Effect of Dehydration on the Local Structure of Framework Silicon Atoms in Zeolites Y Investigated by Solid-State NMR Spectroscopy

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Dedicated to Professor Arndt Simon on the Occasion of his 65th Birthday

Abstract. Recently, high-field shifts of the Si(nAl) signals of 2 to 5 ppm occurring in the $^{29}$Si MAS NMR spectra of non-hydrated zeolites Y were discussed to be caused by i) a variation of the local structure of neighboring AlO$_4$ tetrahedra or ii) the presence of multivalent extra-framework cations. To clarify the reasons for these resonance shifts, zeolites Y with different H- and Al-exchange degrees were investigated by solid-state NMR spectroscopy. The experimental results indicate that the primary reason for a high-field shift of $^{29}$Si MAS NMR signals is the change of O-Al-O bond angles and Al-O bond lengths during the dehydration of AlO$_4$ tetrahedra in the framework of zeolite Y. In contrast, the presence of extra-framework aluminum cations leads only to a strong broadening of the Si(nAl) signals, probably due to $^{29}$Si-$^{27}$Al couplings, and a weak high-field shift of not more than 1 ppm.

Keywords: Zeolites; NMR ($^{29}$Si MAS) spectroscopy; Local structure; Dehydration

1 Introduction

Solid-state NMR spectroscopy is a very sensitive method for the investigation of the local structure of framework atoms in zeolite catalysts. Until now, most of the solid-state NMR investigations of zeolites were performed on hydrated samples [1–12]. In catalytic applications, however, zeolites are always used in the activated, i.e., in the non-hydrated state. The improvement of our knowledge about the properties of zeolite catalysts for applications in the chemical industry, therefore, requires the application of analytical techniques allowing the investigation of activated, i.e., non-hydrated materials.
Recently, the aluminum distribution in steamed and non-hydrated zeolites H-Y was investigated, and in the same study $^{29}\text{Si}$ MAS NMR spectroscopy was applied to determine the framework $n_{\text{Si}}/n_{\text{Al}}$ ratio [18]. Because of high-field shifts of the Si($n$Al) signals in the $^{29}\text{Si}$ MAS NMR spectra of the non-hydrated materials, the framework $n_{\text{Si}}/n_{\text{Al}}$ ratios were determined utilizing the relative intensities in the spectra of rehydrated samples. As a reason for the high-field shift of the Si($n$Al) signals, a variation of the local structure of AlO$_4$ tetrahedra in the vicinity of the resonating silicon atoms and an effect of cationic extra-framework aluminum atoms were discussed. To clarify this issue, Al-exchanged zeolites Y (Al,Na-Y) and a series of zeolites Y (H,Na-Y) with different H$^+$ exchange degrees were investigated by solid-state NMR spectroscopy in the present work. It was found that framework AlO$_4$ tetrahedra in six-membered oxygen rings rather than cationic extra-framework aluminum species are responsible for the strong high-field shifts of Si($n$Al) signals in the $^{29}\text{Si}$ MAS NMR spectra of non-hydrated zeolites Y.

2 Experimental Section

Sample Preparation. Al-exchanged zeolites Al,Na-Y were prepared by exchanging zeolite Na-Y ($n_{\text{Si}}/n_{\text{Al}} = 2.7$, Degussa AG, Hanau, Germany) in an aqueous solution of 1 M Al(NO$_3$)$_3$ at 293 K for 4 h. The pH value of the solution was adjusted to 4 to avoid a dealumination or framework destruction. According to the decrease of the total amount of sodium cations as determined by atomic emission spectroscopy (AES-ICP, Perkin Elmer Plasma 400), 69% of the sodium cations were replaced by aluminum cations in zeolite Al,Na-Y. Prior to the NMR studies, the zeolites Al,Na-Y were evacuated at 433 and 723 K for 12 h under vacuum and sealed in glass ampoules. These samples were denoted as Al,Na-Y/433 and Al,Na-Y/723, respectively.

Zeolites NH$_4$,Na-Y with cation-exchange degrees of 46%, 69%, 77% and 93%, as determined by AES-ICP, were obtained by exchanging zeolite Na-Y one to four times in an aqueous solution of 1 M NH$_4$NO$_3$ at 353 K for 12 h. Subsequently, these samples were calcined at 723 K for 12 h under vacuum ($p \leq 1.5$ Pa) leading to the formation of partially exchanged H-forms of zeolite Y. These samples were sealed in glass ampoules and denoted as H(x),Na-Y, where x is the cation-exchange degree.

By X-ray diffraction (Siemens D5000, CuK$_\alpha$ radiation) and solid-state NMR spectroscopy, the formation of framework defects and extra-framework aluminum species in the different zeolites Al,Na-Y and H(x),Na-Y could be excluded.

Sample Characterization. All samples were investigated by XRD, AES-ICP, $^1\text{H}$, $^{27}\text{Al}$, and $^{29}\text{Si}$ MAS NMR spectroscopy. NMR investigations were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 400.1, 104.2, and 79.46 MHz for $^1\text{H}$, $^{27}\text{Al}$, and $^{29}\text{Si}$ nuclei, respectively. Tetramethylsilane (TMS) was used as a chemical shift standard for $^1\text{H}$ and $^{29}\text{Si}$ MAS NMR spectroscopy, while $^{27}\text{Al}$ MAS NMR shifts were referred to an aqueous solution of 0.5 M Al(NO$_3$)$_3$. $^{29}\text{Si}$ MAS NMR spectra were recorded with a spinning rate of 3.0 to 3.5 kHz and upon a π/2 excitation of 6.0 μs. A longitudinal relaxation time of the $^{29}\text{Si}$ nuclei in non-hydrated samples of ca. 188 s was found. After loading the sample with synthetic air (20 vol. % oxygen and 80 vol. % nitrogen), the longitudinal relaxation time of the $^{29}\text{Si}$ nuclei was decreased to 16 s without any changes in the line shapes and positions of the $^{29}\text{Si}$ MAS NMR signals. Therefore, $^{29}\text{Si}$ MAS NMR studies of non-hydrated samples were performed after adsorption of synthetic air and with a repetition time of 50 s, while 30 s delays were used for fully hydrated samples. $^1\text{H}$ and $^{27}\text{Al}$ MAS NMR spectra were recorded with a sample spinning rate of 10.0 kHz, single-pulse excitations of 2.5 μs, and 0.6 μs, and repetition times of 10 s and 500 μs, respectively. For quantitative $^1\text{H}$ MAS NMR measurements, a non-hydrated zeolite H,Na-Y with an sodium exchange degree of 35% was used as an external standard. Deconvolution and simulation of the NMR spectra were performed using the Bruker softwares WINNMR and WINFIT.

3 Results and Discussion

Investigation of Zeolites Al,Na-Y

In order to elucidate the effect of extra-framework aluminum species on neighboring framework silicon atoms, zeolites Al,Na-Y with a cation exchange degree of 69% were investigated by $^1\text{H}$, $^{27}\text{Al}$, and $^{29}\text{Si}$ MAS NMR spectroscopy (Fig. 1). According to the amount of extra-framework aluminum species introduced by cation exchange, as determined by AES-ICP, the extra-framework aluminum cations preferentially existed as two-fold charged species, such as Al(OH)$_2^{2+}$.

The $^1\text{H}$ MAS NMR spectra of zeolites Al,Na-Y/433 and Al,Na-Y/723 (Fig. 1a) consist of signals at 0.6, 1.8, 2.6, 3.8, and 4.7 ppm due to isolated AlOH groups, SiOH groups at framework defects, hydrogen bonded AlOH groups, bridging OH groups (SiOHAl) in the supercages, and bridging OH groups in the sodalite cages, respectively [19]. Performing a quantitative evaluation of the $^1\text{H}$ MAS NMR intensities, concentrations of 29 SiOHAl/u.c. and 6.5 SiOHAl/u.c. were determined for zeolites Al,Na-Y/433 and Al,Na-Y/723, respectively. These bridging OH groups were formed via the mechanism of Hirschler and Plank [20, 21], i.e., by a dissociation of water molecules in the electrostatic field of multivalent extra-framework cations, as observed for zeolites Mg,Na-Y and Ca,Na-Y [19]. In Scheme 1, the formation of SiOHAl and AlOH groups by this mechanism is explained. Hence, in zeolite Al,Na-Y/433, most of the negative framework charges are compensated by bridging hydroxyl protons (SiOHAl) instead of extra-framework cations. In zeolite Al,Na-Y/723 most of these hydroxyl groups are dehydroxylated again.

The study of zeolites Al,Na-Y/433 and Al,Na-Y/723 by $^{27}\text{Al}$ MAS NMR spectroscopy was performed after dehydration of the calcined samples (indicated by R), while the as-exchanged zeolite Al,Na-Y was investigated without further treatment (Fig. 1b). The $^{27}\text{Al}$ MAS NMR spectra are dominated by the signal of tetrahedrally coordinated framework aluminum atoms at 60 ppm. In the high-field range, a single broad signal or a superposition of a broad and a narrow signal occur at ca. 0 ppm. The broad signal at 0 ppm in the spectra of as-exchanged zeolite Al,Na-Y may be due to Al(OH)(H$_2$O)$_2^{2+}$ complexes (Scheme 1, top). The narrow signal is a hint to the presence of...
Figure 1

(a) $^1$H (a), $^{27}$Al (b), and $^{29}$Si MAS NMR spectra (c) of zeolites Al,Na-Y in different dehydration and rehydration states. Zeolites Al,Na-Y/433 and Al,Na-Y/723 were dehydrated at 433 and 723 K, respectively. Zeolites denoted by -R were rehydrated after the thermal treatment.

$\text{Al(OH)}_3(\text{H}_2\text{O})_3$ complexes shown in Scheme 1, middle. The smaller line width is caused by the more symmetric arrangement of the OH and H$_2$O groups, thus leading to a lower electric field gradient. Cationic extra-framework aluminum complexes, such as Al(OH)(H$_2$O)$_5$$^{2+}$, are influenced by the negative framework charges and have, therefore, a disturbed octahedral coordination. This assignment is supported by the $^{27}$Al MAS NMR spectrum of zeolite Al,Na-Y/723-R, which shows a single broad signal at ca. 0 ppm. In this sample, a rehydration of the Al(OH)$^{2+}$ species (Scheme 1, bottom) leading to Al(OH)(H$_2$O)$_5$$^{2+}$ complexes occurred, while no Al(OH)$_3$(H$_2$O)$_3$ complexes (Scheme 1, middle) are formed. In the $^{27}$Al MAS NMR spectrum of zeolite Al,Na-Y/723-R, an additional broad signal emerges at 30 ppm, which may be due to tetrahedrally coordinated framework aluminum atoms in the vicinity of highly charged extra-framework aluminum species [17]. Based on the experimentally observed decrease of SiOHAl groups and Al(OH)$_3$(H$_2$O)$_3$ complexes, the presence of highly charged aluminum cations, such as Al(OH)$^{2+}$, can be assumed for zeolite Al,Na-Y/723.

In Figure 1c, the $^{29}$Si MAS NMR spectra of zeolite Al,Na-Y and of zeolites Al,Na-Y/433 and Al,Na-Y/723 before and after rehydration are shown. The spectrum of the as-exchanged zeolite Al,Na-Y consists of well resolved signals of Si(0Al), (Si(1Al), Si(2Al), and Si(3Al) silicon species at $-105$, $-100$, $-95$, and $-90$ ppm [22]. In contrast to this finding, the spectrum of zeolite Al,Na-Y/433 shows a broadening of all Si(nAl) signals, which is stronger for the Si(2Al) and Si(3Al) silicon species than for the Si(0Al) and Si(1Al) silicon species. A similar behaviour was found for zeolite Al,Na-Y/723. It could be evidenced by X-ray diffraction that the zeolite framework was not damaged by the cation exchange and thermal treatment. Upon rehydration, the $^{29}$Si MAS NMR spectrum of zeolite Al,Na-Y/433-R is almost recovered and corresponds to the spectrum of the as-exchanged zeolite Al,Na-Y. In contrast, the signals in the...
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The 1H and 29Si MAS NMR spectra of a series of non-hydrated zeolites H(x),Na-Y with different exchange degrees x are shown in Figure 3. The 1H MAS NMR spectra (Fig. 3a) consist of signals of SiOH groups (1.8 ppm), bridging OH groups in the supercages (3.8 ppm), and bridging OH groups in the sodalite cages (4.7 ppm) [19]. A quantitative evaluation of the 1H MAS NMR intensities gives a good agreement with the concentrations of SiOHAl groups calculated using the chemical compositions obtained by AES-ICP. This finding indicates that no damage of the zeolite framework occurred during the cation exchange and calcination of zeolites H(x),Na-Y.

The 29Si MAS NMR spectra of non-hydrated zeolites Na-Y and H(x),Na-Y are shown in Fig. 3b. In the spectrum of the parent zeolite Na-Y, signals occur at −105, −100, −95, and −91 ppm, which are caused by Si(0Al), Si(1Al), Si(2Al), and Si(3Al) silicon species [22]. It should be noted that the relative intensities and resonance positions of these signals do not depend on the hydration state of zeolite Na-Y. With increasing cation exchange degree x of zeolites H(x),Na-Y, all Si(nAl) signals are shifted to higher field and a change in line shape can be observed. In particular, the signals occurring at −95 and −91 ppm show a strong broadening and a decrease in their relative intensities. However, all signals can be completely recovered upon full rehydration or ammonia adsorption (not shown).

A suitable simulation of the 29Si MAS NMR spectrum of non-hydrated zeolite H(93),Na-Y (Fig. 4a) can be reached by applying similar parameters (see Table 1) as those that were used for the simulation of the spectra of steamed and non-hydrated zeolites deH-Y in Ref. [18]. For the Si(3Al) signal, a high-field shift of ca. 5 ppm was found in comparison with the same signal in the spectrum of the hydrated sample (or zeolite Na-Y, see Fig. 3). For the Si(2Al), Si(1Al) and Si(0Al) signals, the high-field shift amounts to ca. 2 ppm. To reach a suitable simulation, a high-field shift of ca. 5 ppm has to be assumed also for some of the Si(2Al) silicon atoms.

The 29Si MAS NMR spectra of the non-hydrated H(4),Na-Y zeolites with lower cation exchange degrees x were simulated by a superposition of the Si(nAl) signals of the non-hydrated H-form of zeolite Y and zeolite Na-Y (Fig. 4b). Also in this case, high-field shifts of the signals of Si(nAl) silicon atoms contributing to the local structure of the H-form of the zeolite occurred (upper trace of simu-
Table 1 Isotropic chemical shifts $\delta$ and relative intensities $I$ of the different Si($n$Al) silicon species obtained by simulation of the $^{29}$Si MAS NMR spectra of zeolites Al,Na-Y/723, Al,Na-Y/723-R, H(93),Na-Y, and H(46),Na-Y and calculated $n_{Si}/n_{Al}$ ratios of the non-hydrated and rehydrated samples. I) and II) are the different Si(2Al)-I and Si(2Al)-II silicon species shown in Figure 5.

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<th>Samples</th>
<th>Si(0Al) ppm</th>
<th>$I/$%</th>
<th>Si(1Al) ppm</th>
<th>$I/$%</th>
<th>Si(2Al) ppm</th>
<th>$I/$%</th>
<th>Si(3Al) ppm</th>
<th>$I/$%</th>
<th>$n_{Si}/n_{Al}$</th>
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<tr>
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<td>9.9</td>
<td>-101.0</td>
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<td>28.1</td>
<td>-91.7</td>
<td>7.0</td>
<td>3.0</td>
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<tr>
<td>Al,Na-Y/723-R:</td>
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<td>12.7</td>
<td>-100.4</td>
<td>49.0</td>
<td>-94.6</td>
<td>26.4</td>
<td>-89.1</td>
<td>7.0</td>
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<tr>
<td>H(93),Na-Y:</td>
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<td>13.9</td>
<td>-102.8</td>
<td>34.6</td>
<td>-101.0</td>
<td>27.8</td>
<td>-95.3</td>
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<tr>
<td>H(46),Na-Y:</td>
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<td>-99.7</td>
<td>23.0</td>
<td>-94.8</td>
<td>22.0</td>
<td>-90.3</td>
<td>2.8</td>
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<tr>
<td>Na-Y set</td>
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<td>14.6</td>
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Figure 3 $^1$H (a) and $^{29}$Si MAS NMR spectra (b) of non-hydrated zeolite H(x),Na-Y with different cation exchange degrees x.

Figure 4 Simulation of the $^{29}$Si MAS NMR spectra of zeolites H(93),Na-Y (a) and H(46),Na-Y (b). The simulation parameters are given in Table 1.

The parameters used for the simulation of the spectrum of zeolite H(46),Na-Y are given in Table 1. A number of $^{27}$Al spin-echo NMR studies of non-hydrated zeolites H-Y demonstrated the strong influence of the adsorption of water or other adsorbate molecules on the quadrupolar parameters of framework aluminum atoms [18, 19, 25–27]. Upon dehydration, the local structure of the framework AlO$_4$ tetrahedra is changed to strongly distorted tetrahedra with characteristics of a threefold oxygen coordination. The change from an M-form of a zeolite (M: Na$^+$, NH$_4^+$ or H$_3$O$^+$) to its H-form (Scheme 2) is accompanied by an increase in the quadrupole coupling constant of the framework aluminum atoms from ca. 6 MHz to ca. 16 MHz [18, 19, 25–27], which corresponds to a decrease of the local symmetry.

As shown by theoretical studies [28], the dehydration of AlO$_4$ tetrahedra and the formation of bridging OH groups is accompanied by a strong increase of the Al-O bond in the Si-OH-Al bridge and significant changes of the O-Al-O
bond angles. Upon rehydration, water molecules are adsorbed at the SiOHAl groups and H$_3$O$^+$ ions are formed, which compensate the negative framework charges instead of SiOHAl groups. This recovers the local symmetry of the AlO$_4$ tetrahedra and leads to a decrease of the electric field gradient at the aluminum site and, therefore, of the $^{27}$Al quadrupole coupling constant. Changes in the local structure of AlO$_4$ tetrahedra certainly influence the chemical environment, i.e., the local structure of neighboring silicon atoms and induce variations of their $^{29}$Si MAS NMR parameters. According to the well-known correlation of the $^{29}$Si NMR shift and the mean Si-O-T bond angle $\alpha$ of framework silicon atoms [22, 29], a change of $\alpha$, e.g., induced by the dehydration of neighboring AlO$_4$ tetrahedra, causes a shift of the $^{29}$Si MAS NMR signals. In addition, it can be expected that the number of different AlO$_4$ tetrahedra and different secondary building units in the local structures of the resonating silicon atoms affect the value of this resonance shift.

In the framework of FAU type zeolites, each silicon atom is surrounded by three four-membered rings and one six-membered ring [30]. Based on NMR investigations of the aluminum ordering in zeolite Y [22, 23], the configurations given in Figure 5 exist. According to this scheme, silicon atoms with 3, 1, and 0 aluminum atoms in the first coordination sphere of T atoms are characterized by only one configuration in each case (Figs. 5a, 5c, and 5d). In contrast, silicon atoms with two aluminum atoms in the first coordination sphere of T atoms are characterized by two different configurations: (i) Both Al atoms are located in the adjacent six-membered ring, such as in Si(2Al)-I, whereas in the other configuration (ii) one Al atom is located in the six-membered ring while another one is located in one of the positions of the four-membered ring, such as in Si(2Al)-II (Fig. 5b). In the local structure of the Si(3Al) silicon atoms, two aluminum atoms are located in the neighboring six-membered ring (Fig. 5a). Also, the configuration Si(2Al)-I has two aluminum atoms in the adjacent six-membered ring (Fig. 5b).

The strong dehydration-induced high-field shift of the $^{29}$Si MAS NMR signal of the Si(3Al) silicon species of ca. 5 ppm indicates that two AlO$_4$ tetrahedra located in six-membered rings cause a significant variation of the local structure of neighboring silicon atoms. This change of the local structure is stronger for the case with one AlO$_4$ tetrahedron in a six-membered ring (Fig. 5c). In agreement with the experimental results, therefore, the $^{29}$Si MAS NMR signal of Si(2Al) silicon species in non-hydrated zeolites H-Y is split into two signals: (i) for the configuration Si(2Al)-I, which is high-field shifted by ca. 5 ppm, and (ii) for the configuration Si(2Al)-II, which is high-field shifted by ca. 2 ppm only. The dehydration-induced high-field shift of the configuration Si(2Al)-II is the same as for Si(1Al) silicon species with one aluminum atom in the adjacent six-membered ring, while the resonance shift of the configuration Si(2A)-I is the same as for Si(3Al) silicon species with two aluminum atoms in the six-membered ring. Hence, the loop configuration and the aluminum ordering in the H-form of zeolites Y are the reasons for the different high-field shifts of the $^{29}$Si MAS NMR signals of Si($n$Al) silicon species upon dehydration of these materials.

4 Conclusions

In this work, the reasons of the resonance shifts and broadenings of the $^{29}$Si MAS NMR signals of Si($n$Al) silicon species in zeolites Y upon dehydration were investigated. To shed light on the origin of these effects, zeolites Na-Y partially exchanged with aluminum cations (Al,Na-Y) and zeolites H($x$),Na-Y with different cation exchange degrees, $x$,
were investigated by solid-state NMR spectroscopy. Depending on the dehydration temperature of zeolites Al,Na-Y, the formation of bridging OH groups via the mechanism of Hirschler and Plank or of extra-framework aluminum cations could be evidenced. In the former case, a high-field shift of the $^{29}$Si MAS NMR signals of the Si($n$Al) silicon atoms of ca. 2 ppm was found, while in the latter case, a strong broadening of these signals occurred. This broadening was explained by $^{29}$Si-$^{27}$Al couplings between framework silicon atoms and extra-framework aluminum cations.

In the $^{29}$Si MAS NMR spectra of non-hydrated zeolites H($x$),Na-Y, a high-field shift of the Si($n$Al) signals by 2 to 5 ppm was observed in comparison with the spectra of the hydrated materials. The value of this high-field shift was found to depend on the aluminum ordering in the local structure of the resonating framework silicon atoms. Two framework AlO$_4$ tetrahedra in the six-membered ring contributing to the local structure of the resonating framework silicon atoms cause a stronger dehydration-induced high-field shift than one AlO$_4$ tetrahedron only. This is due to a larger structural flexibility of six-membered rings in comparison with four-membered rings containing the same number of AlO$_4$ tetrahedra. The above-mentioned finding helps to understand the variation of the $^{29}$Si MAS NMR spectra of H-Y zeolites upon dehydration and rehydration.

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