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# Concentration and acid strength of hydroxyl groups in zeolites La,Na-X and La,Na-Y with different lanthanum exchange degrees studied by solid-state NMR spectroscopy

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**Abstract**

$^1$H MAS NMR spectroscopy was applied for a quantitative investigation of the concentration of hydroxyl groups on lanthanum-exchanged zeolites X and Y as a function of the dehydration temperature. A maximum concentration of Brønsted acidic bridging OH groups (SiOHAl) was reached upon dehydration of zeolites La,Na-X and La,Na-Y at 423 K. Further raise of the dehydration temperature leads to the recombination of the above-mentioned hydroxyl groups, while the dealumination of the framework is negligible. The maximum number of bridging OH groups formed on zeolites La,Na-X and La,Na-Y correlates well with the lanthanum exchange degree. By adsorption of deuterated acetonitrile as a probe molecule, an increase of the acid strength of bridging OH groups in lanthanum-exchanged zeolites X and Y was found. This finding is explained by the polarizing effect of multivalent lanthanum cations, which leads to a withdrawal of electrons from the O–H bonds of Brønsted acid sites in lanthanum-exchanged zeolites with a high concentration of these extra-framework cations.
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*Keywords:* Zeolites La,Na-X and La,Na-Y; Dehydration; Thermal stability; Acid strength; Solid-state NMR spectroscopy

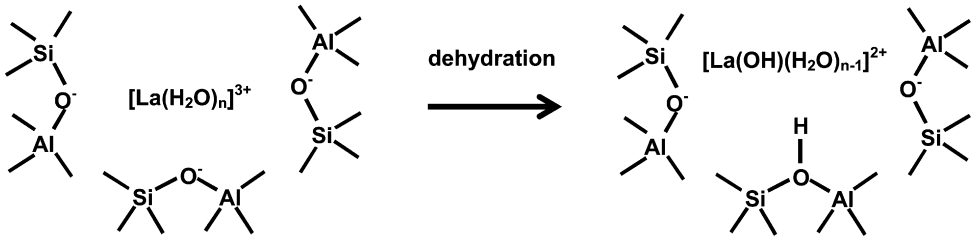
## 1. Introduction

Lanthanum exchange of zeolites is an important procedure for the preparation of acidic zeolite catalysts, e.g., for applications in cracking processes [1] and alkylation reactions [2]. In addition, the ethylbenzene disproportionation on zeolite La,Na-Y was suggested by the Catalysis Commission of the International Zeolite Association (IZA) as a standard reaction for the characterization of acidic zeolites [3]. According to the mechanism of Hirschler and Plank [4], the dissociation of water molecules in the electrostatic fields of multivalent extra-framework cations in zeolites results in the formation of metal OH groups bound to the extra-framework cations and bridging OH groups (SiOHAl) acting as Brønsted acid sites (Scheme 1). Mainly, there are three different ways for releasing water from lanthanum-exchanged zeolites [5]: (i) Release of physisorbed water, (ii) dehydration of lanthanum cations and formation of hydroxyl groups, and (iii) dehydroxylation of the zeolite by a recombination of the above-mentioned hydroxyl groups. The second step leads to the formation of bridging OH groups in the zeolite, while the third one could be accompanied by a damage of the zeolite framework. As shown in earlier $^1$H MAS NMR investigations of zeolites Mg,Na-Y and Ca,Na-Y [6], the concentration and location of zeolitic hydroxyl groups formed via the Hirschler–Plank mechanism strongly depend on the dehydration temperature and the type of multivalent cations.

Lee and Rees [7] studied the effect of dehydration of zeolites La,Na-Y at temperatures of 313–773 K on the location and effective valence of extra-framework lanthanum

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Scheme 1.

cations in these materials. They found that the lanthanum cations, which are initially only sited in the supercages of zeolite La,Na-Y, diffuse through the six-membered rings into the sodalite cages upon dehydration. The apparent charge on the lanthanum cations was reduced from 3+ at 373 K to 2+ at 473–773 K. This charge reduction was fully consistent with the Hirschler–Plank mechanism, i.e. the formation of LaOH groups. Upon dehydration at temperatures between 853 and 1123 K [8], 12 out of 13 extra-framework lanthanum cations in zeolite La,Na-Y were found to occur in the sodalite cages, while the effective charge increased again from 2.2+ to 3+.

The dehydration-induced migration of lanthanum cations in zeolites La,Na-Y from the supercages into the sodalite cages was supported by X-ray studies of Shy et al. [9] and Klein et al. [10]. The observed location of lanthanum cations at sites $I'$ leads to a local strain of framework $SiO_4$ tetrahedra in the vicinity of lanthanum cations as indicated by a resonance shift of the $^{29}$Si MAS NMR signals of these framework silicon atoms to lower chemical shift values by ca. 3 ppm [10–13]. By $^{27}$Al DOR NMR [14] and $^{27}$Al MQMAS NMR [15] spectroscopy of zeolites La,Na-X and La,Na-Y, respectively, it was found that broad signals occurring at 30–45 ppm in the solid-state $^{27}$Al NMR spectra of highly lanthanum-exchanged samples are due to tetrahedrally coordinated framework aluminum atoms in the vicinity of lanthanum cations.

In the present work, the hydroxyl coverage of zeolites La,Na-X and La,Na-Y with different lanthanum exchange degrees and upon dehydration treatments at 393–673 K was quantitatively investigated by $^1$H MAS NMR spectroscopy. In order to study the acid strength and accessibility of hydroxyl groups formed in these materials, deuterated acetonitrile and pyridine, respectively, were adsorbed on the dehydrated materials. By $^{27}$Al and $^{29}$Si MAS NMR spectroscopy of the thermally treated and rehydrated materials, the effect of hydroxylation and recombination of the obtained hydroxyl groups on the zeolite framework was evaluated.

## 2. Experimental section

### 2.1. Preparation of the materials

Zeolites Na-X ($n_{Si}/n_{Al} = 1.3$) and Na-Y ($n_{Si}/n_{Al} = 2.7$) were purchased from Union Carbide Corporation, Tarrytown, NY, USA, and Degussa AG, Hanau, Germany, respectively. Zeolites La,Na-X/42 and La,Na-Y/42 (sodium exchange degrees of 42.5% and 42.3%, respectively) were prepared by a one-fold exchange of zeolites Na-X and Na-Y at 353 K in a 0.1 M aqueous solution of $La(NO_3)_3$. Zeolites La,Na-X/75 and La,Na-Y/74 (sodium exchange degrees of 75.4% and 74.5%, respectively) were obtained by a threefold ion exchange of zeolites Na-X and Na-Y at the same conditions. Subsequently, the materials were washed with demineralized water and dried in the air. The ion-exchange degrees of the lanthanum-exchanged zeolites were determined by atomic emission spectroscopy (ICP-AES). The lanthanum-exchanged zeolites X and Y were dehydrated using the following procedure: Heating with a rate of 20 K/h up to the 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. Using a vacuum line, the dehydrated zeolite samples were quantitatively loaded with 1 probe molecule per bridging OH group.

### 2.2. Spectroscopic characterization

Solid-state MAS NMR spectra were recorded using a Bruker MSL-400 spectrometer at resonance frequencies of 400.1 MHz for $^1$H, 104.3 MHz for $^{27}$Al, and 79.5 MHz for $^{29}$Si nuclei. For the $^1$H and $^{27}$Al MAS NMR studies, a standard 4 mm double-bearing Bruker MAS probe with a sample spinning rate of ca. 8 kHz was used with single-pulse excitation corresponding to $\pi/2$ ($^1$H) and $\pi/6$ ($^{27}$Al) flip angles, and with repetition times of 10 s ($^1$H) and 500 ms ($^{27}$Al). For the $^{29}$Si MAS NMR investigations, a 7 mm double-bearing Bruker MAS standard probe with a single-pulse excitation corresponding to $\pi/2$, a rotation frequency of ca. 3.5 kHz, and a recycle delay of 10 s were applied.

Before starting the $^1$H MAS NMR experiments, the dehydrated samples were filled into 4 mm MAS rotors in a glove box purged with dry nitrogen. Quantitative $^1$H MAS NMR measurements were performed by a comparison of the signal intensities with that of an external intensity standard. The standard sample was a dehydrated zeolite H,Na-Y (exchange degree of 35%) with 1.776 mmol

OH groups per gram and a weight of 58.5 mg. Prior to $^{27}Al$ and $^{29}Si$ 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.

The decomposition and simulation of the NMR spectra were performed using the Bruker software WINNMR and WINFIT.

## 3. Results and discussion

### 3.1. $^1H$ MAS NMR investigation of the OH concentration of dehydrated zeolites La,Na-X and La,Na-Y

As an example, Fig. 1 shows the $^1H$ MAS NMR spectra of zeolites La,Na-X/75 and La,Na-Y/74 dehydrated at temperatures of 393–673 K. The signals occurring at 1.8 ppm and 2.5 to 2.7 ppm in the spectra of zeolites La,Na-X are due to silanol groups (SiOH) and LaOH groups in the supercages ($LaOH^{sup}$), respectively. The signals at 3.6 ppm and 4.6–5.0 ppm are assigned to bridging OH groups in the supercages ($SiOH^{sup}Al$) and sodalite cages ($SiOH^{sod}Al$), respectively, of the faujasite framework. The low-field signals at ca. 6.2 ppm are caused by LaOH groups in the sodalite cages ($LaOH^{sod}$) [14,16]. Upon dehydration at 393 K, the signals at 4.6–5.0 ppm and ca. 6.2 ppm may be superimposed by signals of residual water molecules. Similarly, the $^1H$ MAS NMR spectra of dehydrated zeolites La,Na-Y consist of signals of silanol groups at 1.8 ppm, LaOH groups in the supercages at 2.3–2.9 ppm, bridging OH groups in the supercages and sodalite cages at 3.8–4.0 and 4.8–5.1 ppm, respectively, and LaOH groups in the sodalite cages at ca. 5.8 ppm [14,16]. The assignment of the above-mentioned $^1H$ MAS NMR signals to hydroxyl groups located in the supercages and sodalite cages is supported by the adsorption experiments described in Section 3.2.

In order to determine the influence of the lanthanum exchange degree and the dehydrated temperature on the concentration of OH groups of zeolites La,Na-X and La,Na-Y, a quantitative evaluation of the $^1H$ MAS NMR intensities and simulation of the spectra has been performed. As examples, the simulations of the spectra obtained upon dehydration of zeolites La,Na-X/75 and La,Na-Y/74 at 673 K are shown in Fig. 1, bottom. The results of these evaluations are summarized in Figs. 2 and 3. Upon dehydration at 393 K, first bridging OH groups and lanthanum hydroxyl groups in the supercages ($SiOH^{sup}Al$ and $LaOH^{sup}$, respectively) have been formed as indicated by $^1H$ MAS NMR signals occurring at 3.6–4.0 ppm and 2.3–2.9 ppm, respectively. Due to residual water molecules, the resolution of the $^1H$ MAS NMR spectra is poor and the signals of hydroxyl groups in sodalite cages may be overlapped by the signals of water molecules. Because of the presence of spinning side bands (not shown in the plotted spectral range), however, possible hydrogen exchange processes between water molecules and hydroxyl groups are slow in comparison with the time scale of the MAS

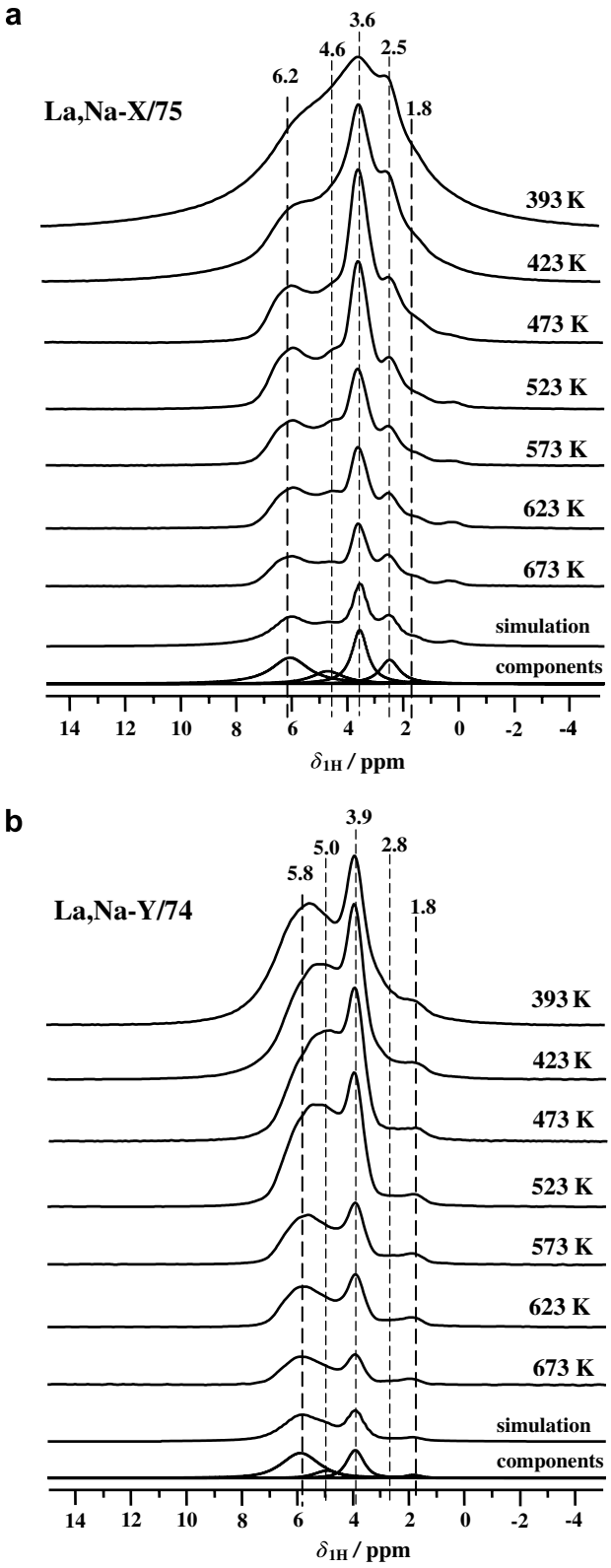



Fig. 1. $^1H$ MAS NMR spectra of zeolites La,Na-X/75 (a) and La,Na-Y/74 (b) dehydrated at temperatures of 393–673 K. As examples, the simulations of the spectra obtained upon dehydration at 673 K are shown (bottom).

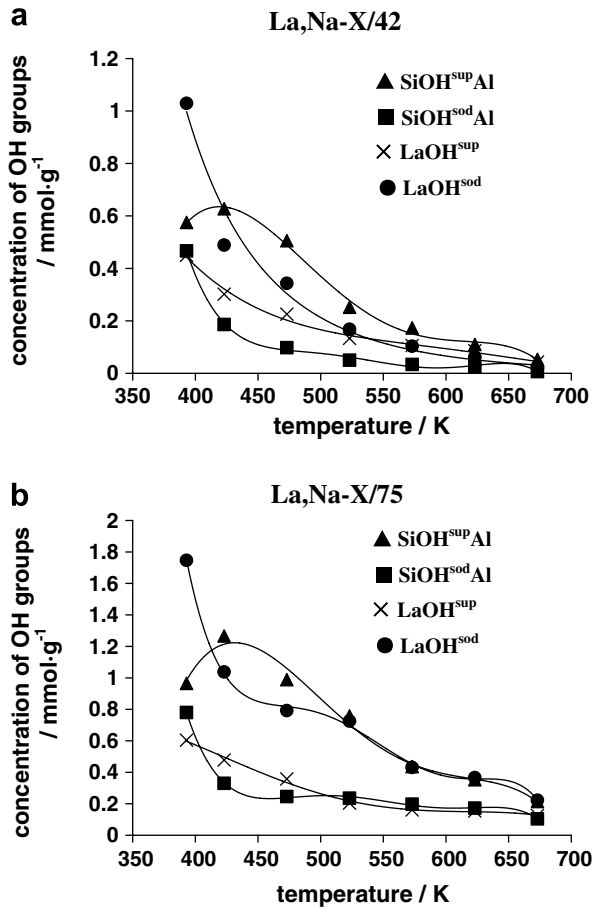



Fig. 2. Concentration of bridging OH groups in the supercages ($SiOH^{sup}Al$) and sodalite cages ($SiOH^{sod}Al$) and of lanthanum OH groups in the supercages ($LaOH^{sup}$) and sodalite cages ($LaOH^{sod}$) of zeolites La,Na-X/42 (a) and La,Na-X/75 (b) as a function of the dehydration temperature (accuracy ±10%).

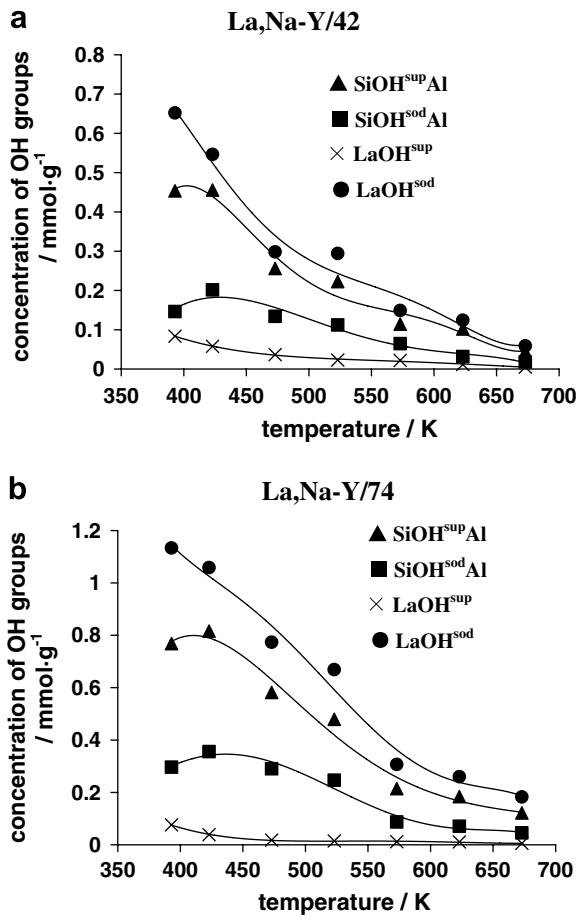



Fig. 3. Concentration of bridging OH groups in the supercages ($SiOH^{sup}Al$) and sodalite cages ($SiOH^{sod}Al$) and of lanthanum OH groups in the supercages ($LaOH^{sod}$) and sodalite cages ($LaOH^{sod}$) of zeolites La,Na-Y/42 (a) and La,Na-Y/74 (b) as a function of the dehydration temperature (accuracy ±10%).

NMR experiment, which allows a quantitative evaluation of the signals visible in the MAS NMR spectra.

Upon increasing the dehydration temperature to 423 K, the maximum concentration of bridging OH groups in the supercages ($SiOH^{sup}Al$) is obtained. For zeolites X and Y with lanthanum exchange degrees of 75% and 74%, this maximum SiOHAl concentration is by a factor of 1.7–1.8 higher than that of the samples with the lower lanthanum exchange degree of 42%. This factor agrees well with the ratio of lanthanum exchange degrees (74%/42% = 1.76). Hence, the number of bridging OH groups formed via the Hirschler–Plank mechanism (see Scheme 1) by the dissociation of water molecules correlates with the number of extra-framework lanthanum cations.

After further increasing the dehydration temperature to $T \geqslant 473$ K, a continuous decrease of the concentration of all types of OH groups occurs. Upon dehydration at 673 K, ca. 80–90% of the hydroxyl groups formed at 423 K via the Hirschler–Plank mechanism are recombined to water, which desorbed from the zeolites due to the thermal treatment.

### 3.2. Accessibility and acidic strength of OH groups in zeolites La,Na-X and La,Na-Y

Deuterated pyridine ($C_5D_5N$) is an often utilized probe molecules for the investigation of the accessibility of hydroxyl groups in acidic zeolites [14,16]. Fig. 4 shows the $^1H$ MAS NMR spectra of dehydrated (473 K) zeolites La,Na-X/42, La,Na-X/75, La,Na-Y/42, and La,Na-Y/74 recorded before and after loading with $C_5D_5N$. After adsorption of $C_5D_5N$, preferentially the signals occurring at 2.5 ppm and 3.6–3.9 ppm are affected by the probe molecules. This finding supports the assignment of the above-mentioned LaOH and SiOHAl groups to hydroxyl protons located in the supercages. Due to the high acid strength of SiOHAl groups in zeolites La,Na-X and La,Na-Y, a protonation of the basic probe molecules occurs leading to signals of pyridinium ions ($C_5D_5NH^+$) at 14–16 ppm [14,16].

Due to the low base strength of acetonitrile, the adsorption of this probe molecule in the deuterated state ($CD_3CN$) on zeolite catalysts allows the discrimination of Brønsted acidic bridging OH groups with different acid strengths. In this case, the adsorbate-induced resonance

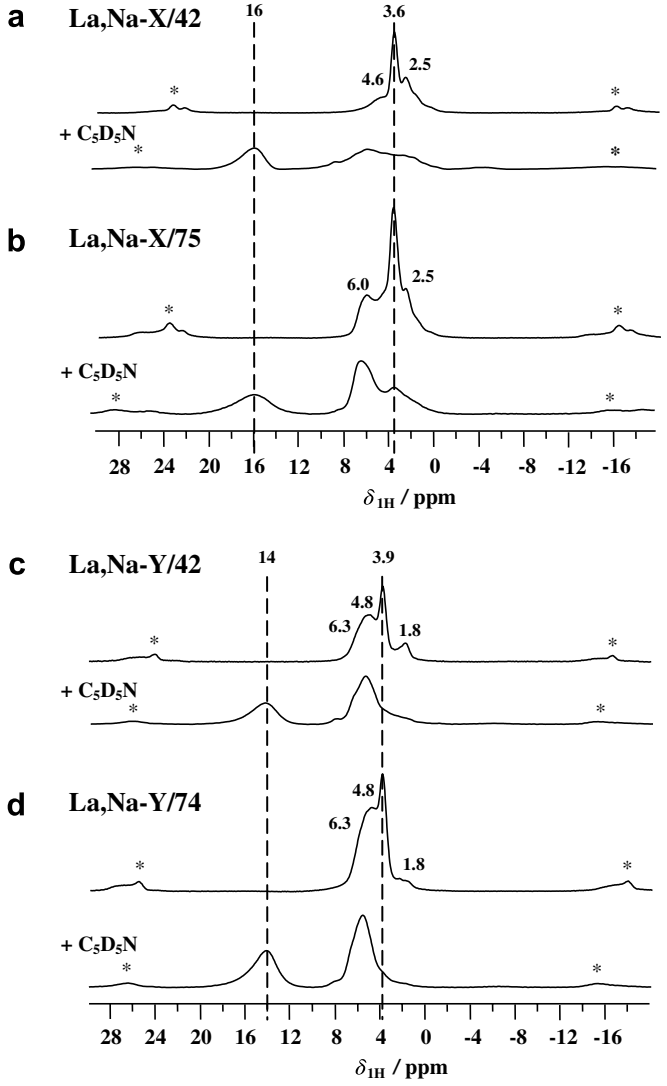



Fig. 4. $^1$H MAS NMR spectra of dehydrated (473 K) zeolites La,Na-X/42 (a), La,Na-X/75 (b), La,Na-Y/42 (c), and La,Na-Y/74 (d) recorded before (top) and after (bottom) loading with deuterated pyridine ($C_5D_5N$). Asterisks denote spinning side-bands.

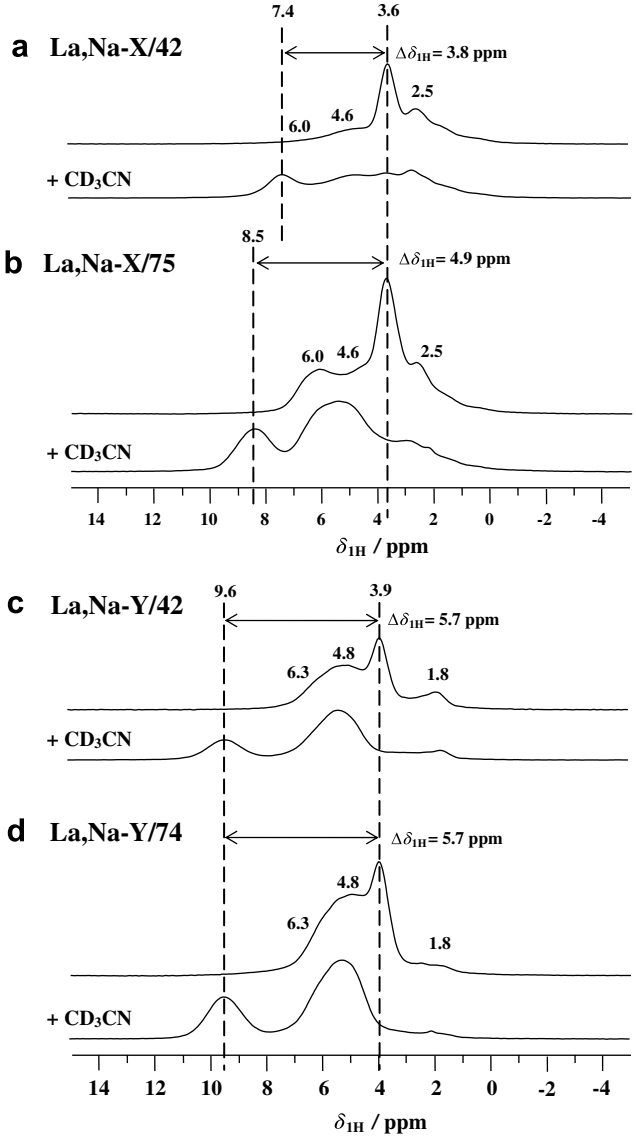



Fig. 5. $^1$H MAS NMR spectra of dehydrated (473 K) zeolites La,Na-X/42 (a), La,Na-X/75 (b), La,Na-Y/42 (c), and La,Na-Y/74 (d) recorded before (top) and after (bottom) loading with deuterated acetonitrile ($CD_3CN$). Asterisks denote spinning side-bands.

shift $\Delta\delta_{1H}$ of the $^1$H MAS NMR signal of SiOHAl groups is utilized as a measure of the acid strength [17–20]. A strong resonance shift corresponds to a high acid strength. The interaction of acetonitrile with the Brønsted acidic hydroxyl groups occurs via an O–H···N-type hydrogen bonding [19,20]. Upon adsorption of $CD_3CN$ on zeolite H-ZSM-5 ($n_{Si}/n_{Al} = 52$) a resonance shift of $\Delta\delta_{1H} =$ 7.1 ppm was observed [17], while adsorption of this probe molecule on zeolites H-Y with $n_{Si}/n_{Al}$ ratios of 5.8 and 2.7 leads to resonance shifts of $\Delta\delta_{1H} = 6.4$ and 5.1 ppm, respectively [17,18].

Fig. 5 shows the $^1$H MAS NMR spectra of dehydrated (473 K) zeolites La,Na-X/42, La,Na-X/75, La,Na-Y/42, and La,Na-Y/74 recorded before and after loading with $CD_3CN$. For zeolites La,Na-X/42 and La,Na-X/75, the signals of bridging OH groups in the supercages occurring at 3.6 ppm are shifted to 7.4 ppm and 8.5 ppm corresponding to resonance shifts of $\Delta\delta_{1H} = 3.8$ ppm and $\Delta\delta_{1H} =$ 4.9 ppm, respectively. The $\Delta\delta_{1H}$ value was found to increase with increasing lanthanum exchange degree for zeolites La,Na-X. This finding implies a higher acid strength of Brønsted acid sites in zeolites La,Na-X with increasing lanthanum exchange degree.

Upon adsorption of $CD_3CN$ on zeolites La,Na-Y/42 and La,Na-Y/74, the $^1$H MAS NMR signals of bridging OH groups in the supercages of both materials show an adsorbate-induced resonance shift of $\Delta\delta_{1H} = 5.7$ ppm. This value is higher than the resonance shift $\Delta\delta_{1H}$ obtained for zeolite H-Y with the same $n_{Si}/n_{Al}$ ratio ($\Delta\delta_{1H} = 5.1$ ppm [18]). However, no effect of the lanthanum exchange degree on the acid strength of bridging OH groups in zeolites La,Na-Y could be found.

Generally, the Brønsted acid sites in zeolites La,Na-Y ($\Delta\delta_{1H} = 5.7$ ppm) have a higher acid strength than those in zeolites La,Na-X ($\Delta\delta_{1H} = 3.8$ to 4.9 ppm). Zeolites La,Na-Y ($n_{Si}/n_{Al} = 2.7$) and zeolites La,Na-X ($n_{Si}/n_{Al} = 1.3$) are characterized by the same framework type (faujasite), but different $n_{Si}/n_{Al}$ ratios [21]. The higher mean electronegativity of zeolites Y with the lower aluminum content results in a higher acid strength of the Brønsted sites in this material in comparison with those in zeolites X. Likewise, different extra-framework cations may affect the mean electronegativity of the zeolite framework [21].

### 3.3. $^{27}$Al MAS NMR investigation of zeolites La,Na-X and La,Na-Y

Fig. 6 shows the $^{27}$Al MAS NMR spectra of hydrated zeolites La,Na-X and La,Na-Y obtained after thermal treatment at 673 K and rehydration at room temperature. All spectra are dominated by the signal of tetrahedrally coordinated framework aluminum atoms at 58–60 ppm [22]. In the spectra of samples dehydrated at 673 K and rehydrated at room temperature, an additional signal of octahedrally coordinated aluminum atoms appears at 0–2 ppm with a maximum relative intensity of 3%. This signal is due to extra-framework aluminum species [22] or framework aluminum atoms at defect sites [23]. The low intensity of this signal indicates that only a negligible dealumination or damage of the framework of zeolites La,Na-X and La,Na-Y can exist before rehydration of the samples under study, i.e. upon formation of hydroxyl groups via the Hirschler–Plank mechanism and subsequent recombination of these hydroxyl groups during the thermal treatment at 673 K.

Depending on the lanthanum exchange degree and the thermal treatment, an additional broad signal is observed at ca. 40 ppm, the increase of which obviously occurs at the expense of the signal at 58 to 60 ppm. Simulation of the $^{27}$Al MAS NMR spectra of zeolites La,Na-X leads to the relative intensities of this broad signal given in Fig. 6. In the spectra of zeolites La,Na-Y, the broad signals at ca. 40 ppm are much weaker and were, therefore, not evaluated. The broad signal at ca. 40 ppm is due to framework aluminum atoms in the vicinity of lanthanum cations as shown in Scheme 2 [15]. According to Lee and Rees [7], most of the lanthanum cations in strongly dehydrated zeolites with faujasite structure are located in the sodalite cages, possibly at sites $I'$ [9,10]. The highly charged lanthanum cations cause a polarizing effect and induce an electric field gradient at the sites of neighboring framework aluminum atoms [15]. The increase of the quadrupolar interaction of the corresponding framework aluminum atoms causes the experimentally observed resonance shift of the $^{27}$Al MAS NMR signal at 58–60 ppm by ca. 20 ppm to lower chemical shift values. Interestingly, the change of the lanthanum exchange degree of zeolites La,Na-X from 42% to 75% is accompanied by an increase of the relative intensities of the broad signal from 46% to 65%.

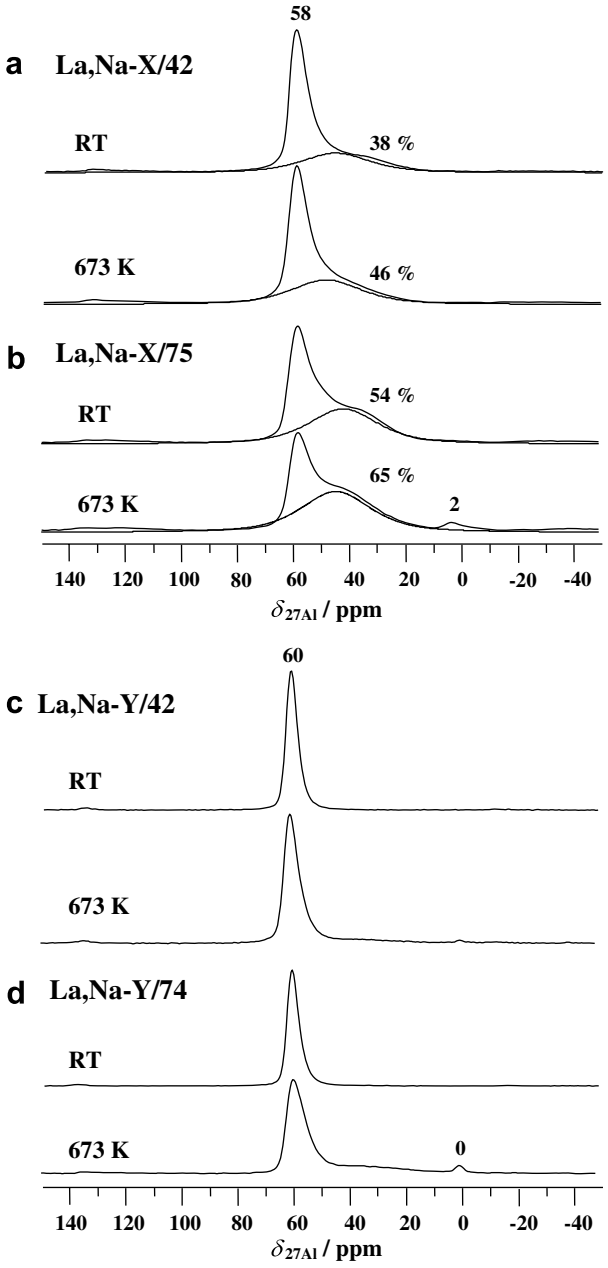
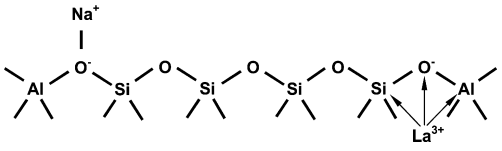



Fig. 6. $^{27}$Al MAS NMR spectra of hydrated zeolites La,Na-X/42 (a), La,Na-X/75 (b), La,Na-Y/42 (c), and La,Na-Y/74 (d) upon drying at room temperature (top) and after thermal treatment at 673 K (bottom).




Scheme 2.

### 3.4. $^{29}$Si MAS NMR investigation of zeolites La,Na-X and La,Na-Y

In Fig. 7, the $^{29}$Si MAS NMR spectra of hydrated zeolites La,Na-X and La,Na-Y recorded upon thermal

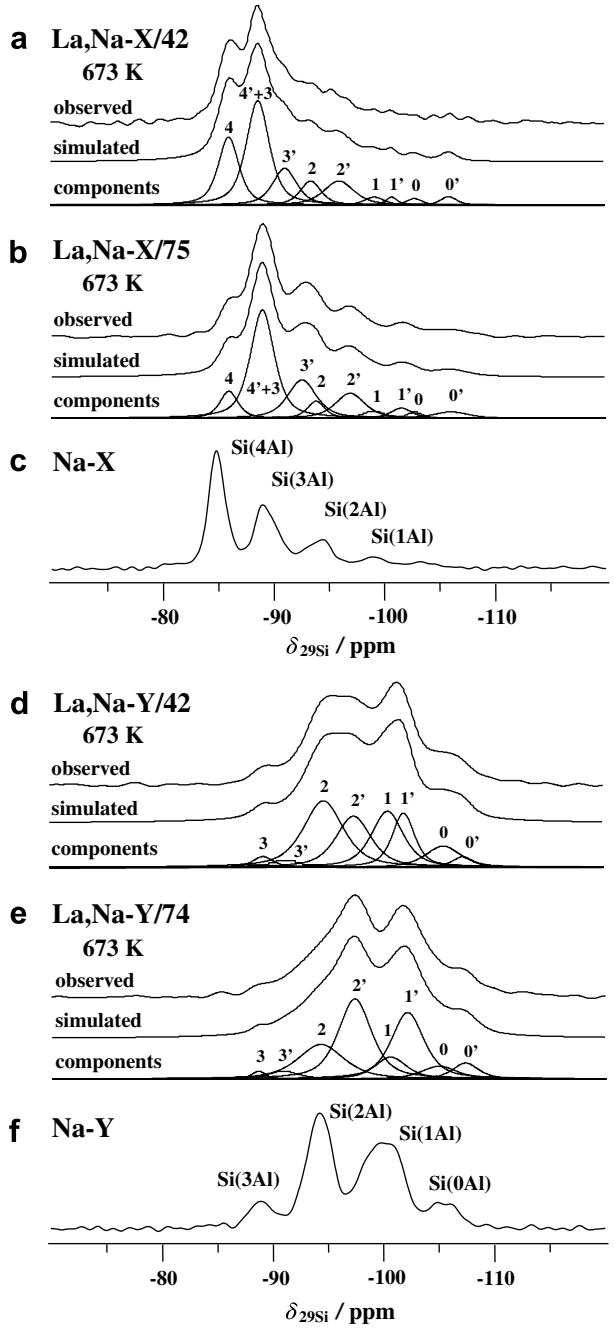



Fig. 7. $^{29}$Si MAS NMR spectra of hydrated zeolites La,Na-X/42 (a), La,Na-X/75 (b), La,Na-Y/42 (d), and La,Na-Y/75 (e) after thermal treatment at 673 K and of the parent zeolites Na-X (c) and Na-Y (f).

treatment at 673 K are depicted. For comparison, Fig. 7c and f show the spectra of the parent zeolites Na-X and Na-Y, respectively. Generally, the $^{29}$Si MAS NMR spectra of zeolites Na-X and Na-Y consist of signals of framework silicon atoms at Si($n$Al) sites, where $n$ is the number of framework aluminum atoms in the second coordination sphere of T atoms. The $^{29}$Si MAS NMR signals of Si($n$Al) silicon atoms with different numbers $n$ are split by ca. 5 ppm [22]. In agreement with previous studies [11–15], the lanthanum exchange of zeolites X and Y leads to a resonance shift of some of the Si($n$Al) signals by ca. 3 ppm to lower chemical shift values. In Fig. 7a, b, d and e, the shifted signals are assigned by numbers $n'$.

Since dealumination of the framework of zeolites La,Na-X and La,Na-Y due to lanthanum exchange and thermal treatment can be neglected (see Section 3.3), the simulation of the $^{29}$Si MAS NMR spectra in Fig. 7 was performed in such a manner that $n_{Si}/n_{Al}$ ratios of 1.3 and 2.7 were obtained for all zeolites X and Y, respectively. With this assumption, contents of the shifted Si($n$Al) signals of 50% and 74% for zeolites La,Na-X/42 and La,Na-X/75, respectively, and 38% and 66% for zeolites La,Na-Y/42 and La,Na-Y/74, respectively, were obtained. These contents of the shifted Si($n$Al) signals are comparable with the lanthanum exchange degrees of the corresponding zeolites.

It is well-known that the resonance positions of $^{29}$Si MAS NMR signals of Si($n$Al) species are not only affected by the number $n$ of aluminum atoms in the second coordination sphere of T atoms, but also by the Si–O–T angle [24,25]. Since $^{29}$Si nuclei are characterized by a spin $I = 1/2$, they are insensitive for the electric field gradients caused by neighboring lanthanum cations. Hence, the resonance shift of the Si($n$Al) signals in the $^{29}$Si MAS NMR spectra of zeolites La,Na-X and La,Na-Y is caused by a local framework strain due to the lanthanum cations in the sodalite cages, which leads to changes of the Si–O–T angles. Since the contents of the shifted Si($n$Al) signals are similar for zeolites La,Na-X and La,Na-Y, changes of the Si–O–T angles cannot be the primary reason for the exchange-induced variation of the acid strength of Brønsted sites.

## 4. Conclusions

By quantitative $^{1}$H MAS NMR spectroscopy, the hydroxyl coverage of zeolites La,Na-X and La,Na-Y with different lanthanum exchange degrees was studied as a function of the dehydration temperatures in the range of 393–673 K. The formation of acidic bridging OH groups and lanthanum OH groups according to the Hirschler–Plank mechanism, i.e. by the dissociative adsorption of water at the multivalent lanthanum cations, was found to be a reversible process. The maximum number of bridging OH groups occurs upon dehydration of zeolites La,Na-X and La,Na-Y at 423 K. A further raise of the dehydration temperature leads to a recombination of the hydroxyl groups on the above-mentioned zeolites and a negligible dealumination of the framework only. The number of maximum bridging OH groups formed on zeolites La,Na-X and La,Na-Y via the Hirschler–Plank mechanism correlates well with the lanthanum exchange degree.

By adsorption of deuterated acetonitrile ($CD_3CN$) as a probe molecule and $^{1}$H MAS NMR spectroscopy, an acid strength of the bridging OH groups in zeolite La,Na-Y was found, which is higher than that of bridging OH groups in zeolite H-Y with same $n_{Si}/n_{Al}$ ratio and significantly higher than the acid strength of bridging OH groups in zeolites

La,Na-X. In addition, the acid strength of bridging OH groups in zeolites La,Na-X depends on the lanthanum exchange degree.

$^{29}$Si MAS NMR spectroscopy indicated that lanthanum cations in dehydrated zeolites La,Na-X and La,Na-Y cause a local framework strain in both types of zeolites in a similar manner. On the other hand, a polarizing effect of the multivalent lanthanum cations on framework aluminum atoms was observed by $^{27}$Al MAS NMR spectroscopy. According to Carvajal et al. [26], the above-mentioned polarizing and inductive effect of lanthanum cations causes a withdrawal of electrons from the O–H bonds of Brønsted acid sites in lanthanum-exchanged zeolites. Hence, the polarizing effect of lanthanum cations may be the reason of the enhanced acid strength of bridging OH groups observed for lanthanum-exchanged zeolites Y and the different acid strengths of bridging OH groups in zeolites La,Na-X with different lanthanum-exchange degrees.

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