Characterization and Acidic Properties of Aluminum-Exchanged Zeolites X and Y

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Zeolites Al,Na−X and Al,Na−Y with defined numbers of extraframework aluminum cations were prepared by exchange in an aqueous solution of aluminum nitrate. A maximum concentration of Brønsted acidic bridging OH groups in supercages ($SiOH^{sup}Al$) was reached upon dehydration of zeolites Al,Na−X and Al,Na−Y at 423 K. Further raising of the dehydration temperature led to a dehydroxylation of zeolites due to the recombination of aluminum hydroxyl groups with hydroxyl protons of bridging OH groups. High-field ^{27}Al multiple-quantum magic-angle spinning (MQMAS) NMR spectroscopy was utilized to study zeolites Al,Na−X/61 and Al,Na−Y/63 dehydrated at 423 K. Second-order quadrupolar effect parameters of 10.1−11.0 MHz for tetrahedrally coordinated framework aluminum atoms, compensated in their negative charge by hydroxyl protons ($\mathbf{Al^{IV}}/H^+$) and aluminum cations ($\mathbf{Al^{IV}}/Al^{x+}$), 3.6−4.4 MHz for tetrahedrally coordinated framework aluminum atoms compensated by sodium cations ($\mathbf{Al^{IV}}/Na^+$), and 5.6−7.6 MHz for pentacoordinated extraframework aluminum cations ($\mathbf{Al^{x+}}$ **cat.**) were obtained. Comparison of the number of AlOH groups with the number of pentacoordinated extraframework aluminum cations determined by one-dimensional high-field ^{27}Al MAS NMR spectroscopy gave a ratio near 1:1. This finding and the five-fold coordination of the cationic extraframework aluminum species hint to the presence of $HO-Al^+-O-Al^+-OH$ compounds, but also a minor number of $Al(OH)_2^+$ and AlO^+ species could exist. The enhanced acid strength of bridging OH groups in zeolites Al,Na−X and Al,Na−Y in comparison with zeolites H,Na−X and H,Na−Y, as found by adsorption of acetonitrile, may be due to a polarizing effect of cationic extraframework aluminum species in the vicinity of Brønsted acid sites.

Introduction

Due to the strongly acidic properties of zeolites, these solid catalysts are widely used in the hydrocarbon processing industry.[1] In heterogeneously catalyzed reactions, Brønsted and Lewis acid sites of zeolites play an important role as active surface sites. Brønsted acid sites acting as proton donors consist of hydroxyl protons covalently bonded to oxygen atoms bridging framework silicon and aluminum atoms.[2] Lewis acid sites acting as electron pair acceptors are extraframework species, e.g., formed by cation exchange or caused by steaming to create lattice defects and extraframework aluminum clusters.[3] The change in the distribution of framework aluminum atoms affects the acid strength of the hydroxyl groups in zeolite. Framework aluminum atoms with no second-neighbor aluminum atoms are responsible for strong Brønsted acid sites.[4] Moreover, the presence of multivalent extraframework cations acting as Lewis acid sites is discussed, as it is thought to play an important role in the creation of strong Brønsted acid sites in zeolites.

Multivalent lanthanum cations in lanthanum-exchanged zeolites are proposed to influence the framework via a polarizing or inductive effect, i.e., a withdrawing of electrons from the framework hydroxyl groups, which leads to an increase of the strength of the Brønsted acid sites in their vicinity.[4−6] Vayssilov and Rusch reported that charge compensation by alkali or alkaline-earth metal cations instead of protons can stabilize the deprotonated form of the zeolite.[7] This effect leads to a decrease of the deprotonation energy,[7] which corresponds to an increase of the acid strength of the bridging OH groups. In addition, the combination of Brønsted and Lewis acid sites, e.g., by a coordination of extraframework aluminum species at the bridging oxygen atom of SiOHAl groups, was suggested to be the reason for the enhanced acidity of zeolites.[8] On the other hand, Mota et al. reported that only $Al(OH)_2^+$ increases the acid strength of neighboring Brønsted acid sites by hydrogen bonding between extraframework aluminum hydroxyls and oxygen atoms of the formed AlO_4^- tetrahedral and no Brønsted/Lewis synergism, as discussed by Mirodatos and Barthomeuf,[8] was found.[9]

Extraframework aluminum species may occur as Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, AlOOH, $Al(OH)_3$, and Al_2O_3.[10] Among these compounds, the cationic extraframework aluminum species Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2^+$ act as strong Lewis acid sites,[10] which may directly initiate the hydrocarbon conversion via hydride abstraction.[11]

Solid-state NMR spectroscopy is an important method for the investigation of the oxygen coordination, local symmetry, and concentration of aluminum species at framework and extraframework positions in zeolites.[5,6,12−17] To reach a suitable resolution of ^{27}Al solid-state NMR spectra, zeolites are often studied in the hydrated state.[5,6] However, the hydration of calcined samples may result in changes of the coordination state and nature of the aluminum species in zeolites with high aluminum content and of extraframework aluminum species.[14]

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Therefore, ^{27}Al solid-state NMR investigation of dehydrated zeolites is an interesting approach to obtain direct insight into the surface sites responsible for the catalytic activity of these materials. However, such investigations are limited by the strong line broadening due to the quadrupolar interactions of aluminum nuclei with spin $I = {}^5/_2$. Nowadays, ^{27}Al high-speed magic-angle spinning (MAS) NMR and multiple-quantum MAS (MQMAS) NMR spectroscopy in high magnetic fields, such as $B_0 = 17.6$ T, allows the separation of signals caused by different aluminum species with strong quadrupolar interactions, making these approaches powerful tools for characterizing dehydrated zeolites.[14,17,18]

Aluminum-exchanged zeolites are attractive acidic catalysts, because of the presence of Lewis acidic extraframework aluminum species as well as Brønsted acid sites formed via the Hirschler−Plank mechanism by dissociation of water molecules in the electrostatic field of cations.[19] In the present work, solid-state NMR spectroscopy is utilized to study the different aluminum species in aluminum-exchanged zeolites X and Y in the dehydrated state and to investigate the concentration, distribution, and strength of Brønsted acid sites. The hydroxyl coverage of zeolites Al,Na−X and Al,Na−Y with different aluminum exchange degrees and upon dehydration treatments at 393−673 K was quantitatively investigated by ^{1}H MAS NMR spectroscopy. Deuterated acetonitrile and pyridine were adsorbed as probe molecules on the dehydrated zeolites to study the acid strength and accessibility of hydroxyl groups formed in these materials. The framework and extraframework aluminum species in dehydrated zeolites Al,Na−X and Al,Na−Y were investigated by ^{27}Al high-speed MAS NMR and MQMAS NMR spectroscopy in a magnetic field $B_0 = 17.6$ T. For the first time, the strength of Brønsted acid sites in aluminum-exchanged zeolites was quantitatively compared with those of H-form and lanthanum-exchanged zeolites. These experiments demonstrate the effect of Lewis acidic extraframework species, as existing in dealuminated materials, on the acidity of these catalysts.

Experimental Section

1. Preparation of the Materials. Zeolites Na−X ($n_{Si}/n_{Al} = 1.3$) of Union Carbide Corporation, Tarrytown, NY, and Na−Y ($n_{Si}/n_{Al} = 2.7$) of Degussa AG, Hanau, Germany, were 1- or 2-fold exchanged in a 1.0 M aqueous solution of $Al(NO_3)_3$ at 293 K for 4 h. The pH value of the solution was adjusted to 4 to avoid dealumination or destruction of the framework. The obtained ion-exchanged zeolites were washed by demineralized water until no nitrate ions were detected. Then they were dried in the air at 353 K. The ion-exchange degrees of aluminum-exchanged zeolites Al,Na−X/32, Al,Na−X/61, Al,Na−Y/34, and Al,Na−Y/63 were determined by atomic emission spectroscopy (ICP-AES) to 31.6, 60.8, 34.0, and 63.2%, respectively. These zeolite materials were dehydrated using the following procedure: Heating with a rate of 20 K/h up to temperatures of 393 to 673 K and evacuation at a pressure of $p < 10^{-2}$ mbar for 12 h.

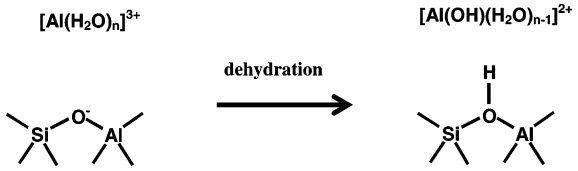
Acetonitrile-d_3 (99.9% deuterated) and pyridine-d_5 (99.5% deuterated) were purchased from ACROS and EURISO, respectively. With the use of a vacuum line, the dehydrated zeolite samples were quantitatively loaded with one probe molecule per bridging OH group.

2. Spectroscopic Characterization. ^{1}H and ^{29}Si MAS NMR studies were carried out on a Bruker MSL 400 spectrometer at resonance frequencies of 400.13 and 79.49 MHz, respectively. ^{1}H MAS NMR spectra were recorded with a standard 4 mm double-bearing Bruker MAS probe, a sample spinning rate of ca. 8 kHz, a corresponding single-pulse $\pi/2$ excitation, and a repetition time of 10 s. ^{29}Si MAS NMR investigations were performed with a 7 mm double-bearing Bruker MAS standard probe, a rotation frequency of ca. 4 kHz, a recycle delay of 10 s, and after a single-pulse $\pi/2$ excitation. ^{27}Al high-speed MAS NMR and ^{27}Al MQMAS NMR experiments were carried out on a Bruker Avance 750 ($B_0 = 17.6$ T) spectrometer at the resonance frequency of 195.4 MHz using a 2.5 mm MAS NMR probe with a sample spinning frequency of ca. 30 kHz. The one-dimensional spectra were recorded upon single-pulse $\pi/12$ exitation with a pulse duration of 0.34 μs. The DFS-enhanced ^{27}Al MQMAS NMR spectra were obtained applying the split-t_1 echo pulse sequence with hard pulses of 3.3 and 13.7 μs and an rf field strength corresponding to the nutation frequency of 125 kHz and a soft pulse of 47 μs with a nutation frequency of 10 kHz. The experiment repetition time was 2 s.

Before starting the ^{1}H and ^{27}Al MAS NMR measurements, the dehydrated samples were placed into 4 and 2.5 mm MAS rotors, respectively, in a glovebox purged with dry nitrogen. For quantitative ^{1}H MAS NMR measurements, a nonhydrated zeolite H,Na−Y (ammonium exchange degree of 35%) with 1.776 mmol OH groups per gram and a weight of 58.5 mg was used as an external intensity standard. Prior to ^{29}Si MAS NMR studies, the samples were exposed to an atmosphere that was saturated with vapor of a $Ca(NO_3)_2$ solution at ambient temperature to be fully hydrated. These studies indicated that no significant dealumination of zeolites X and Y occurred as a result of aluminum exchange.

Bruker software packages *WINNMR* and *WINFIT* were utilized for the decomposition and simulation of the NMR spectra. The transformation and evaluation of MQMAS spectra were performed using *XWINNMR*.

SCHEME 1



Results and Discussion

1. Concentration of OH Groups on Dehydrated Zeolites Al,Na−X and Al,Na−Y. According to the Hirschler−Plank mechanism,[19] the dehydration of zeolites exchanged with multivalent metal cations results in the generation of Brønsted acid sites in the pores and cavities (Scheme 1). Water molecules dissociate in the local electrostatic fields of multivalent metal cations, which leads to the formation of OH groups at the metal cations (e.g., AlOH) and hydroxyl protons bound to oxygen bridges between framework silicon and aluminum atoms. These bridging hydroxyl groups (SiOHAl) are the catalytically active Brønsted sites of acidic zeolites.

By quantitative evaluation of the ^{1}H MAS NMR intensities obtained before and after dehydration, the number of water molecules desorbed during dehydration was determined. The curve of desorbed water at temperatures of 300 to 673 K (Figure 1) shows a sharp and intense maximum at 393 K and two weak maxima at ca. 473 and 573 K. Three different reasons were suggested for the water release from ion-exchanged zeolites:[20] (i) Release of physisorbed water, (ii) dehydration of multivalent cations, and (iii) dehydroxylation of the zeolite. Dehydration at 300 to 393 K causes the desorption of physisorbed water molecules responsible for the strong maximum at 393 K

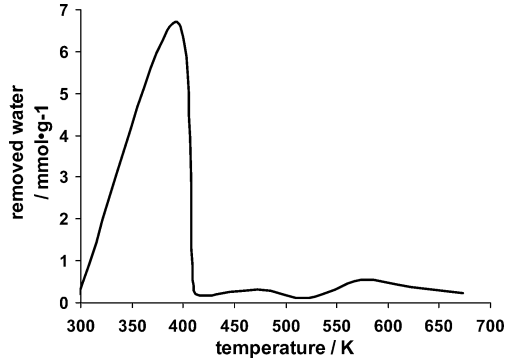


Figure 1. Number of water molecules desorbed during dehydration of zeolite Al,Na−Y/63 at temperatures of 300 to 673 K.

(i). The weak maximum at ca. 473 K is caused by the desorption of water molecules, which are more strongly bound, such as to multivalent cations (ii). Upon dehydration at 573 K, the hydroxyl groups formed via the Hirschler−Plank mechanism are dehydroxylated by the recombination of AlOH and bridging hydroxyl groups (iii).[6] These hydroxyl groups are formed after the desorption of most of the physisorbed water molecules and only if a few water molecules are coordinated to the strongly polarizing multivalent cations. ^{1}H MAS NMR spectroscopy is a very suitable method for the quantitative evaluation of this combined dehydration, hydroxylation, and dehydroxylation process.

Figure 2 shows ^{1}H MAS NMR spectra of zeolites Al,Na−X and Al,Na−Y recorded upon dehydration at 473 and 673 K. The signals occurring at $\delta_{1H} = 0.4$ and 2.5 ppm in the spectra of zeolites Al,Na−X are due to AlOH groups. The signal at $\delta_{1H} = 1.7$ ppm is caused by SiOH groups, while the signals at $\delta_{1H} = 3.6$ and 4.6 ppm are assigned to bridging OH groups in the supercages ($SiOH^{sup}Al$) and sodalite cages ($SiOH^{sod}Al$), respectively, of the faujasite framework. Similarly, the ^{1}H MAS NMR spectra of dehydrated zeolites Al,Na−Y consist of signals of AlOH groups at $\delta_{1H} = 0.6$ and 2.7 ppm, silanol groups at $\delta_{1H} = 1.9$ ppm, and bridging OH groups in the supercages and sodalite cages at $\delta_{1H} = 3.9$ and 4.9 ppm, respectively.[23,24]

In order to determine the influence of the aluminum exchange degree and the dehydrated temperature on the concentration of OH groups of zeolites Al,Na−X and Al,Na−Y, a quantitative evaluation of the ^{1}H MAS NMR intensities and simulation of the spectra has been performed. The results of these investigations are summarized in Figures 3 and 4. Upon dehydration at 393 K, the first signals of bridging OH and AlOH groups formed via the pathway in Scheme 1 occur, which is indicated by signals at $\delta_{1H} = 3.6$ and 2.5 ppm, respectively, for zeolites Al,Na−X, and at $\delta_{1H} = 3.9$ and 2.7 ppm, respectively, for zeolites Al,Na−Y. After dehydration at low temperatures, the resolution of the ^{1}H MAS NMR analysis is poor and the signals of hydroxyl groups are broadened by rapid exchange with residual water molecules.

With increasing dehydration temperature, the concentration of SiOHAl groups in the supercages ($SiOH^{sup}Al$) increases and reaches a maximum at 423 K. In agreement with previous studies on lanthanum-exchanged zeolites,[6] the number of Brønsted acid sites correlates with the number of extraframework cations. The maximum numbers of SiOHAl groups in zeolites Al,Na−X/61 and Al,Na−Y/63 are, by a factor of 1.7 to 1.8, higher than those of zeolites Al,Na−X/32 and Al,Na−Y/34. This factor agrees well with the ratio of exchange degrees (Al,Na−X, 61%/32% = 1.90; Al,Na−Y, 63%/34% = 1.85).

Upon further increase of the dehydration temperatures, a continuous decrease of the concentration of OH groups occurs

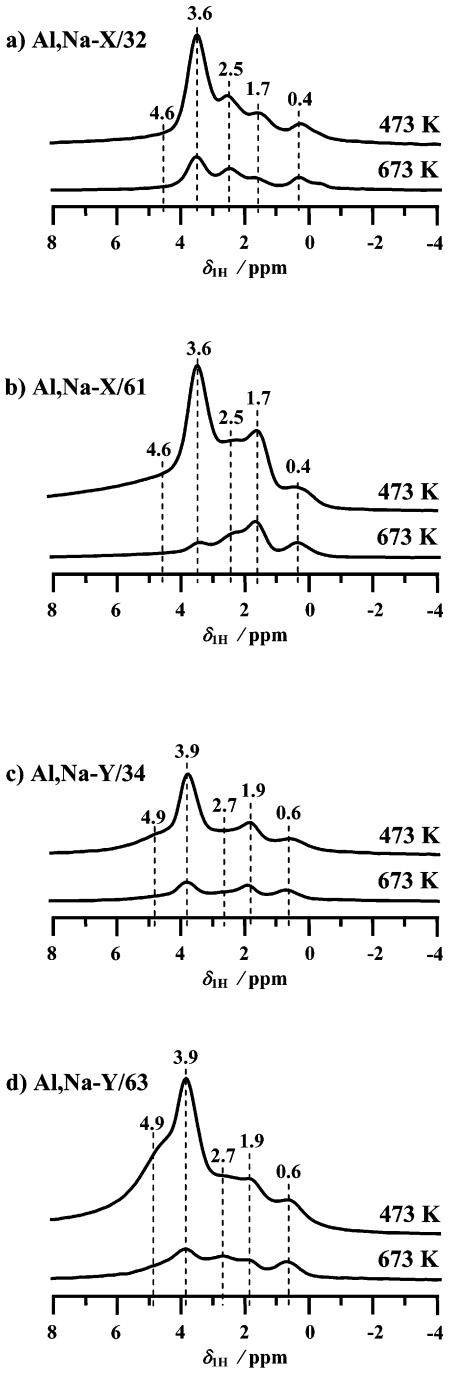


Figure 2. ^{1}H MAS NMR spectra of zeolites Al,Na−X/32 (a), Al,Na−X/61 (b), Al,Na−Y/34 (c), and Al,Na−Y/63 (d) dehydrated at 473 and 673 K.

combined with an ongoing dehydration of the zeolites (compare Figures 1, 3, and 4). This finding indicates that the dehydroxylation of AlOH and SiOHAl groups has started. After increasing the temperature to $T = 573$ K, the concentration of bridging OH groups strongly decreases, e.g., according the mechanism shown in Scheme 2. At 673 K, ca. 80 to 90% of bridging OH groups formed via the Hirschler−Plank mechanism recombined to water, which desorbed from the zeolites as a result of thermal treatment.

Considering the ratio of the number of AlOH and SiOHAl groups formed in zeolites Al,Na−X and Al,Na−Y upon dehydration at 393 to 673 K, generally more SiOHAl groups than AlOH groups were observed. However, their ratio should be 1:1 according to the Hirschler−Plank mechanism. Therefore,

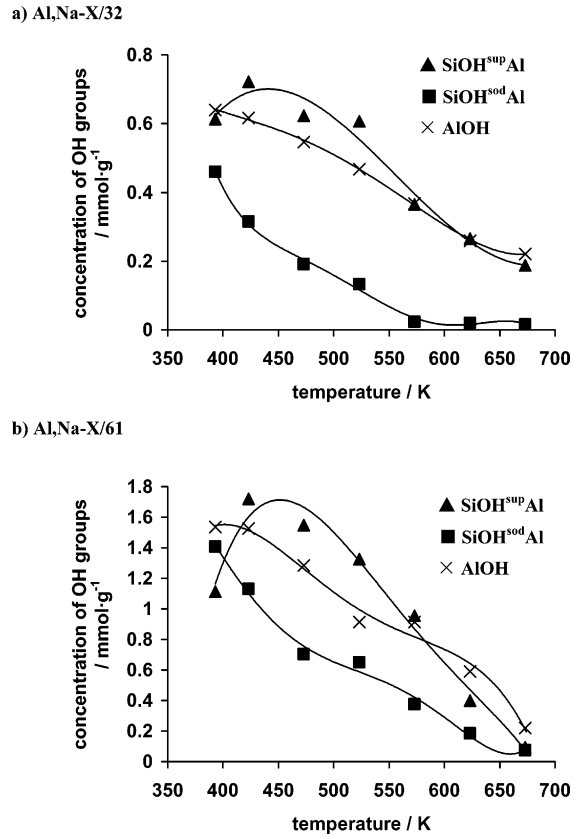


Figure 3. Concentration of bridging OH groups in supercages ($SiOH^{sup}$-Al) and sodalite cages ($SiOH^{sod}Al$) and of aluminum OH groups (AlOH) in zeolites Al,Na−X/32 (a) and Al,Na−X/61 (b) plotted as a function of the dehydration temperature (accuracy ±10%). (Al,Na−X/32, 0.0771 mmol u.c. per gram; Al,Na−X/61, 0.0791 mmol u.c. per gram.)

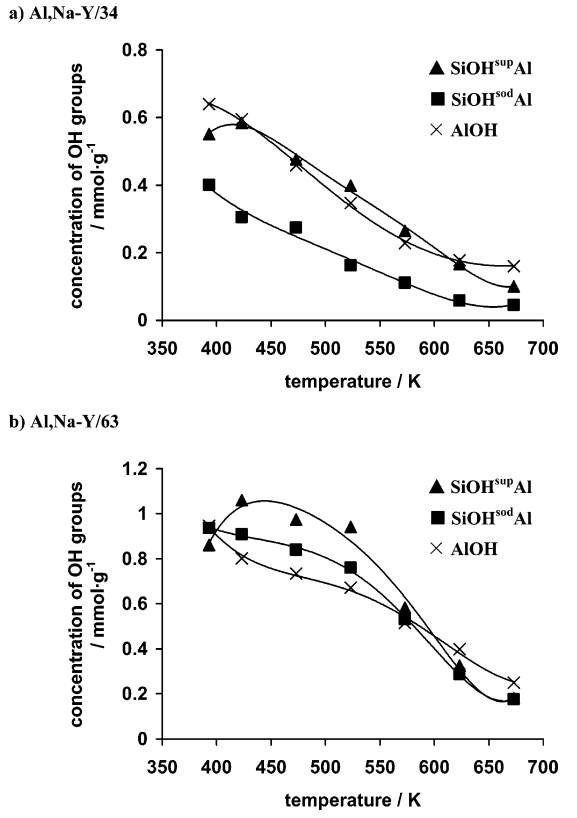
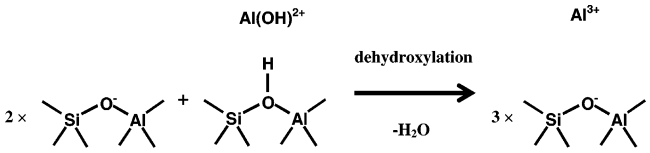


Figure 4. Concentration of bridging OH groups in supercages ($SiOH^{sup}$-Al) and sodalite cages ($SiOH^{sod}Al$) and of aluminum OH groups (AlOH) in zeolites Al,Na−Y/34 (a) and Al,Na−Y/63 (b) plotted as a function of the dehydration temperature (accuracy ±10%). (Al,Na−Y/34, 0.0805 mmol u.c. per gram; Al,Na−Y/63, 0.0819 mmol u.c. per gram.)

an additional mechanism must exist leading to a decrease of the number of AlOH groups. A possible explanation could be the formation of $Al(OH)_2^+$ species in combination with two SiOHAl groups. In a further step, some of the $Al(OH)_2^+$ species are dehydroxylated to AlO^+ under the formation of water molecules, which is desorbed from the zeolite. Since that total number of positive charges at the extraframework aluminum species does not increase in this case, the dehydroxylation of $Al(OH)_2^+$ species is not necessarily accompanied by a dehydroxylation of SiOHAl groups.

2. Accessibility and Acidic Strength of OH Groups in Al,Na−X and Al,Na−Y Zeolites. To understand the catalytic function of acid zeolites, it is necessary to consider not only the number of acid sites but also their accessibility and acid strength. Therefore, deuterated pyridine (C_5D_5N) was introduced as a probe molecule to characterize the accessibility of OH groups formed in the zeolites.[6,21−23] Figure 5 shows the ^{1}H MAS NMR spectra of dehydrated (473 K) zeolites Al,Na−X/32, Al,Na−X/61, Al,Na−Y/34, and Al,Na−Y/63 recorded before and after loading with C_5D_5N. The assignments of the signals in the spectra obtained before C_5D_5N adsorption are the same as those for the spectra in Figure 2. After adsorption of C_5D_5N on dehydrated zeolites Al,Na−X and Al,Na−Y, the accessible Brønsted acid sites are involved in the protonation of pyridine to form the pyridinium ions $C_5D_5NH^+$, which results in a broad peak at δ_{1H} = 15−16 ppm.[6] Simultaneously, the signals of SiOHAl groups interacting with probe molecules disappeared. In the case of zeolites Al,Na−X and Al,Na−Y, signals of SiOHAl groups at δ_{1H} = 3.6−3.9 ppm disappear upon adsorption of deuterated pyridine, which indicates that these hydroxyl groups are located in the supercages. According to the molecular diameter of 0.68 nm, pyridine molecules cannot enter the six-ring windows of the sodalite cages.

SCHEME 2



Acetonitrile is a weak base and, therefore, suitable to discriminate Brønsted sites with different acid strength. Brønsted sites interact with acetonitrile via O−H···N-type hydrogen bonding. The application of deuterated acetonitrile (CD_3CN) allows ^{1}H MAS NMR studies of Brønsted acid sites without an overlapping of signals due to a probe molecule. The resonance shift $\Delta\delta_{1H}$ of the ^{1}H MAS NMR signal of SiOHAl groups upon adsorption of CD_3CN is utilized as a measure of the acid strength of the corresponding hydroxyl protons.[6,24−28] A strong resonance shift corresponds to a high acid strength.

Figure 6 shows the ^{1}H MAS NMR spectra of dehydrated (473 K) zeolites Al,Na−X/32, Al,Na−X/61, Al,Na−Y/34, and Al,Na−Y/63 recorded before and after loading with CD_3CN. In the case of zeolites Al,Na−X/32 and Al,Na−X/61, the signals of bridging OH groups in the supercages shift from δ_{1H} = 3.6 to 7.4 and 8.0 ppm corresponding to $\Delta\delta_{1H}$ values of 3.8 and 4.4 ppm, respectively. Upon adsorption of CD_3CN on zeolites Al,Na−Y/34 and Al,Na−Y/63, this resonance shift $\Delta\delta_{1H}$ is 5.3 ppm in both cases. These adsorbate-induced resonance shifts $\Delta\delta_{1H}$ are lower than those obtained upon adsorption of CD_3CN on lanthanum-exchanged zeolites ($\Delta\delta_{1H}$ = 3.8 and 4.9 ppm for La,Na−X/42 and La,Na−X/75 and $\Delta\delta_{1H}$ = 5.7 ppm for

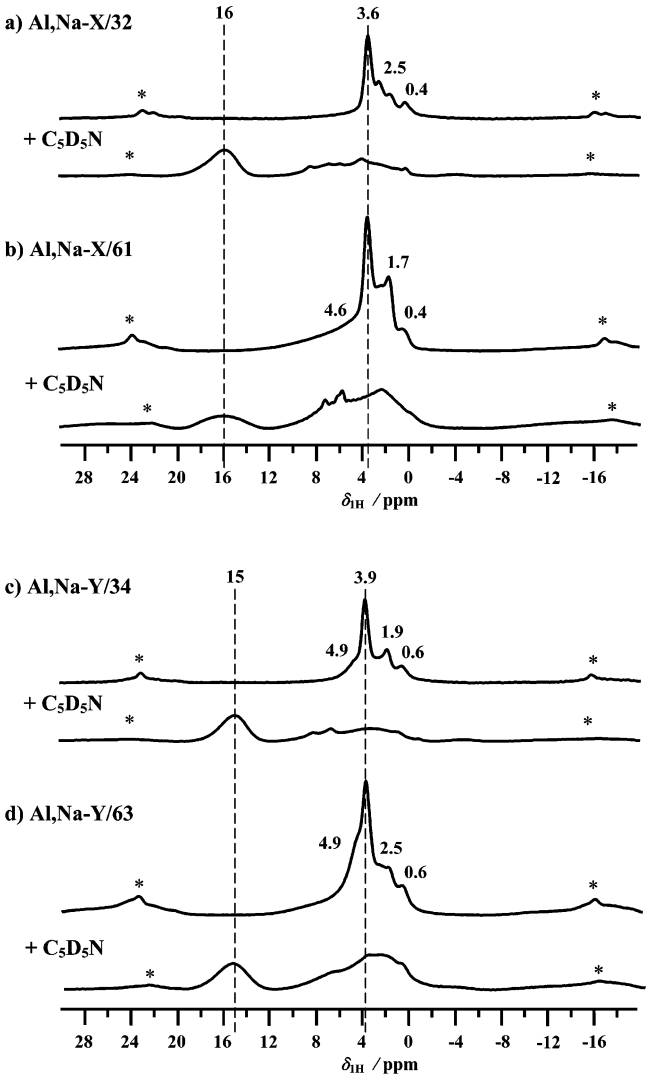


Figure 5. ^{1}H MAS NMR spectra of dehydrated (473 K) zeolites Al,Na−X/32 (a), Al,Na−X/61 (b), Al,Na−Y/34 (c), and Al,Na−Y/63 (d) recorded before (top) and after (bottom) loading with deuterated pyridine (C_5D_5N). Asterisks denote spinning side bands.

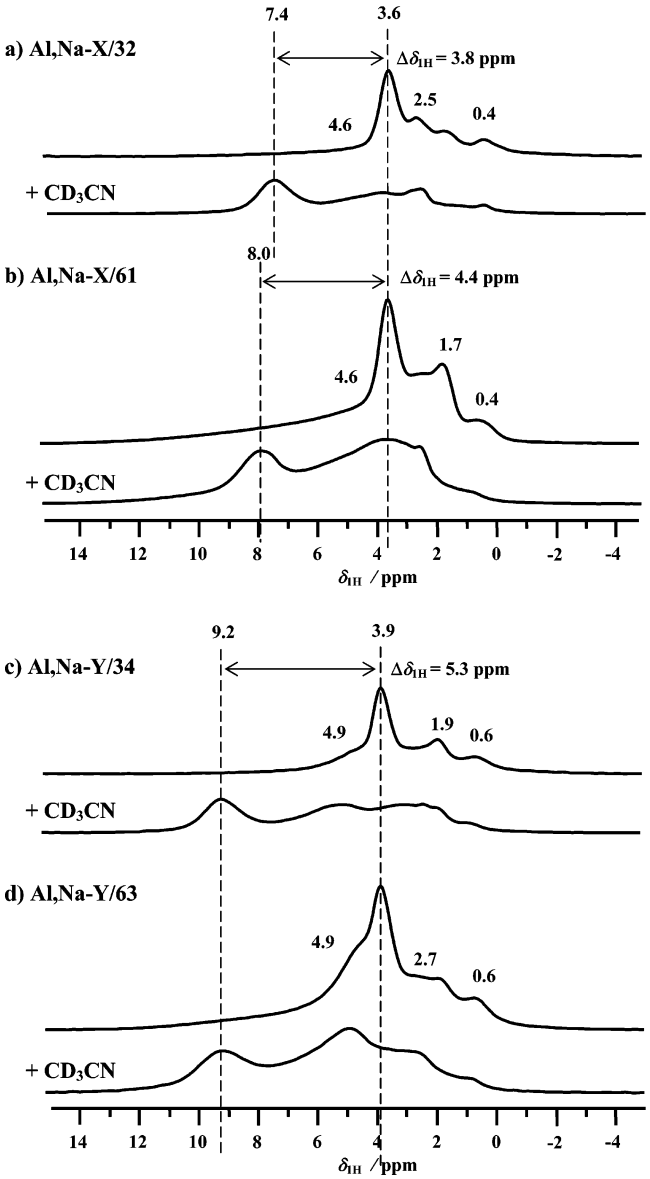


Figure 6. ^{1}H MAS NMR spectra of dehydrated (473 K) zeolites Al,Na−X/32 (a), Al,Na−X/61 (b), Al,Na−Y/34 (c), and Al,Na−Y/63 (d) recorded before (top) and after (bottom) loading with deuterated acetonitrile (CD_3CN).

La,Na−Y/42 and La,Na−Y/74).[6] On the other hand, the adsorbate-induced resonance shifts $\Delta\delta_{1H}$ observed for zeolites Al,Na−X and Al,Na−Y are significantly higher than the values obtained for zeolite X ($\Delta\delta_{1H}$ = 3.6 ppm, see Figure S1, Supporting Information) and zeolite Y ($\Delta\delta_{1H}$ = 5.1 ppm)[25] in their H forms.

Zeolites X (n_{Si}/n_{Al} = 1.3) and Y (n_{Si}/n_{Al} = 2.7) are characterized by the same framework type (faujasite), but different framework n_{Si}/n_{Al} ratios. The higher average electronegativity of zeolite Y having the higher framework n_{Si}/n_{Al} ratio results in a higher acid strength of Brønsted sites in comparison with those in zeolites X.[29] This is the reason for the higher acid strength of Brønsted sites in zeolites H,Na−Y ($\Delta\delta_{1H}$ = 5.1 ppm) and Al,Na−Y ($\Delta\delta_{1H}$ = 5.3 ppm) in comparison with Brønsted sites in zeolites H,Na−X ($\Delta\delta_{1H}$ = 3.6 ppm) and Al,Na−X ($\Delta\delta_{1H}$ = 3.8 to 4.4 ppm). In addition, extraframework cations may enhance the acid strength of zeolites by affecting the electronegativity of the zeolite framework.[29]

In the present study, the $\Delta\delta_{1H}$ value was found to increase with increasing aluminum exchange degree, i.e., for zeolites Al,Na−X/32 and Al,Na−X/61. However, no effect of the aluminum exchange degree on the acid strength of bridging OH groups in zeolites Al,Na−Y was found. This phenomenon was also detected in previous investigations for lanthanum-exchanged zeolites X and Y.[6] Zeolite X ($Al_{83.0}Si_{109.0}O_{384.0}\cdot xH_2O$) has significantly more framework aluminum atoms in comparison with Y ($Al_{51.9}Si_{140.1}O_{384.0}\cdot xH_2O$). At similar aluminum exchange degrees, therefore, the number of extraframework aluminum atoms is 1.6 times higher in zeolite Al,Na−X compared with zeolite Al,Na−Y. This may cause a stronger polarizing effect of extraframework aluminum species on Brønsted acid sites in zeolite X in comparison with zeolite Y.[5]

3. Solid-State ^{27}Al NMR Investigations of Dehydrated Zeolites Al,Na−X and Al,Na−Y. The comparison of the results of quantitative ^{1}H MAS NMR investigations of dehydrated zeolites Al,Na−X and Al,Na−Y with the distribution of the various aluminum species investigated by ^{27}Al solid-state NMR spectroscopy requires studies under identical conditions. Therefore, the ^{27}Al MQMAS NMR spectra shown in Figure 7 were recorded using zeolites Al,Na−X/61 (a) and Al,Na−Y/63 (b) dehydrated at 473 K, i.e., under the same conditions as the studies in Sections 1 and 2.

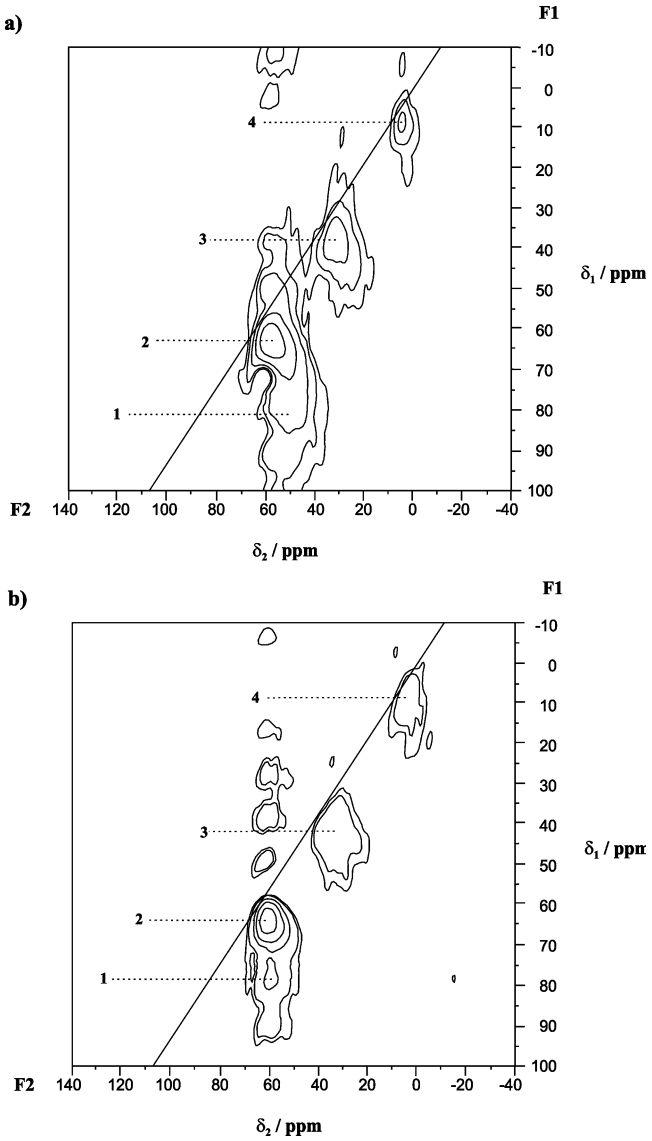


Figure 7. ^{27}Al MQMAS NMR spectra of dehydrated (473 K) zeolites Al,Na−X/61 (a) and Al,Na−Y/63 (b).

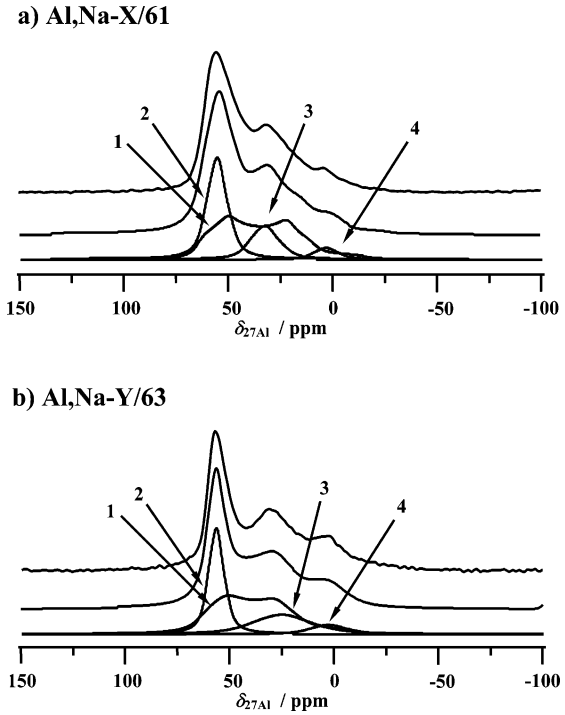


Figure 8. ^{27}Al high-speed MAS NMR spectra of dehydrated (473 K) zeolites Al,Na−X/61 (a) and Al,Na−Y/63 (b). The experimental spectra (top) are compared with the simulated spectra (bottom).

TABLE 1: Resonance Positions δ_1 and δ_2 along the *F*1 and *F*2 Dimensions, Chemical Shifts δ_{cs}, and Second-Order Quadrupolar Effect Parameters SOQE of Signals 1 to 4 Obtained by Evaluation of the ^{27}Al MQMAS NMR Spectra of Dehydrated Zeolites Al,Na−X/61 and Al,Na−Y/63 in Figure 7

zeolite	signal	δ_1/ppm	δ_2/ppm	δ_{CS}/ppm	SOQE/MHz
Al,Na−X/61	1	80	50	69	11.0
	2	64	58	61	4.4
	3	38	30	35	5.6
	4	8	0	5	5.6
Al,Na−Y/63	1	80	55	71	10.1
	2	64	60	62	3.6
	3	44	30	39	7.6
	4	10	0	6	6.2

The ^{27}Al MQMAS NMR spectrum of dehydrated zeolite Al,Na−X/61 shows four signals at chemical shifts δ_1 of ca. 75 ppm (signal 1), 64 ppm (signal 2), 38 ppm (signal 3), and 8 ppm (signal 4) in the *F*1 dimension (Figure 7a). In the spectrum of zeolite Al,Na−Y/63, similar signals occur at chemical shifts δ_1 of ca. 78 ppm (signal 1), 64 ppm (signal 2), 44 ppm (signal 3), and 10 ppm (signal 4) in the *F*1 dimension (Figure 7b). Along the *F*2 dimension, these signals are shifted to the resonance positions δ_2 due to second-order quadrupolar shift. On the basis of the shift values δ_1 and δ_2 summarized in Table 1, columns 3 and 4, and utilizing the evaluation procedure described by Rocha et al.,[34] the chemical shifts δ_{cs} (Table 1, column 5) and the second-order quadrupolar effect parameters SOQE (Table 1, column 6) were calculated. The second-order quadrupolar effect parameter SOQE differs from the quadruopole coupling constant C_{qcc} by a factor of $[1 + (\eta^2/3)]^{1/2}$ with the asymmetry parameter η, which is often on the order of 1. The second-order quadrupolar effect parameters obtained by high-field ^{27}Al MQMAS NMR spectroscopy of dehydrated zeolites Al,Na−X/61 and Al,Na−Y/63 are in the range of 4.4−11.0 MHz and 3.6−10.1 MHz, respectively.

On the basis of results of earlier investigations of aluminum species in zeolites H−Y and Al,Na−Y,[14,35] signal 1 with the highest quadrupole coupling constant of $C_{qcc} = 10-11$ MHz is assigned to a superposition of signals caused by tetrahedrally coordinated framework aluminum atoms compensated in their negative charge by hydroxyl protons of SiOHAl groups ($\mathbf{Al^{IV}}$/H^+) and by extraframework aluminum cations ($\mathbf{Al^{IV}}$/Al^{x+}). The weak quadrupolar interaction of aluminum atoms responsible for signal 2 ($C_{qcc} = 3.6$ to 4.4 MHz) indicates that this signal is due to tetrahedrally coordinated framework aluminum atoms compensated by extraframework sodium cations ($\mathbf{Al^{IV}}$/Na^+).[35] The chemical shift of 35−39 ppm and the quadrupole coupling constant of 5.6−7.6 MHz found for signal 3 agree well with the spectroscopic parameters of cationic extraframework aluminum species ($\mathbf{Al^{x+}}$ **cat.**) investigated in an earlier study.[14] According to their chemical shift value, these cationic aluminum species are pentacoordinated, which may be due to a coordination to the oxygen atoms of AlOH groups and to framework oxygen atoms near framework aluminum.[30] This coordination was proposed to be the reason for the strong quadrupolar broadening observed for the $\mathbf{Al^{IV}}$/Al^{x+} species contributing to signal 1 in the spectra of dehydrated zeolites Al,Na−X/61 and Al,Na−Y/63. Finally, signal 4 indicates the presence of octahedrally coordinated aluminum atoms ($\mathbf{Al^{VI}}$). Since residual water molecules may occur in zeolites X and Y dehydrated at

TABLE 2: Relative Intensities *I* and Concentration n_{Al} of Aluminum Species in Dehydrated (473 K) Zeolites Al,Na−X/61 and Al,Na−Y/63 Determined by Simulating the ^{27}Al High-Speed MAS NMR Spectra in Figure 8 (Accuracy of ±10%)

		signal			
		1	2	3	4
assignment		**Al^{IV}**/H$^+$ **Al^{IV}**/Al^{x+}	**Al^{IV}**/Na$^+$	**Al^{x+} cat.**	Al^{VI}
Al,Na−X/61	*I* (%)	42.9	37.8	16.9	2.4
($n_{Al,total}$ = 100.0)	n_{Al} (Al/u.c.)	42.9	37.8	16.9	2.4
Al,Na−Y/63	*I* (%)	47.6	30.8	18.9	2.7
($n_{Al,total}$ = 62.9)	n_{Al} (Al/u.c.)	29.9	19.4	11.9	1.7

473 K, the weak signal 4 could be due to extraframework aluminum cations (pentacoordinated), which are additionally coordinated to one residual water molecule. Another possibility is the formation of extraframework aluminum oxide clusters caused by slight dealumination of the framework during the aluminum exchange and dehydration.[14]

The relative intensities of signals 1 to 4 were determined by ^{27}Al high-speed MAS NMR spectroscopy of dehydrated (473 K) zeolites Al,Na−X/61 and Al,Na−Y/63 at B_0 = 17.6 T. The corresponding spectra are shown in Figure 8. The simulation of these spectra was performed using signals with the chemical shifts and C_{qcc} values obtained by MQMAS NMR spectroscopy. In Table 2, a summary of the relative intensities *I* and the corresponding numbers n_{Al} of aluminum species in the dehydrated zeolites is given. All spectra are dominated by the signal of tetrahedrally coordinated framework aluminum atoms (**Al^{IV}**/H$^+$, **Al^{IV}**/Al^{x+} and **Al^{IV}**/Na$^+$). The octahedrally coordinated aluminum atoms (**Al^{VI}**) were observed with a maximum relative intensity of 2.4%, which indicates a low number of residual water upon dehydration at 473 K and extraframework aluminum oxide clusters. The contents of pentacoordinated extraframework aluminum cations are of ca. 17 to 19% intensity.

The comparison of the number of AlOH groups of 17.1 and 9.1 OH/u.c. (Figures 3b and 4b) with the number of extraframework aluminum cations (**Al^{x+} cat.**) of 16.9 and 11.9 Al/u.c. (column 5 of Table 2) for zeolites Al,Na−X/61 and Al,Na−Y/63 dehydrated at 473 K, respectively, indicates that a significant number of these cations exhibit one hydroxyl group ($AlOH^{2+}$). Differences between the above-mentioned numbers can be explained by AlO^+ species, which are formed by the dehydration of $Al(OH)_2^+$ species (see Section 1).

On the basis of ^{1}H DQ MAS NMR experiments (DQ = double-quantum) and the theoretical calculations, the extraframework aluminum species $Al(OH)_3$ and $AlOH^{2+}$ located in the supercages were found. In the sodalite cages, exclusively $AlOH^{2+}$ species exist.[36] The pentacoordination of extraframework aluminum species (^{27}Al MAS NMR shift of δ_{CS} = 35 ppm) with one OH group per aluminum atom ($AlOH^{2+}$) could be explained by the formation of HO−Al$^+$−O−Al$^+$−OH compounds. In this case, the extraframework aluminum cations may be located at SI′ positions and coordinate to three framework oxygen atoms of the nearest six-membered oxygen ring. One additional extraframework bridging oxygen atom at the SI position and one hydroxyl oxygen atom at each extraframework aluminum atom can lead to the pentacoordination. In the case of AlO^+ species, e.g., a location at SIII sites near four-membered oxygen rings and the coordination to one additional extraframework oxygen atom could be thought to reach a pentacoordination of these cationic extraframework aluminum species.

Cationic extraframework aluminum species coordinated to framework oxygen atoms near Brønsted acid sites may cause a polarizing effect[5] and stabilize the deprotonated zeolite.[7] This could lead to the enhanced acid strength of bridging OH groups in zeolites Al,Na−X and Al,Na−Y in comparison with those in zeolites H,Na−X and H,Na−Y (see Section 2).

Conclusions

On zeolites Al,Na−X and Al,Na−Y, the formation of acidic bridging OH groups (SiOHAl: δ_{1H} = 3.6−3.9 ppm and 4.6−4.9 ppm) and aluminum hydroxyl groups (AlOH: δ_{1H} = 2.5−2.7 ppm) starts at ca. 393 K. The maximum number of SiOHAl groups occurs upon dehydration of zeolites Al,Na−X and Al,Na−Y at 423 K. This correlates well with the aluminum exchange degree. A further raise of the dehydration temperature leads to a dehydroxylation of zeolites, i.e., recombination of the aluminum hydroxyl group with a proton at a bridging OH group.

As found by ^{27}Al MAS NMR spectroscopy, only a negligible dealumination or damage of the framework occurs on zeolites Al,Na−X and Al,Na−Y upon aluminum exchange and dehydration. The C_{qcc} values obtained by high-field ^{27}Al MQMAS NMR spectroscopy of zeolites Al,Na−X/61 and Al,Na−Y/63 dehydrated at 423 K are 10.1−11.0 MHz for framework aluminum atoms compensated in their negative charge by hydroxyl protons (**Al^{IV}**/H$^+$) and aluminum cations (**Al^{IV}**/Al^{x+}), 3.6−4.4 MHz for framework aluminum atoms compensated by sodium cations (**Al^{IV}**/Na$^+$), and 5.6−7.6 MHz for extraframework aluminum cations (**Al^{x+} cat.**). Comparison of the number of AlOH groups, as determined by ^{1}H MAS NMR spectroscopy, with the number of extraframework aluminum cations (**Al^{x+} cat.**), as obtained by ^{27}Al high-speed MAS NMR spectroscopy, indicates that a significant number of these cations exhibit one hydroxyl group.

The acid strength of bridging OH groups in zeolites Al,Na−X and Al,Na−Y was studied by adsorption of CD_3CN as probe molecule. The adsorbate-induced resonance shifts of hydroxyl protons indicate that zeolites Al,Na−X and Al,Na−Y have a higher acid strength than zeolites H−X and H−Y, but a lower one than lanthanum-exchanged zeolites X and Y. Multivalent extraframework cations may be the reason for the enhanced acid strength of zeolites by a polarizing effect on SiOHAl groups acting as Brønsted acid sites.

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Supporting Information Available: Acid strength of zeolite H,Na−X; ^{27}Al and ^{29}Si MAS NMR investigations of hydrated zeolites. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information of

Characterization and Acidic Properties of Aluminum-exchanged Zeolites X and Y

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1. Acid strength of OH groups in and zeolite H,Na-X

Fig. S1 shows the ^{1}H MAS NMR spectra of dehydrated (723 K) zeolite H,Na-X/62.3 recorded before and after loading with CD_3CN. The signal of bridging OH groups in the supercages occurring at 3.6 ppm is shifted to 7.2 ppm corresponding to low-field shifts of $\Delta\delta_{1H}$ = 3.6 ppm.

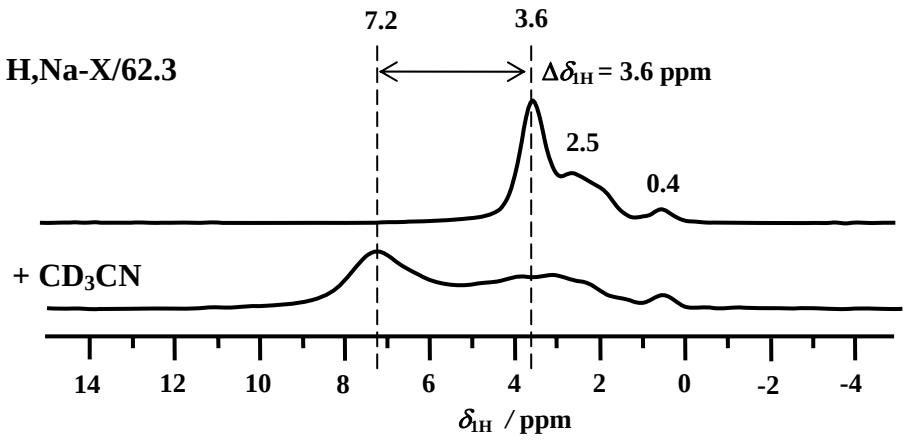


Figure S1. ^{1}H MAS NMR spectra of dehydrated (723 K) zeolite H,Na-X/62.3 recorded before (top) and after (bottom) loading with deuterated acetonitrile (CD_3CN).

2. ^{29}Si MAS NMR investigation of zeolites Al,Na-X and Al,Na-Y

Generally, the presence of large extra-framework cations in zeolites can lead to a local framework strain accompanied by a distortion of the Si-O-T bond angles in their vicinity.[1] The cation-induced local framework distortion leads to a resonance shift of Si(*n*Al) signals, e.g. by *ca.* 3 ppm to lower shift values as observed for lanthanum-exchanged zeolites X and Y.[1,4] In this case, the ^{29}Si MAS NMR chemical shifts of Si(*n*Al) species are not only affected by the number *n* of aluminum atoms in the next coordination sphere of T atoms, but also by the Si-O-T angles.[2,3]

In Fig. S2, characteristic ^{29}Si MAS NMR spectra of zeolites Al,Na-X and Al,Na-Y, rehydrated after thermal treatment at 673 K are shown. No obvious resonance shifts of the ^{29}Si MAS NMR signals were found in these spectra. The similar phenomenon was observed by Radeglia and Engelhardt for zeolite Al,Na-Y/69 dehydrated at 423 to 723 K.[5] In this case, no or only weak cation-induced shifts (maximum 1 ppm) occurred in the ^{29}Si MAS NMR spectra.[5] However, with the increasing aluminum exchange degree, a broadening of the Si(*n*Al) signals in the spectra of zeolites Al,Na-X/61 and Al,Na-Y/63 occurs in Fig. S2. This broadening could be caused by ^{29}Si-^{27}Al couplings.[5] The evaluation of the relative intensities in Fig. S2 led to n_{Si}/n_{Al} ratios of 1.3, 1.6, 2.7, and 2.8 for zeolites Al,Na-X/32, Al,Na-X/61, Al,Na-Y/34, and Al,Na-Y/63, respectively. These results indicate that no or only very weak dealumination and damage of the zeolite framework occurred upon aluminum-exchange, dehydration, and rehydration.

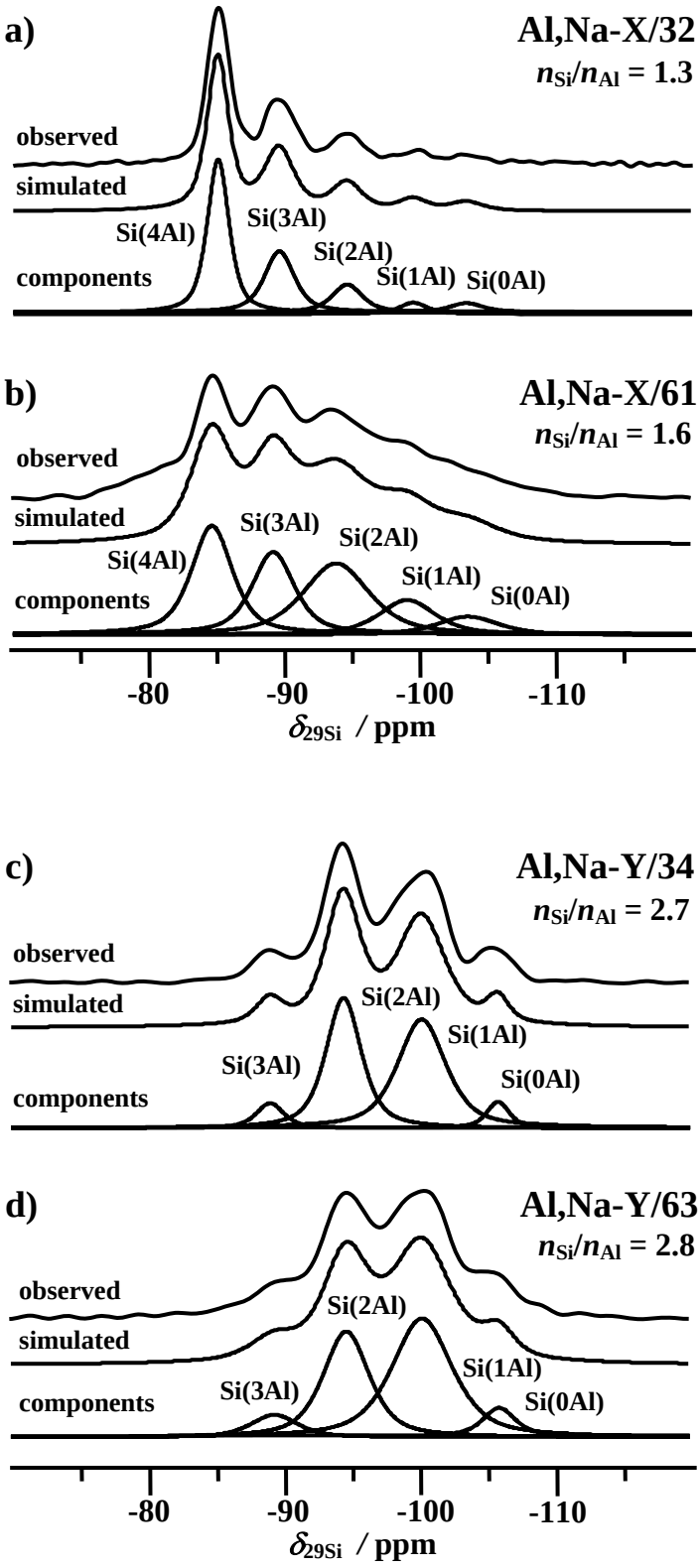


Figure S2. ^{29}Si MAS NMR spectra of hydrated zeolites Al,Na-X/32 (a), Al,Na-X/61 (b), Al,Na-Y/34 (c), and Al,Na-Y/63 (d) after thermal treatment at 673 K.

3. ^{27}Al MAS NMR investigation of hydrated zeolites Al,Na-X and Al,Na-Y

Fig. S3 shows the ^{27}Al MAS NMR spectra of zeolites Al,Na-X/32 (a), Al,Na-X/61 (b), Al,Na-Y/34 (c), and Al,Na-Y/63 (d), rehydrated after thermal treatment at 673 K. All spectra are dominated by the signal of tetrahedrally coordinated framework aluminum atoms at 60 ppm. The broad peak at 30 ppm in the ^{27}Al MAS NMR spectra of zeolites Al,Na-X/61 and Al,Na-Y/63 could be caused by tetrahedrally coordinated framework aluminum atoms in the vicinity of highly charged extra-framework aluminum species.[6] The signal at 3 ppm is due to hydrated extra-framework aluminum species, such as $Al(OH)(H_2O)_5^{2+}$ complexes.[6] The narrow peak at 0 ppm for zeolites Al,Na-Y is caused by $Al(OH)_3(H_2O)_3$ complexes.[6] Again, no significant dealumination was observed by ^{27}Al MAS NMR spectroscopy of the aluminum-exchanges, dehydrated, and reahydrated zeolites X and Y.

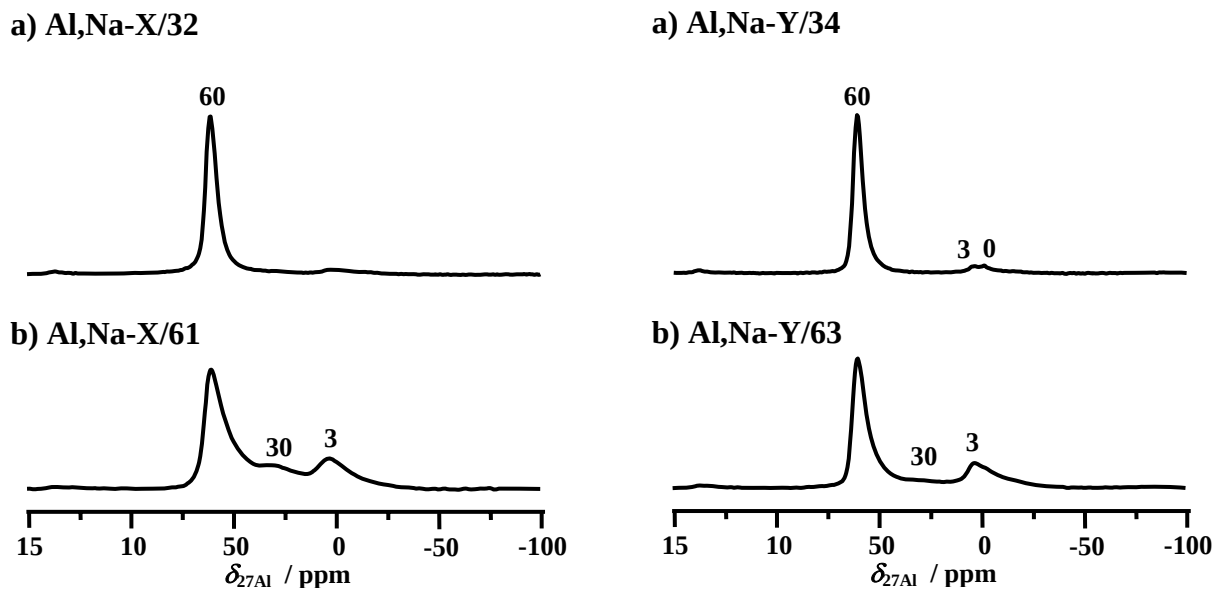


Figure S3. ^{27}Al MAS NMR spectra of hydrated zeolites Al,Na-X/32 (a), Al,Na-X/61 (b), Al,Na-Y/34 (c), and Al,Na-Y/63 (d) after thermal treatment at 673 K.

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