiments were carried out applying the $p_1\text{--}\tau_1\text{--}p_2\text{--}\tau_2$ spin-echo pulse sequence introduced by Kunwar et al.²⁵ with $p_1 = p_2 = 0.61$ μs , $\tau_1 = 10$ μs , and $\tau_2 = 9$ μs . ²⁷Al spin-echo NMR experiments with repetition times of 500 ms to 5 s indicated that quantitative studies of nonhydrated samples require a repetition time of at least 2 s. ¹H MAS NMR spectra were recorded with a 4 mm MAS rotor system, a sample spinning rate of 10.0 kHz, and a repetition time of 10 s and after a $\pi/2$ single-pulse excitation of 4.5 μs . The decomposition and simulation of NMR spectra were performed using the Bruker software WINNMR and WINFIT. All dealuminated zeolites Y were investigated by ICP-AES to determine the total amounts of aluminum atoms.

Results and Discussion

²⁹Si MAS NMR Investigations of Nonhydrated and Hydrated Zeolites H-Y and deH-Y. Characteristic ²⁹Si MAS NMR spectra of dealuminated, nonhydrated zeolites Y are shown in Figure 1, top. The spectrum of nonhydrated zeolite H-Y (Figure 1a, top), i.e., of zeolite $\text{NH}_4\text{-Y}$ after calcination in the dealumination equipment without subsequent steaming, consists of a dominating signal at -102 ppm with a low-field shoulder at -97 ppm and a high-field shoulder at -107 ppm. No signals occur at -90 and -95 ppm, which are indicative for Si(3Al) and Si(2Al) sites in hydrated zeolites Y.²⁹ The ²⁹Si MAS NMR spectrum recorded after hydration of the non-

hydrated zeolite H-Y (Figure 1a, bottom) shows signals characteristic for zeolite Y with a framework $n_{\text{Si}}/n_{\text{Al}}$ ratio of 2.7 as obtained by simulation. The agreement between the framework $n_{\text{Si}}/n_{\text{Al}}$ ratio determined by ^{29}Si MAS NMR spectroscopy and the bulk $n_{\text{Si}}/n_{\text{Al}}$ ratio obtained by ICP-AES indicates that hydration of the nonhydrated zeolite H-Y is not accompanied by damage of the framework. However, the formation of octahedrally coordinated framework aluminum species, as described by Wouters et al.,^{17,18} cannot be excluded.

It is important to note that the total intensities of the ^{29}Si MAS NMR spectra of the nonhydrated zeolites (Figure 1, top spectra) are equal to those of the hydrated materials (Figure 1, bottom spectra). This indicates that a high-field shift of the ^{29}Si MAS NMR signals of $\text{Si}(n\text{Al})$ sites with large numbers n occurs in the spectra of nonhydrated zeolites Y. Comparison of the ^{29}Si MAS NMR spectra of strongly dealuminated zeolites Y in the nonhydrated and hydrated states (Figure 1c,d) shows that the above-mentioned high-field shift is weaker for $\text{Si}(0\text{Al})$ and $\text{Si}(1\text{Al})$ signals than for $\text{Si}(2\text{Al})$ and $\text{Si}(3\text{Al})$ signals.

There are various possible reasons for a resonance shift of the ^{29}Si MAS NMR signals of $\text{Si}(n\text{Al})$ sites. As proposed by van Bokhoven et al.,³¹ the presence of large cations, such as lanthanum cations or charged extraframework aluminum species, can lead to a local framework strain accompanied by a distortion of the $\text{Si}-\text{O}-\text{T}$ bond angles in their vicinity. The above-mentioned cationic species would be preferentially located in the neighborhood of negative framework charges, i.e., $\text{Si}(n\text{Al})$ sites with a large number n of aluminum atoms in the first coordination sphere of T atoms. According to the well-known relationship between the mean $\text{Si}-\text{O}-\text{T}$ bond angle and the ^{29}Si NMR shift, therefore, a cation-induced local framework distortion would lead to a resonance shift preferentially of the signals of $\text{Si}(3\text{Al})$ and $\text{Si}(2\text{Al})$ sites in zeolites Y.²⁹ In this case, the high-field shift of the ^{29}Si MAS NMR signals of $\text{Si}(3\text{Al})$ and $\text{Si}(2\text{Al})$ species in nonhydrated zeolites Y would be an indication for the presence of cationic extraframework species.

On the other hand, already the ^{29}Si MAS NMR spectrum of nonhydrated zeolite H-Y shows a significant high-field shift of the signals of $\text{Si}(3\text{Al})$ and $\text{Si}(2\text{Al})$ sites (Figure 1a). Since there is no extraframework aluminum in this material, only the dehydration of the framework may be a reason for the distortion of $\text{Si}-\text{O}-\text{Al}$ bond angles. The experimentally observed broadening of the ^{27}Al NMR signals of framework aluminum atoms in nonhydrated zeolite Y indicates a strong strain of AlO_4 tetrahedra. This strain of AlO_4 tetrahedra is caused by changes in the $\text{O}-\text{Al}-\text{O}$ bond angles and $\text{Al}-\text{O}$ bond lengths.³² Therefore, also the $\text{Si}-\text{O}-\text{Al}$ bond angles of neighboring silicon atoms must be influenced by a dehydration and hydration of AlO_4 tetrahedra. Considering the strong influence of the dehydration on the ^{29}Si MAS NMR spectrum of zeolite H-Y, the strain of nonhydrated AlO_4 tetrahedra has the stronger influence on the $\text{Si}-\text{O}-\text{Al}$ bond angles than the presence of cationic extraframework species.

The strong overlap of the signals of different $\text{Si}(n\text{Al})$ sites in the spectra of nonhydrated zeolites Y made a quantitative evaluation complicated. Therefore, ^{29}Si MAS NMR spectra of hydrated samples (Figure 1, bottom spectra) were used to determine the relative intensities $I_{\text{Si}(n\text{Al})}$ of $\text{Si}(n\text{Al})$ sites and to calculate the framework $n_{\text{Si}}/n_{\text{Al}}$ ratios and amounts of framework aluminum atoms summarized in Table 1, columns 2 and 3, respectively. A simulation of the ^{29}Si MAS NMR spectra of nonhydrated zeolites Y using the $I_{\text{Si}(n\text{Al})}$ values obtained for the hydrated samples gave a good agreement assuming a high-field shift of ca. 5.5 ppm for the signals of $\text{Si}(3\text{Al})$ and part of the

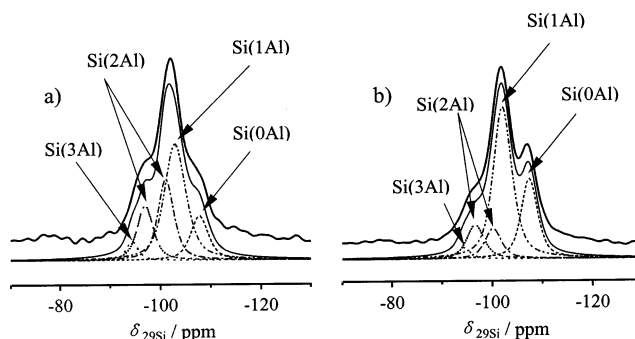


Figure 2. Simulation of the ^{29}Si MAS NMR spectra of nonhydrated zeolites deH-Y/7.4 (a) and deH-Y/31.1 (b) using the relative intensities $I_{\text{Si}(n\text{Al})}$ obtained by an evaluation of the spectra of hydrated samples.

$\text{Si}(2\text{Al})$ sites and 1.5–2.0 ppm for the signals of $\text{Si}(0\text{Al})$, $\text{Si}(1\text{Al})$, and part of the $\text{Si}(2\text{Al})$ sites (Figure 2). The framework $n_{\text{Si}}/n_{\text{Al}}$ ratios and amounts of framework aluminum atoms given in Table 1, therefore, are valid for both nonhydrated and hydrated zeolites Y. The range of the high-field shift of the $\text{Si}(2\text{Al})$ signals depends on the location of the neighboring two framework aluminum atoms in a four-membered or six-membered oxygen ring.²⁹ In the latter case it can be expected that the local structure of six-membered oxygen rings is more flexible, leading to a larger high-field shift of the signals of $\text{Si}(2\text{Al})$ sites. This also explains the large high-field shift of $\text{Si}(3\text{Al})$ signals in the spectra of nonhydrated samples, since $\text{Si}(3\text{Al})$ sites always possess two neighboring aluminum atoms located in a six-membered oxygen ring.²⁹

Van Bokhoven et al. observed a hydration-induced conversion of 3-fold-coordinated framework aluminum species into tetrahedrally coordinated atoms,¹⁶ which cannot be excluded in the present work. The amounts of framework aluminum atoms given in Table 1, column 3, therefore, may also contain 3-fold-coordinated framework species existing in the nonhydrated samples. On the other hand, since no insertion of extraframework aluminum species into the zeolite framework as a result of hydration occurs, the total amounts of aluminum in zeolites Y determined by ICP-AES and the amounts of framework aluminum atoms obtained by ^{29}Si MAS NMR spectroscopy (Table 1, column 3) allow the calculation of the amounts of extraframework aluminum species summarized in Table 1, column 4.

^{27}Al Spin-Echo NMR Studies of Nonhydrated Zeolites H-Y and deH-Y. Figure 3 shows characteristic ^{27}Al spin-echo NMR spectra of the dealuminated and nonhydrated zeolites deH-Y under study. The simulation of these spectra gave the quadrupole coupling constants, C_{QCC} , and the asymmetry parameters, η_{Q} , summarized in Table 2, columns 2, 3, 5, and 6. The amounts of aluminum atoms n in columns 4 and 7 were determined using the nonhydrated zeolite H-Y as an external intensity standard. As known from previous studies, quadrupolar patterns with C_{QCC} values of 13–16 MHz (signal 1) are characteristic for tetrahedrally coordinated framework aluminum atoms in the local structure of bridging OH groups.^{26,27} The narrow signal 2 ($C_{\text{QCC}} = 6.4$ MHz) in the ^{27}Al spin-echo NMR spectrum of nonhydrated zeolite H-Y is due to framework aluminum atoms which are compensated by residual sodium cations (3.5 Na^+ ions per unit cell). To calculate the amounts of framework aluminum atoms in Table 2, column 8, therefore, an amount of 3.5 aluminum atoms per unit cell was added (compare with column 4).

After a strong dealumination of zeolite H-Y, the intensity of the broad quadrupolar pattern (signal 1) due to tetrahedrally

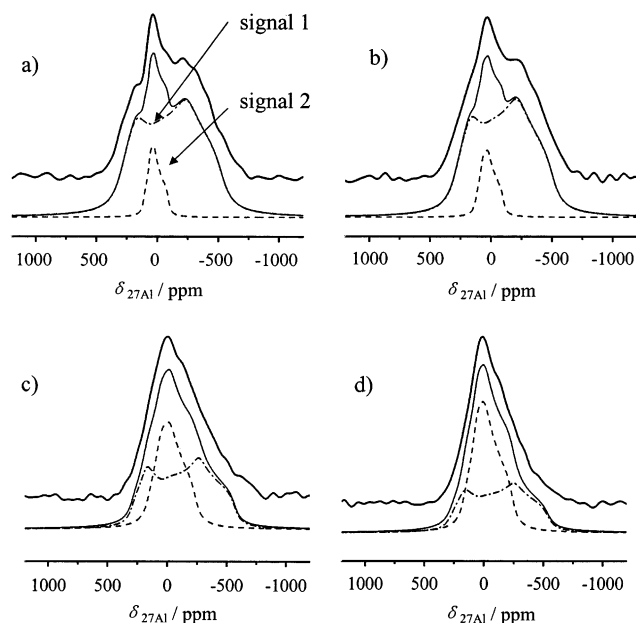


Figure 3. ^{27}Al spin-echo NMR spectra of nonhydrated zeolites H-Y (a), deH-Y/7.4 (b), deH-Y/31.1 (c), and deH-Y/81.5 (d). Experimental spectra (top) are compared with simulated spectra (bottom).

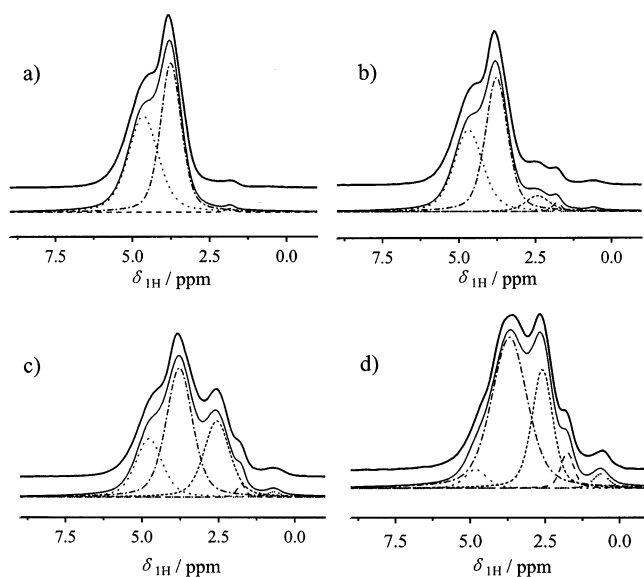


Figure 4. ^1H MAS NMR spectra of nonhydrated zeolites H-Y (a), deH-Y/7.4 (b), deH-Y/31.1 (c), and deH-Y/81.5 (d). Experimental spectra (top) are compared with simulated spectra (bottom).

coordinated framework aluminum atoms decreased, while the narrow pattern (signal 2) increased. For strongly dealuminated samples, the narrow signal 2 is characterized by a quadrupole coupling constant of ca. 9 MHz which agrees with the C_{QCC} values of extraframework aluminum species in dehydrated zeolites H-ZSM-5 published by Freude et al.²⁶

Generally, the electric field gradient at an aluminum position is caused by the electric charge distribution in the surroundings. The conversion of a tetrahedrally coordinated aluminum atom, such as in zeolite Na-Y (C_{QCC} = ca. 5 MHz), into an aluminum atom in a strained AlO_4 tetrahedron, such as in the local structure of a bridging OH group, is accompanied by an increase of the C_{QCC} value of ca. 10 MHz.^{26,27} The conversion of this tetrahedrally coordinated framework aluminum atom into a 3-fold-coordinated framework aluminum species, therefore, should be accompanied by a further increase of the quadrupole

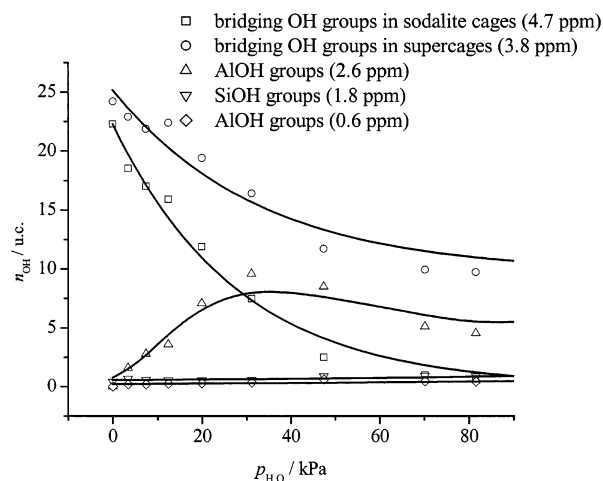


Figure 5. Amounts of hydroxyl groups in nonhydrated zeolites Y plotted as a function of the water vapor pressure during the steaming.

TABLE 1: Framework $n_{\text{Si}}/n_{\text{Al}}$ Ratios (Column 2) and Number of Framework Aluminum Atoms Per Unit Cell (Column 3) in Zeolites H-Y and deH-Y (^{29}Si MAS NMR Spectroscopy), Number of Extraframework Aluminum Species Per Unit Cell (Column 4) Calculated from the Total Amount of Aluminum (ICP-AES) and the Values in Column 3, Total Amounts of Bridging OH Groups before (Column 5) and after (Column 6) an Ammonia Adsorption/Desorption Treatment (^1H MAS NMR Spectroscopy), and Amounts of Tetrahedrally Coordinated Framework Aluminum Atoms (Column 7) Calculated by the Values in Column 3 and the Difference between the Values in Columns 5 and 6

sample	$n_{\text{Si}}/n_{\text{Al}}^a$	$n_{\text{fr Al}}^a/\text{uc}$	$n_{\text{ex Al}}^a/\text{uc}$	$n_{\text{SiOHAl}}^{\text{before b/}}/\text{uc}$	$n_{\text{SiOHAl}}^{\text{after b/}}/\text{uc}$	$n_{\text{Al}}^{\text{IV}}/\text{uc}$
H-Y	2.7	51.7		46.5		
deH-Y/3.4	2.8	50.1	1.9	41.4	43.0	48.5
deH-Y/7.4	2.9	48.6	3.4	38.9	39.2	48.3
deH-Y/12.4	3.0	48.4	3.6	38.3	38.8	47.9
deH-Y/19.9	3.3	45.0	7.0	31.3	34.4	41.9
deH-Y/31.1	4.0	38.2	13.8	23.8	25.7	36.3
deH-Y/47.4	4.8	33.0	19.0	14.2	20.4	26.8
deH-Y/70.1	5.4	30.0	22.0	10.9	17.4	23.5
deH-Y/81.5	6.0	27.6	24.4	10.5	17.3	20.8

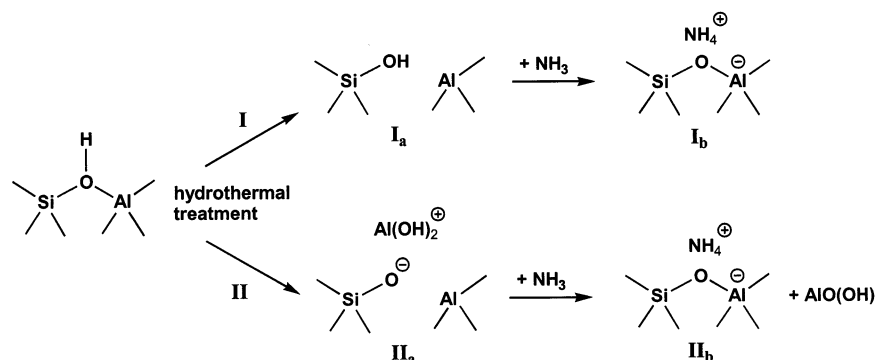
^a Accuracy of $\pm 2\%$. ^b Accuracy of $\pm 5\%$.

coupling constant to a C_{QCC} value larger than ca. 15 MHz. However, no such ^{27}Al spin-echo NMR signal could be observed in the present study. Therefore, no determination of 3-fold-coordinated framework aluminum species was possible by ^{27}Al spin-echo NMR spectroscopy.

^1H MAS NMR Investigations of the Hydroxyl Coverage of Nonhydrated Zeolites H-Y and deH-Y. The ^1H MAS NMR spectra of nonhydrated zeolites H-Y and deH-Y consist of signals of AlOH groups at 0.6 and 2.6 ppm, SiOH groups at 1.8 ppm, and bridging OH groups in supercages and sodalite cages at 3.8 and 4.7 ppm, respectively (Figure 4). The amounts of different hydroxyl groups as a function of the water vapor pressure during the steaming are given in Figure 5. It is interesting to note that dealumination of the zeolite framework is not accompanied by a strong increase of defect SiOH groups, but rather a strong increase of AlOH groups occurring at 2.6 ppm. Concomitantly, the amounts of bridging OH groups decrease, and this effect is more pronounced for SiOHAl groups located in the sodalite cages than for SiOHAl groups located in the supercages.

As found in previous investigations, ammonia adsorption on nonhydrated zeolites Y leads to a conversion of disturbed framework aluminum species into tetrahedrally coordinated

SCHEME 1



framework aluminum atoms. Upon desorption of ammonia, an increase in the amount of bridging OH groups was observed.²¹ In the present work, therefore, an ammonia adsorption/desorption treatment and ¹H MAS NMR spectroscopy were utilized to determine, in an indirect manner, the amounts of disturbed framework aluminum atoms in dealuminated and nonhydrated zeolites Y as a function of the water vapor pressure during the steaming. In Table 1, the total amounts of bridging OH groups in nonhydrated zeolites Y before (column 5) and after (column 6) the ammonia adsorption/desorption treatment are compared. These values show that ca. 1–6 aluminum atoms per unit cell occur as disturbed framework aluminum species upon steaming under low and high vapor pressures, respectively. The qualitative behavior of the amount of disturbed framework aluminum species agrees well with the behavior of 3-fold-coordinated framework aluminum atoms in the nonhydrated zeolites studied by van Bokhoven et al.¹⁶

The amounts of disturbed framework aluminum species determined by an ammonia adsorption/desorption treatment and ¹H MAS NMR spectroscopy were used to calculate the real amounts of tetrahedrally coordinated framework aluminum atoms in nonhydrated zeolites Y (Table 1, column 7).

Discussion of the State of Aluminum Species in Nonhydrated Zeolites deH-Y. The present multinuclear solid-state NMR investigation clearly evidences that tetrahedrally coordinated framework aluminum atoms in nonhydrated zeolites Y exist as strained AlO₄ tetrahedra. In agreement with earlier studies, quadrupole coupling constants of ca. 15 MHz were found, which are significantly higher than those of framework aluminum species in nonhydrated zeolites in the Na⁺ form ($C_{\text{QCC}} = \text{ca. } 5 \text{ MHz}$).^{24,26,27} The behavior of the experimentally determined asymmetry parameters η_{Q} , given in Table 2, agrees well with that of parameters η_{Q} obtained by quantum-chemical calculations.³² According to these calculations, the parameter η_{Q} is larger for AlO₄ tetrahedra with cationic extraframework species in their vicinity (signal 2) than for strained AlO₄ tetrahedra in the local structure of bridging OH groups (signal 1).³²

Within the accuracy of ²⁹Si MAS NMR and ²⁷Al spin-echo NMR spectroscopies, the total amounts of framework aluminum atoms obtained by these methods agree well. Both methods, however, were not able to separate signals due to 3-fold-coordinated framework aluminum species in the nonhydrated samples. By an ammonia adsorption/desorption treatment and ¹H MAS NMR spectroscopy, it was shown that up to 6.5 framework aluminum atoms per unit cell exist in a disturbed coordination, probably in a 3-fold one, which can be transformed into a tetrahedral coordination, leading to the formation of a corresponding number of bridging OH groups.

One possibility to convert the aluminum atom in a ≡Si-OH-Al≡ bridge into a 3-fold-coordinated framework aluminum

TABLE 2: Quadrupole Coupling Constants, C_{QCC} , and Asymmetry Parameters, η_{Q} , Determined by Simulation of the ²⁷Al Spin-Echo NMR Spectra of Nonhydrated Zeolites H-Y and deH-Y^a

sample	signal 1			signal 2			$n_{\text{fr Al}}/ \text{uc}$
	$C_{\text{QCC}}/ \text{MHz}$	η_{Q}	n^b/ uc	$C_{\text{QCC}}/ \text{MHz}$	η_{Q}	n^b/ uc	
H-Y	14.7	0.4	46.3	6.4	0.75	5.7	49.8
deH-Y/3.4	14.6	0.4	45.3	7.3	0.8	6.7	48.8
deH-Y/7.4	14.3	0.4	45.6	6.9	0.7	6.4	49.1
deH-Y/12.4	14.7	0.35	42.1	7.9	0.8	9.9	45.6
deH-Y/19.9	14.6	0.35	35.5	8.5	0.7	16.5	39.0
deH-Y/31.1	15.0	0.35	30.3	9.1	0.7	21.7	33.8
deH-Y/47.4	14.4	0.35	28.4	8.8	0.75	23.6	31.9
deH-Y/70.1	14.5	0.35	25.6	8.7	0.7	26.4	29.1
deH-Y/81.5	14.6	0.35	23.2	9.1	0.75	28.8	26.7

^a The amounts n of aluminum atoms in columns 4 and 7 were calculated from the relative intensities of signal 1. In column 8, the amounts of framework aluminum atoms ($n_{\text{fr Al}}$) are given taking into account 3.5 framework aluminum atoms per unit cell which are compensated by residual sodium cations. ^b Accuracy of $\pm 5\%$.

atom is the formation of a Q³ silicon species coordinated to one hydroxyl group (pathway I in Scheme 1), causing a ²⁹Si MAS NMR signal at ca. -100 ppm.²⁹ Considering the low amount of SiOH groups determined by ¹H MAS NMR spectroscopy (Figures 4 and 5), however, the presence of such Q³ species can be neglected. Another possibility is the coordination of an extraframework aluminum species, such as Al(OH)₂⁺, at the silicon atom of the ≡Si-OH-Al≡ bridge (pathway II in Scheme 1). In this case, the corresponding silicon atom should occur as a Q⁴ signal in the ²⁹Si MAS NMR spectrum. After an ammonia adsorption/desorption treatment, the ≡Si-OH-Al≡ bridge is healed and the Al(OH)₂⁺ species is converted to an AlO(OH) species.

In the ²⁷Al spin-echo NMR spectra of nonhydrated zeolites Y, no signal broader than that of strained AlO₄ tetrahedra (signal 1) was observed. The latter finding may indicate that 3-fold-coordinated aluminum species at framework defects are characterized by a quadrupole coupling constant similar to that of tetrahedrally coordinated aluminum atoms in nonhydrated H⁺-form zeolites. This explanation is supported by the agreement of the total amounts of framework aluminum atoms determined by ²⁹Si MAS NMR and ²⁷Al spin-echo NMR spectroscopies in the present study (compare Tables 1, column 3, and 2, column 8).

The difference in the amounts of tetrahedrally coordinated aluminum atoms in nonhydrated zeolites Y (Table 1, column 7) and bridging OH groups (Table 1, column 5) is strong evidence for the presence of cationic extraframework species. These cationic extraframework species cannot be accounted for in the 3.5 residual sodium cations per unit cell (n_{Na}). In the

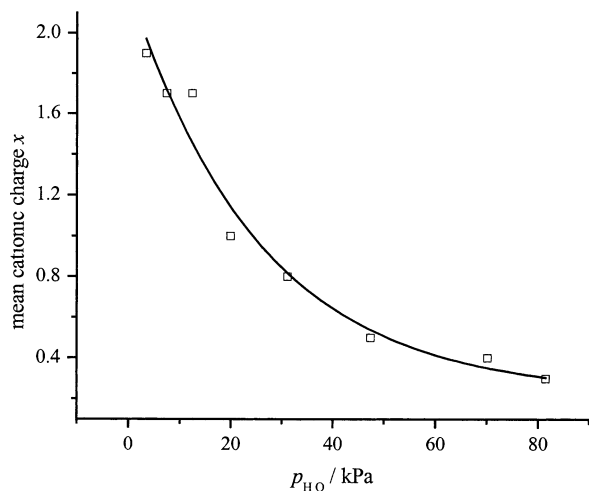


Figure 6. Behavior of the mean cationic charge x per extraframework aluminum atom in nonhydrated zeolites Y calculated after eq 1 and plotted as a function of the water vapor pressure during the steaming.

case of strongly dealuminated zeolites Y, the amount of cationic extraframework charges necessary to compensate the negative framework charges increases up to ca. 12 per unit cell. This finding indicates the formation of cationic extraframework aluminum species during the steaming. By eq 1 and using the

$$x = (n_{\text{Al}}^{\text{IV}} - n_{\text{Na}} - n_{\text{SiOHAl}}) / n_{\text{ex Al}} \quad (1)$$

corresponding values summarized in Table 1, the mean cationic charge x per extraframework aluminum can be estimated. The behavior of the mean cationic charge per extraframework aluminum atom obtained in this way for nonhydrated zeolites Y dealuminated under water vapor pressures of 3.4–81.5 kPa is given in Figure 6. The mean cationic charge per extraframework aluminum atom is found to decrease from ca. +2 to ca. +0.5 with increasing severity of the steaming. Performing a Rietveld refinement of the X-ray pattern of a weakly dealuminated zeolite Y in the dehydrated state, Gola et al. found extraframework aluminum atoms in the state of Al^{3+} cations on SI' positions in the sodalite cages.²² This indicates that a mean cationic charge of ca. +2 according to Figure 6 is caused by a variety of highly charged cationic species. However, it can be generally stated that the probability of the occurrence of extraframework aluminum species with a high cationic charge is significantly higher after a weak steaming of zeolite Y than after a strong steaming and vice versa.

Conclusions

By a combination of different methods of solid-state NMR spectroscopy, the state of aluminum atoms in dealuminated and nonhydrated zeolites Y was investigated. ^{29}Si MAS NMR and ^{27}Al spin-echo NMR spectroscopies were utilized for a quantitative determination of the total amounts of aluminum atoms in the framework of nonhydrated zeolites Y. The amounts of disturbed framework aluminum atoms, probably 3-fold-coordinated species, were obtained in an indirect way, i.e., via an ammonia adsorption/desorption treatment of the nonhydrated materials and application of ^1H MAS NMR spectroscopy. The discrepancy between the amounts of tetrahedrally coordinated framework aluminum atoms, responsible for negative framework charges, and the amounts of charge-compensating residual sodium cations and bridging hydroxyl protons allowed the estimation of the mean cationic charge of extraframework aluminum species. This mean cationic charge per extraframe-

work aluminum atom in nonhydrated zeolites Y was found to depend on the strength of steaming. It will be the objective of further investigations to clarify the ^{27}Al NMR spectroscopic parameters of 3-fold-coordinated aluminum species in the framework of nonhydrated zeolites.

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft, Max-Buchner-Forschungsförderung, Fonds der Chemischen Industrie, and Volkswagen-Stiftung Hannover is gratefully acknowledged.

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