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Influence of the lanthanum exchange degree on the concentration and acid strength of bridging hydroxyl groups in zeolites La,Na-X

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ABSTRACT

^{1}H MAS NMR spectroscopy was applied for the quantitative investigation of the concentration of hydroxyl groups in zeolites La,Na-X with different lanthanum-exchange degrees as a function of the dehydration temperature. A maximum concentration of Brønsted acidic bridging OH groups (SiOHAl) corresponding to *ca.* 1 OH per lanthanum cation was reached upon dehydration of zeolites La,Na-X at 423 to 473 K. Further raise of the dehydration temperature led to a dehydroxylation of the above-mentioned zeolites, while the dealumination of the framework was negligible. By adsorption of deuterated acetonitrile as probe molecule, a significant increase of the acid strength of bridging OH groups was found with increasing lanthanum exchange degree. This finding is explained by the polarizing effect of the multivalent lanthanum cations, which leads to a withdrawal of electrons from the O-H bonds of Brønsted acid sites in zeolites La,Na-X possessing a high concentration of these multivalent extra-framework cations.

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]. According to the mechanism of Hirschler and Plank [3], 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 extra-framework cations and bridging OH groups (SiOHAl) acting as Brønsted acid sites. Mainly, there are three different ways for releasing water from lanthanum-exchanged zeolites [4]: (i) Release of physisorbed water, (ii) dehydration of lanthanum cations and formation of hydroxyl groups, and (iii) dehydroxylation of the zeolites. The second step leads to the formation of bridging OH groups in the zeolite, while the third one could result in a dealumination of the zeolite framework and the formation of Lewis acid sites. As shown in earlier ^{1}H MAS NMR investigations of zeolites Mg,Na-Y and Ca,Na-Y [5], the concentration and location of zeolitic hydroxyl groups formed *via* the mechanism of Hirschler and Plank strongly depend on the dehydration temperature and the type of multivalent cations.

Lee and Rees [6] studied the effect of dehydration of zeolites La,Na-Y at temperatures of 313 to 773 K on the location and effective valency of extra-framework lanthanum 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 to 773 K. This charge reduction was fully consistent with the mechanism of

Hirschler and Plank, i.e., the formation of LaOH groups. Upon dehydration at temperatures between 853 and 1123 K [7], 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.* [8] 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 high-field shift of the ^{29}Si MAS NMR signals of these framework silicon atoms by *ca.* 3 ppm [9-12]. By ^{27}Al DOR NMR [13] and ^{27}Al MQMAS NMR [14] spectroscopy of zeolites La,Na-X and La,Na-Y it was found that broad signals occurring at 30 to 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 with different lanthanum exchange degrees and upon dehydration treatments at 393 to 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.

2. EXPERIMENTAL PART

Zeolite Na-X (n_{Si}/n_{Al} = 1.3) was purchased from Union Carbide Corporation, Tarrytown, NY, USA. Zeolite La,Na-X/42 (lanthanum exchange degree of 42.5%) was prepared by a one-fold exchange of zeolite Na-X at 353 K in a 0.1 M aqueous solution of $La(NO_3)_3$. Zeolite La,Na-X/75 (lanthanum exchange degree of 75.4%) was obtained by a threefold ion exchange of zeolite Na-X under the same conditions. Subsequently, the materials were washed with demineralized water and dried in air at 293 K. The ion-exchange degrees of the lanthanum-exchanged zeolites were determined by atomic emission spectroscopy (ICP-AES). The lanthanum-exchanged zeolites X 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. Using a vacuum line, the dehydrated zeolite samples were quantitatively loaded with 1 probe molecule per bridging OH group.

^{1}H MAS NMR spectra were recorded using a Bruker MSL-400 spectrometer at resonance frequencies of 400.1 MHz and with a standard 4 mm double-bearing Bruker MAS probe. The measurements were performed with a sample spinning rate of *ca.* 8 kHz, with a single-pulse excitation corresponding to $\pi/2$, and a repetition time of 10 s. 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. Decomposition and simulation of the NMR spectra were performed using the Bruker software WINNMR and WINFIT.

3. RESULTS AND DISCUSSION

3.1. ^{1}H MAS NMR studies of the OH concentration of dehydrated zeolites La,Na-X

As an example, Figure 1 shows the ^{1}H MAS NMR spectra of zeolite La,Na-X/75 dehydrated at temperatures of 473 and 673 K. The signals occurring at 1.8 ppm and 2.5 ppm are due to silanol groups (SiOH) and LaOH groups in the supercages (LaOH^{sup}), respectively. The signals at 3.6 ppm 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 structure. The low-field signals at *ca.* 6.2 ppm are caused by LaOH groups in the sodalite cages (LaOH^{sod}) [13,15]. The assignment of the above-mentioned ^{1}H MAS NMR signals to hydroxyl groups located in the supercages and sodalite cages is supported by the adsorption experiments described in Section 3.2.

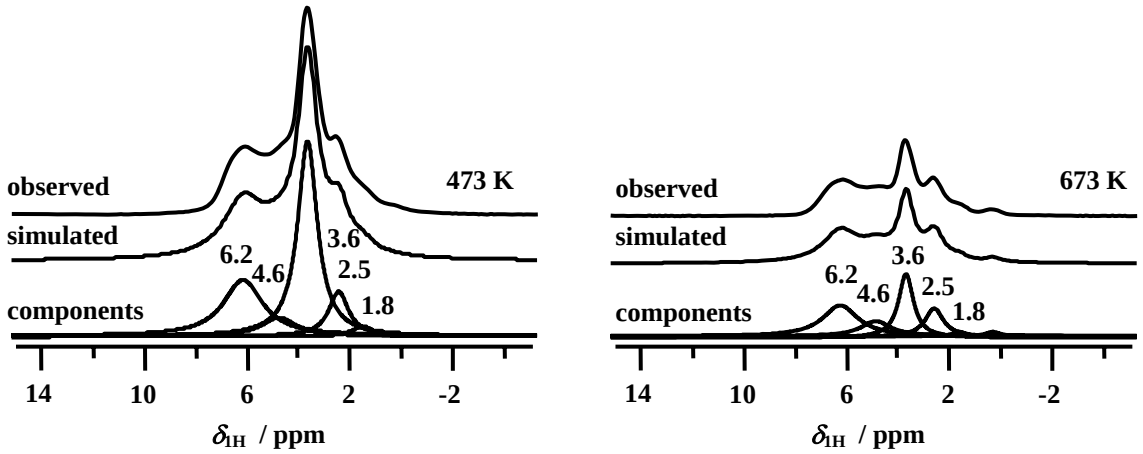


Fig. 1. ^{1}H MAS NMR spectra of zeolite La,Na-X/75 dehydrated at temperatures 473 (left) and 673 K (right).

In order to determine the influence of the lanthanum exchange degree and the dehydration temperature on the concentration of OH groups in zeolites La,Na-X, quantitative evaluation of the ^{1}H MAS NMR intensities and simulation of the spectra were performed. The results of these investigations are summarized in Table 1. Upon dehydration at 393 K, first bridging OH groups and lanthanum hydroxyl groups in the supercages (SiOH^{sup}Al and LaOH^{sup}, respectively) were formed. However, due to residual water molecules, the resolution of the ^{1}H MAS NMR spectra was poor and the signals of SiOH^{sod}Al and LaOH^{sod} groups were partially overlapped by the signal of water molecules.

Upon increasing the dehydration temperature to 423 K, the maximum concentration of bridging OH groups in the supercages (SiOH^{sup}Al) was obtained. For the zeolite La,Na-X with the lanthanum exchange degree of 75 %, this maximum SiOHAl concentration is by a factor of 1.87 higher than that of the sample with the lanthanum exchange degree of 42 %. This factor agrees well with the ratio of the number of lanthanum cations introduced by the exchange (75 % / 42 % = 1.79). Hence, the number of bridging OH groups formed *via* the mechanism of Hirschler and Plank, i.e., by the dissociation of water molecules, correlates with the number of extra-framework lanthanum cations.

Table 1 Concentration of OH groups in zeolites La,Na-X/42 and La,Na-X/75 dehydrated at temperatures between 393 and 673 K

Zeolite	Temp. / K	Concentration of OH groups / mmol g^{-1}			
		$SiOH^{sup}Al$	$SiOH^{sod}Al$	$LaOH^{sup}$	$LaOH^{sod}$
La,Na-X/42	393	0.5753	0.4665	0.4501	1.0293
	423	0.6774	0.1360	0.3018	0.4891
	473	0.5059	0.0978	0.2255	0.3432
	523	0.2521	0.0500	0.1331	0.1680
	573	0.1729	0.0339	0.1058	0.1033
	623	0.1098	0.0266	0.0859	0.0622
	673	0.0535	0.0067	0.0431	0.0234
La,Na-X/75	393	0.9652	0.7795	0.6038	1.7469
	423	1.2665	0.3301	0.4775	1.0378
	473	0.9888	0.2458	0.3575	0.7919
	523	0.7581	0.2357	0.2046	0.7255
	573	0.4367	0.1973	0.1607	0.4309
	623	0.3529	0.1722	0.1539	0.3667
	673	0.2142	0.1041	0.1257	0.2228

Upon a further increase of the dehydration temperature to $T \geq 473$ K, a continuous decrease of the concentration of all kinds of OH groups occurred. Upon dehydration at 673 K, *ca.* 80 to 90 % of the hydroxyl groups formed *via* the mechanism of Hirschler and Plank were recombined to water, which desorbed from the zeolites due to the thermal treatment.

The quantitative evaluation and comparison of the total ^{1}H MAS NMR intensities of zeolites La,Na-X allows the determination of the number of desorbed water molecules as a function of the dehydration temperature. In Figure 2, these values are given for zeolite La,Na-X/75 dehydrated at 393 to 673 K. In this curve, a strong maximum of water desorption occurs at *ca.* 393 K and two weak maxima can be observed at *ca.* 473 and 573 K. The strong maximum at 393 K is attributed to the desorption of weakly physisorbed water molecules previously located in supercages. According to Figure 1 and the values given in Table 1, the peak at 473 K is due to the desorption of water molecules, which are more strongly adsorbed at lanthanum cations located in sodalite cages. This assignment is supported by the decrease of the ^{1}H MAS NMR signal at *ca.* 6.2 ppm due to $LaOH^{sod}$. Upon thermal treatment at 573 K, the hydroxyl groups formed *via* the mechanism of Hirschler and Plank were dehydroxylated, i.e., a recombination of LaOH groups with hydroxyl protons of bridging hydroxyl groups occurred. Correspondingly, the signals at 2.5 and 6.2 ppm due to LaOH groups and at 3.6 and 4.6 caused by bridging OH groups were decreased. The recombination of these hydroxyl groups leads to the formation of water molecules, which desorb at *ca.* 573 K. By ^{27}Al MAS NMR spectroscopy could be evidenced that dehydration of zeolites La,Na-X at 673 K and subsequent rehydration is accompanied by negligible dealumination of the zeolite framework. Only a very weak signal of octahedrally coordinated aluminum atoms occurred at 0 ppm in the spectra of samples obtained after the above-mentioned procedure (not shown).

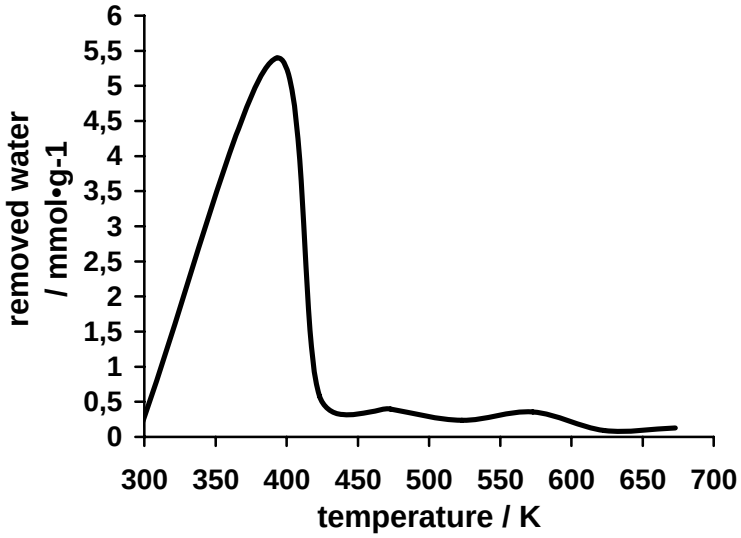


Fig. 2. Number of water molecules desorbed from zeolite La,Na-X/75 upon thermal treatments at 393 to 673 K.

3.2. Accessibility and acid strength of OH groups in zeolites La,Na-X

Deuterated pyridine (C_5D_5N) is an often applied probe molecule for the investigation of the accessibility of hydroxyl groups in acidic zeolites [13,15]. Figure 3 shows the ^{1}H MAS NMR spectra of zeolites La,Na-X/42 and La,Na-X/75, dehydrated at 473 K and 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 ppm were 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. Because of the high acid strength of SiOHAl groups, a protonation of the basic probe molecules occurred, which led to signals of pyridinium ions ($C_5D_5NH^+$) at *ca.* 16 ppm [13,15].

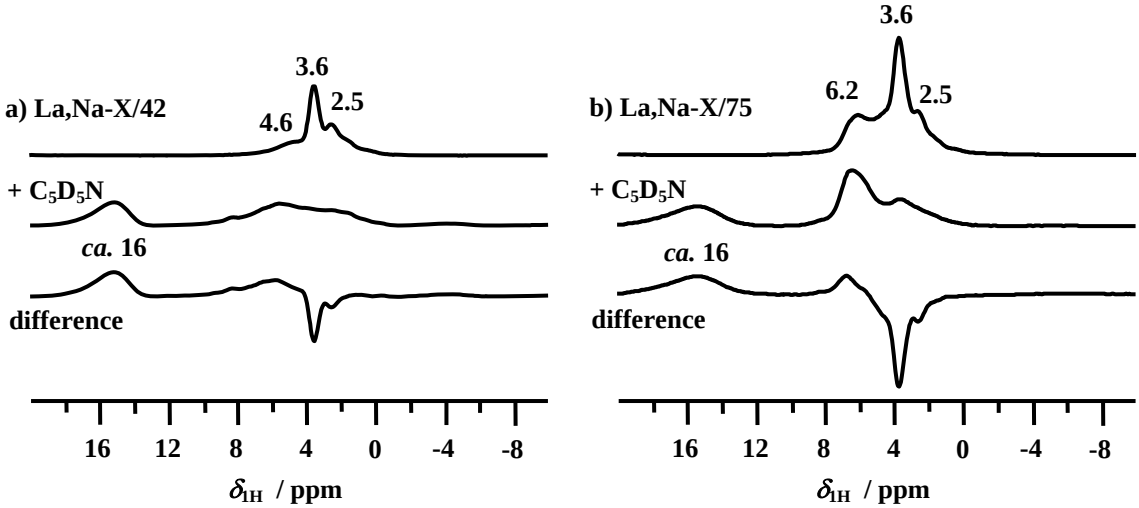


Fig. 3. ^{1}H MAS NMR spectra of dehydrated (473 K) zeolites La,Na-X/42 (a) and La,Na-X/75 (b) recorded before (top) and after (middle) loading with deuterated pyridine (C_5D_5N). At bottom, the difference spectrum is shown.

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 low-field shift $\Delta\delta_{1H}$ of the ^{1}H MAS NMR signal of SiOHAl groups is utilized as a measure of the acid strength [16-19]. A strong low-field shift $\Delta\delta_{1H}$ corresponds to a high acid strength. The interaction of acetonitrile molecules with the Brønsted acidic hydroxyl groups occurs *via* an OH···N-type hydrogen bonding [18,19]. Upon adsorption of CD_3CN on zeolite H-ZSM-5 (n_{Si}/n_{Al} = 52), a low-field shift of $\Delta\delta_{1H}$ = 7.1 ppm was observed, while adsorption of this probe molecule on zeolite H-Y (n_{Si}/n_{Al} = 5.8) led to a low-field shift of $\Delta\delta_{1H}$ = 6.4 ppm [17].

Figure 4 shows the ^{1}H MAS NMR spectra of zeolites La,Na-X/42 and La,Na-X/75 dehydrated at 473 K and 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 low-field shifts of $\Delta\delta_{1H}$ = 3.8 ppm and $\Delta\delta_{1H}$ = 4.9 ppm, respectively. This finding implies a higher acid strength of Brønsted acid sites in zeolites La,Na-X with increasing lanthanum exchange degree, but a significantly lower acid strength in comparison with zolites H-ZSM-5 and H-Y.

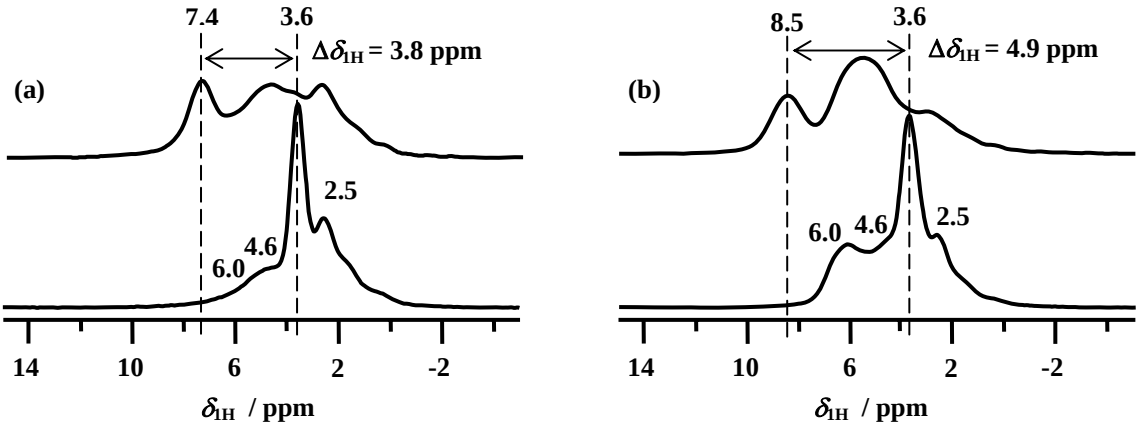


Fig. 4. ^{1}H MAS NMR spectra of dehydrated (473 K) zeolites La,Na-X/42 (a) and La,Na-X/75 (b) recorded before (bottom) and after (top) loading with deuterated acetonitrile (CD_3CN).

4. CONCLUSIONS

By quantitative ^{1}H MAS NMR spectroscopy, the hydroxyl coverage of zeolites La,Na-X with different lanthanum exchange degrees was studied as a function of the dehydration temperature in the range of 393 to 673 K. The formation of lanthanum OH groups and acidic bridging OH groups occurred according to the mechanism of Hirschler and Plank, i.e., by the dissociative adsorption of water at the multivalent lanthanum cations. The maximum number of bridging OH groups was found upon dehydration of zeolites La,Na-X at 423 K. This number of bridging OH groups correlates well with the lanthanum exchange degree. Dehydration at temperatures higher than 473 K led to a dehydroxylation of the above-mentioned zeolites *via* a recombination of lanthanum OH groups and bridging OH groups to water molecules. This process is responsible for water desorption maxima at *ca.* 473 and 573 K and is accompanied by a negligible dealumination of the zeolite framework. Hence, the formation of hydroxyl groups on zeolites La,Na-X *via* the mechanism of Hirschler and Plank is a fully reversible process.

By adsorption of deuterated acetonitrile (CD_3CN) as probe molecule and ^1H MAS NMR spectroscopy, an acid strength of the bridging OH groups in zeolites La,Na-X was determined, which is lower than that of bridging OH groups in zeolites H-Y and H-ZSM-5. It was found that the acid strength of bridging OH groups in zeolites La,Na-X strongly depends on the lanthanum exchange degree.

The lanthanum cations in dehydrated zeolite La,Na-X were proposed to cause a local framework strain. On the other hand, these cations have a polarizing effect on framework aluminum atoms. According to Carvajal *et al.* [20], the above-mentioned polarizing and inductive effect of lanthanum cations leads to 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 different acid strengths of bridging OH groups observed for zeolites La,Na-X with different lanthanum exchange degrees.

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