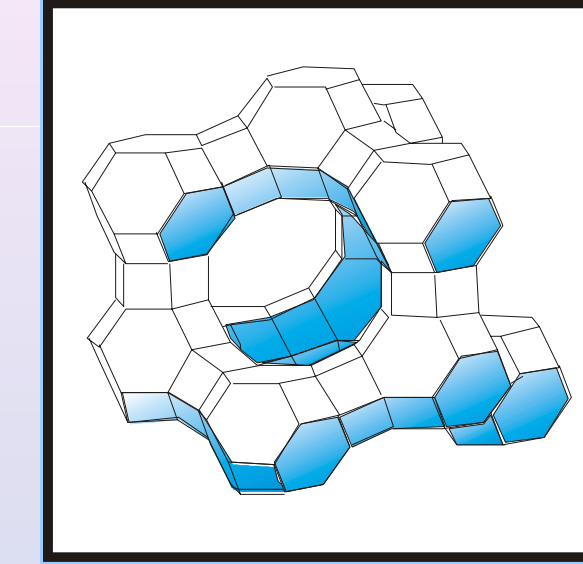


INFLUENCE OF THE COORDINATION CHANGE OF ALUMINUM ATOMS ON THE BRØNSTED ACIDITY OF DEALUMINATED ZEOLITES Y

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INTRODUCTION

Generally, the catalytic behavior of aluminosilicate-type zeolites strongly depends on the distribution of aluminum atoms on framework and extra-framework positions. Studying dealuminated zeolite H-Beta by solid-state NMR spectroscopy, a change of the aluminum coordination from octahedral to tetrahedral was found upon adsorption of a strong base [1].

After steaming of zeolite H-Y with low water vapor pressures, a formation of framework-related AlOH groups at octahedrally coordinated aluminum species was observed [2]. Again, adsorption of ammonia converted these aluminum species back to a tetrahedral coordination. In the present work, the relationship between the coordination change of aluminum species in dealuminated zeolites Y and the amount of Brønsted acid sites in these materials was investigated by spectroscopic techniques.

EXPERIMENTAL

• Zeolite NH₄-Y was obtained by **ion exchange** of a commercial Na-Y sample (Degussa, $n_{\text{Si}}/n_{\text{Al}} = 2.7$) in a 1 M aqueous NH₄NO₃ solution, until an exchange degree of 93 % was reached.

• Zeolite NH₄-Y was **dealuminated** at 813 K in a flow of nitrogen (200 cm³/min) through a horizontal quartz glass tube saturated with water vapor at temperatures of 40 to 98 °C (corresponding to $p_{\text{H}_2\text{O}} = 7.4$ to 94.3 kPa). The dealuminated zeolites Y were denoted according to the saturator temperature (in °C) in the experiment, e.g. DAY98.

• To study the coordination change of the aluminum atoms, the materials were dehydrated at 723 K, **loaded with ammonia** (50 kPa) for 1.5 h, and subsequently evacuated at room temperature for 10 min.

• All samples were **characterized** in the hydrated state by XRD, AES, ²⁹Si and ²⁷Al MAS NMR spectroscopy. Before the ¹H MAS NMR investigations the zeolites were dehydrated at 723 K.

• 1D **NMR** studies were carried out on a Bruker MSL-400 spectrometer at resonance frequencies of 400.1 MHz, 104.3 MHz and 79.5 MHz for ¹H, ²⁷Al and ²⁹Si, respectively. ²⁷Al 3QMAS NMR investigations were performed on a Bruker Avance 500 WB spectrometer at a resonance frequency of 130.3 MHz using a 3-pulse-sequence with z-filter [3].

RESULTS AND DISCUSSION

²⁹Si MAS NMR spectroscopy: From the relative intensities of the Si(*n*Al)-signals the framework aluminum content per unit cell (N_{Al}) can be calculated [4]. For the zeolites NH₄-Y, DAY40, DAY80 and DAY98, N_{Al} -values of 51.8/uc, 49.4/uc, 42.9/uc and 31.0/uc were found according to a stronger dealumination of these zeolites with increasing partial pressure of water vapor during the steaming process. Ammonia loading had only a minor influence on these results.

²⁷Al 3QMAS NMR spectroscopy: As a prerequisite for the quantitative evaluation of 1D ²⁷Al MAS NMR spectra the ²⁷Al quadrupolar parameters of all aluminum species were determined [5]. Fig. 1 shows the ²⁷Al 3QMAS NMR spectra of the dealuminated zeolite DAY98 and DAY98N (sample after ammonia loading). These 2D spectra show two different signals of tetrahedrally coordinated aluminum species (Al^{IVa} and Al^{IVb}) with completely different quadrupolar parameters (noticeable as the distance between the center of a signal and the diagonal line in Fig. 1). In addition a signal of octahedrally coordinated aluminum atoms (Al^{VI}), and, after loading the sample with ammonia (zeolite DAY98N), an additional peak of five-fold coordinated aluminum species occurs.

The quadrupolar parameters (isotropic chemical shift δ_{iso} and second-order quadrupolar effect parameter *SOQE*) derived from the ²⁷Al 3QMAS NMR spectra are:

- Al^{IVa}: $\delta_{\text{iso}} = 62$ ppm, *SOQE* = 2.2 MHz
- Al^{IVb}: $\delta_{\text{iso}} = 61$ ppm, *SOQE* = 6.7 MHz
- Al^{VI}: $\delta_{\text{iso}} = 31$ ppm, *SOQE* = 3.3 MHz
- Al^{IV}: $\delta_{\text{iso}} = 0$ ppm, *SOQE* = 2.0 MHz

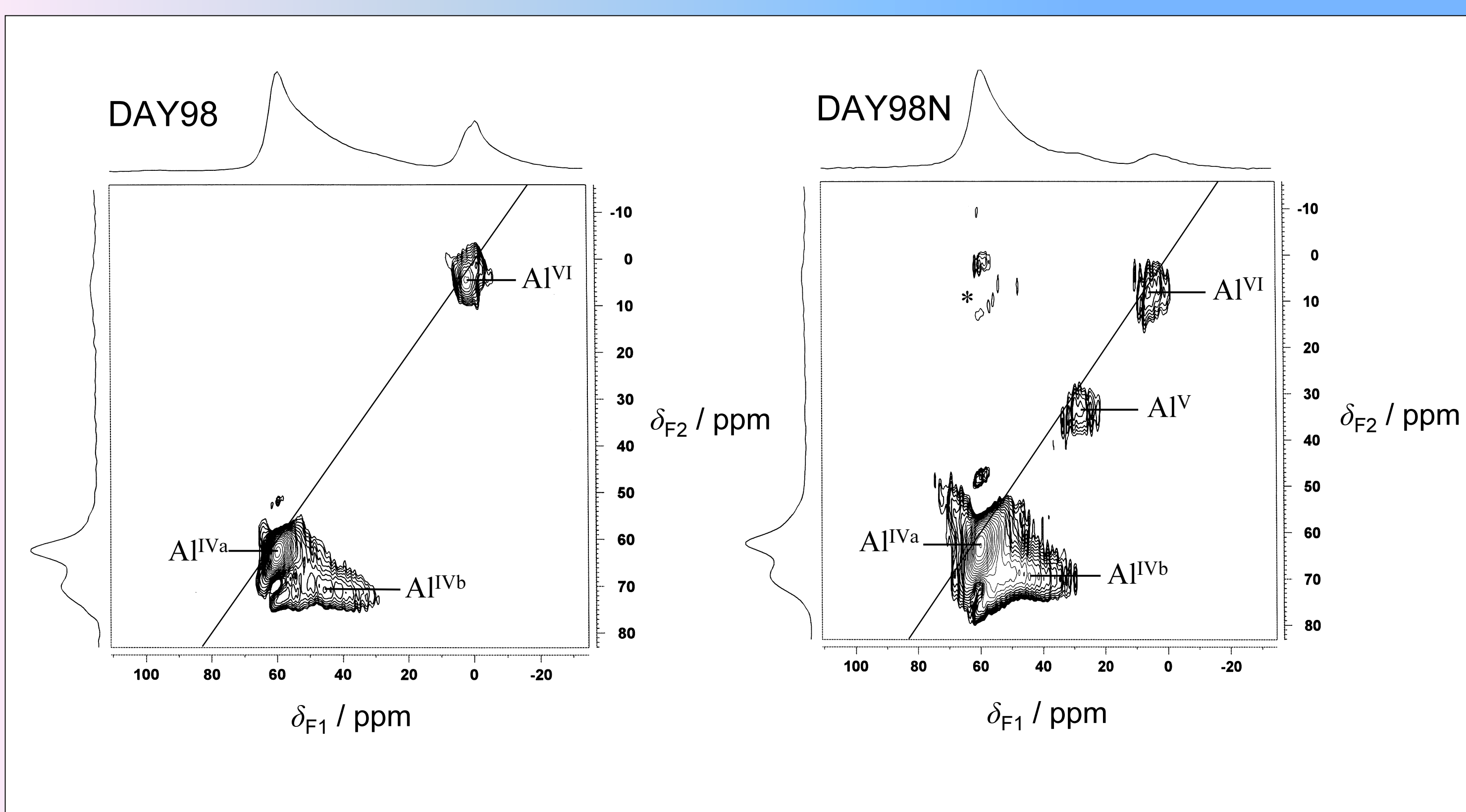


Fig. 1: ²⁷Al 3QMAS NMR spectra of dealuminated zeolite DAY98 before (left) and DAY98N after (right) loading with ammonia; * spinning side band.

1D ²⁷Al MAS NMR spectroscopy: With the quadrupolar parameters of the four different aluminum species and a correction of Massiot et al. [6], taking into account the signal intensity distribution to central and satellite transitions and also to spinning side bands, it was possible to simulate the 1D ²⁷Al MAS NMR spectra of the dealuminated zeolites quantitatively. Fig. 2 shows the ²⁷Al MAS NMR spectra (including the simulations) of zeolite DAY98 before (b) and after (a) loading of the sample with ammonia. Part c) of Fig. 2 is the difference of these two spectra. It was possible to perform the simulation without introducing an Al^{IV} signal, which can be understood in terms of a very low contribution of this signal to the whole intensity in the ²⁷Al 3QMAS NMR spectrum. Table 1 gives the results of the simulations for zeolite NH₄-Y and the dealuminated samples before and after the ammonia loading. Comparison of the amount of aluminum atoms in the different coordinations with the framework aluminum contents, calculated from ²⁹Si MAS NMR spectra, shows that the influence of a reversible coordination change upon ammonia loading has to be taken into account.

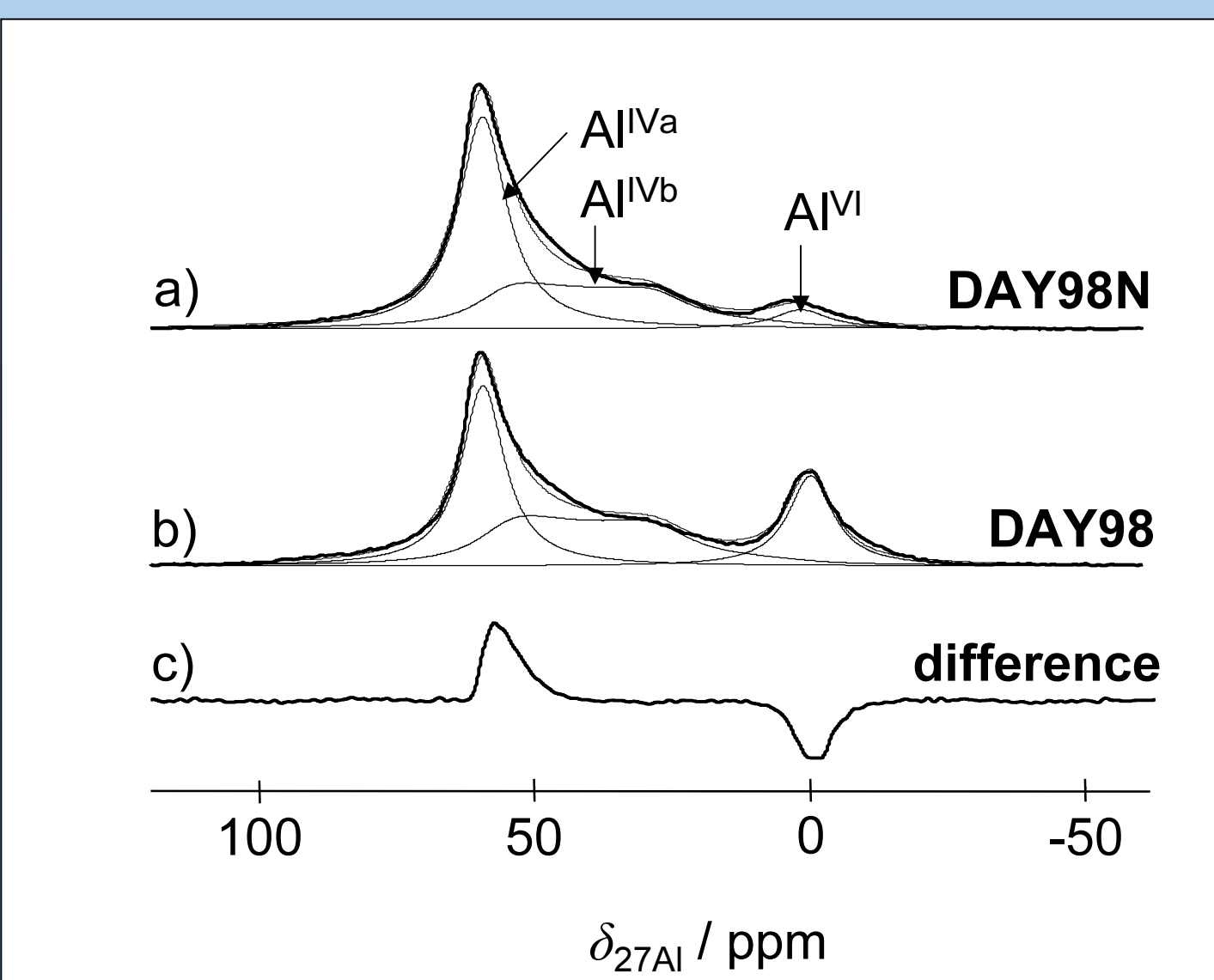


Fig. 2: ²⁷Al MAS NMR spectra and simulations of zeolite DAY98 a) after and b) before ammonia loading; c) difference spectrum of a) and b).

By interpreting the Al^{IVa} signal in terms of framework aluminum atoms, the Al^{IVb} signal as distorted tetrahedral aluminum atoms, and the Al^{VI} signal as octahedral extra-framework aluminum, the discrepancy between $N_{\text{Al, IVa}}$ before the ammonia loading and the framework aluminum content, derived from ²⁹Si MAS NMR spectra can be eliminated within an accuracy of 10 %.

¹H MAS NMR spectroscopy: Simulation and quantitative evaluation of ¹H MAS NMR spectra (Table 2) yield amounts of Brønsted acid sites (SiOHAl groups), AlOH, and SiOH groups per unit cell. Surprisingly, upon steaming the amount of SiOHAl decreases strongly for weak dealumination and increases again with a more severe hydrothermal treatment. The latter can be explained by the existence of highly charged extra-framework aluminum ions, compensating the negative framework charge, in the case of weak dealumination (DAY40). In DAY80 and DAY98, Brønsted acid sites rather than condensed extra-framework aluminum ions with a low charge act as compensating species.

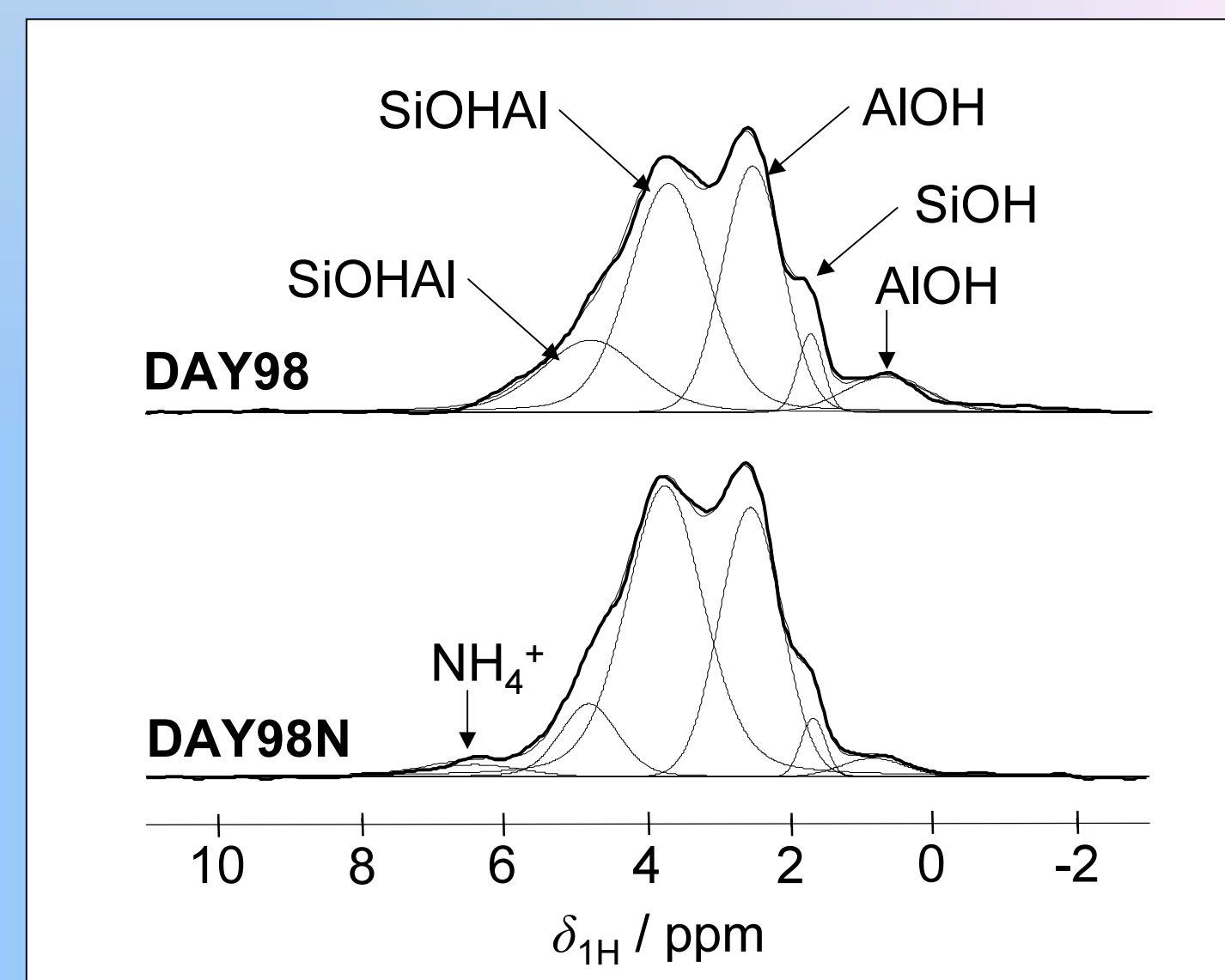


Fig. 3: ¹H MAS NMR spectra and simulations of the dealuminated and dehydrated zeolite DAY98 before and DAY98N after ammonia loading.

Table 1: Amounts of aluminum atoms per unit cell in Al^{IVa}, Al^{IVb}, and Al^{VI} coordination for zeolite NH₄-Y and the dealuminated zeolites before and after ammonia loading

sample	$N_{\text{Al, IVa}} / \text{uc}$	$N_{\text{Al, IVb}} / \text{uc}$	$N_{\text{Al, VI}} / \text{uc}$
NH ₄ -Y	52.0	-	-
DAY40	41.4	-	10.6
DAY80	32.2	10.2	9.6
DAY98	20.3	21.2	10.5
DAY40N	49.8	-	2.2
DAY80N	39.3	9.9	2.8
DAY98N	28.2	20.9	2.9

Table 2: Amounts of SiOHAl, AlOH and SiOH groups per unit cell for zeolite H-Y and the dealuminated zeolites before and after the ammonia loading

sample	$N_{\text{SiOHAl}} / \text{uc}$	$N_{\text{AlOH}} / \text{uc}$	$N_{\text{SiOH}} / \text{uc}$
H-Y	45.8	-	0.9
DAY40	5.6	5.4	1.8
DAY80	14.4	12.1	1.5
DAY98	18.5	12.0	1.4
DAY40N	4.2	4.9	0.4
DAY80N	22.8	11.4	1.1
DAY98N	22.8	13.7	1.1

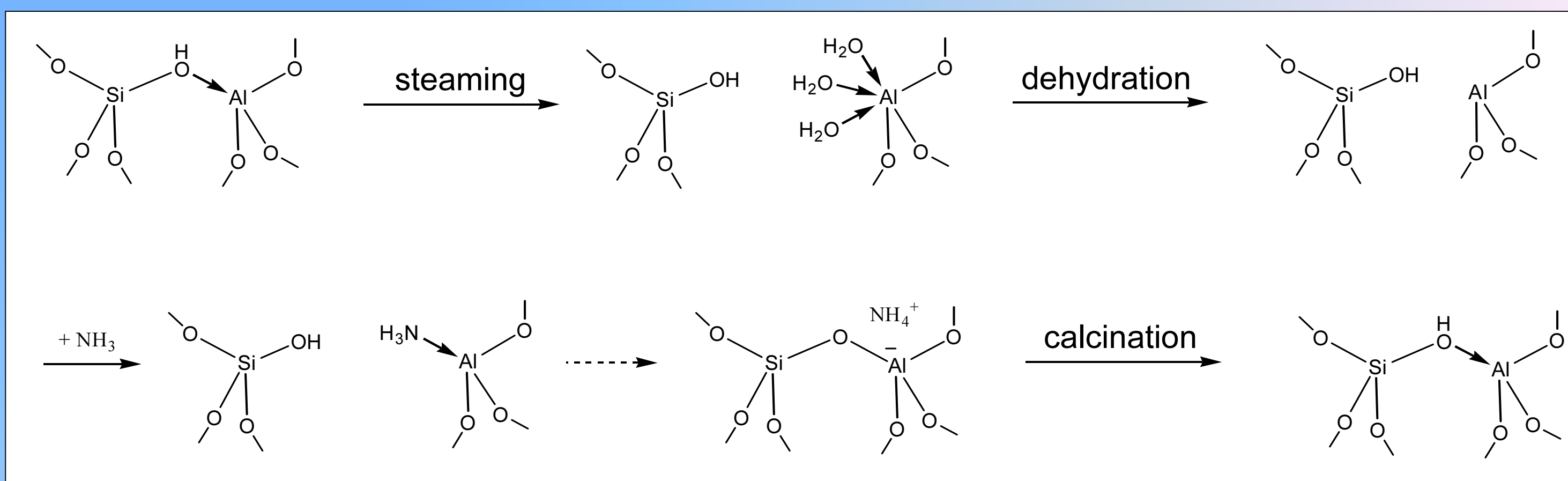


Fig. 4: Mechanism of reversible coordination change of framework aluminum atoms upon steaming, dehydration, and subsequent ammonia loading of zeolites Y and its influence on the Brønsted acidity.

Mechanism of coordination change: The above results can be accounted for by a mechanism shown in Fig. 4. Upon steaming, octahedrally coordinated framework aluminum is formed, which can, after dehydration in the presence of a strong base (ammonia), be converted back to tetrahedrally coordinated aluminum atoms in the local structure of bridging SiOHAl groups.

CONCLUSIONS

- Quantitative determination of aluminum species with different quadrupolar parameters in hydrothermally treated zeolites Y.
- Influence of the coordination change of framework aluminum atoms on ²⁷Al MAS NMR spectra and the amount of Brønsted acid sites.
- Proposed mechanism of the coordination change of partially hydrolyzed framework aluminum atoms and the possibility to recover the Brønsted acidity upon ammonia loading.

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Financial support of this work by Max-Buchner-Forschungstiftung and Deutsche Forschungsgemeinschaft is gratefully acknowledged.