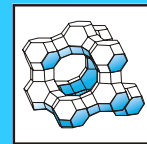


# Influence of the Lanthanum Exchange Degree on the Concentration and Acid strength of Bridging Hydroxyl Groups in Zeolites La, Na-X

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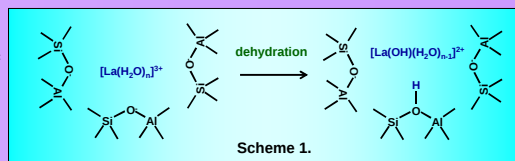
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## Introduction

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 the extra-framework cations and bridging OH groups (SiOHAl) acting as Brønsted acid sites (Scheme 1). The concentration and location of zeolitic hydroxyl groups formed via the above-mentioned mechanism depend strongly on the dehydration temperature and the type of multivalent cations. [4].

In the present work, the hydroxyl coverage of X-type zeolites with different lanthanum exchange degrees was quantitatively investigated by  $^1\text{H}$  MAS NMR spectroscopy. Deuterated acetonitrile and pyridine were used to probe the acid strength and accessibility of these bridging OH groups.



## Results and Discussion

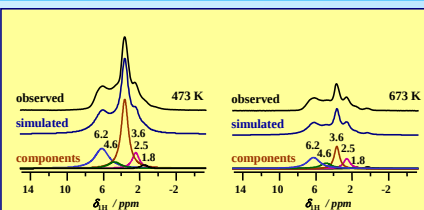


Fig. 1.  $^1\text{H}$  MAS NMR spectra of zeolite La,Na-X/75 dehydrated at temperatures 473 K (left) and 673 K (right).

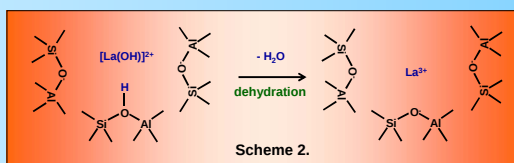
Table 1: Assignments of  $^1\text{H}$  MAS NMR spectra in Fig. 1.

| Signals /ppm | Assignments                                                                  |
|--------------|------------------------------------------------------------------------------|
| 1.8          | silanol groups (SiOH)                                                        |
| 2.5          | LaOH groups in supercages ( $\text{LaOH}^{\text{sup}}$ )                     |
| 3.6          | bridging OH groups in supercages ( $\text{SiOH}^{\text{sup}}\text{Al}$ )     |
| 4.6          | bridging OH groups in sodalite cages ( $\text{SiOH}^{\text{sod}}\text{Al}$ ) |
| 6.2          | LaOH groups in the sodalite cages ( $\text{LaOH}^{\text{sod}}$ )             |

From Fig. 2:

➤ At 393 K, first bridging OH groups and lanthanum hydroxyl groups in the supercages ( $\text{SiOH}^{\text{sup}}\text{Al}$  and  $\text{LaOH}^{\text{sup}}$ ) have been formed. The signals of  $\text{SiOH}^{\text{sod}}\text{Al}$  and  $\text{LaOH}^{\text{sod}}$  groups are partially overlapped by the signals of water molecules.

➤ At 423 K, the maximum concentration of bridging OH groups in the supercages ( $\text{SiOH}^{\text{sup}}\text{Al}$ ) is obtained. The concentration of  $\text{SiOH}^{\text{sup}}\text{Al}$  in La,Na-X/75 is by a factor of 1.72 higher than that in La,Na-X/42. This factor agrees well with the ratio of lanthanum exchange degrees ( $75\% / 42\% = 1.79$ ). Hence, the number of bridging OH groups formed via the Hirschler-Plank mechanism (Scheme 1) correlates with the number of extra-framework lanthanum cations.



➤ At  $T \geq 473$  K, a continuous decrease of the concentration of all types of OH groups occurs. Upon dehydration at 673 K, ca. 80 to 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 (Scheme 2).

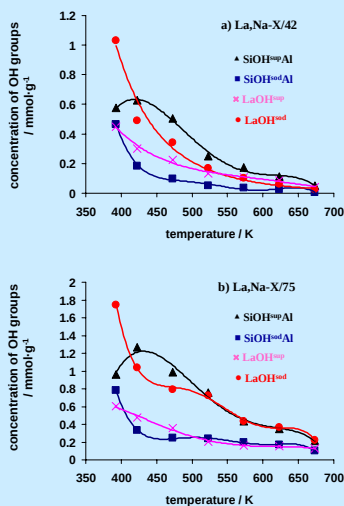


Fig. 2. Concentration of  $\text{SiOH}^{\text{sup}}\text{Al}$ ,  $\text{SiOH}^{\text{sod}}\text{Al}$ ,  $\text{LaOH}^{\text{sup}}$  and  $\text{LaOH}^{\text{sod}}$  in zeolites La,Na-X/42 (a) and La,Na-X/75 (b) as a function of the dehydration temperature (accuracy  $\pm 10\%$ ).

Fig. 4 shows:

★ The acid strength of Brønsted acid sites in zeolites La,Na-X increases with lanthanum exchange degree.

★ The polarizing and inductive effect of the multivalent lanthanum cations causes a withdrawal of electrons from the O-H bonds of Brønsted acid sites in lanthanum-exchanged zeolites. (Scheme 3).

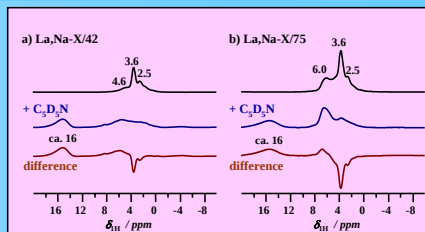
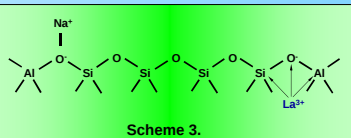


Fig. 3.  $^1\text{H}$  MAS NMR spectra of dehydrated (473 K) zeolites La,Na-X/42 (a) and La,Na-X/75 (b) recorded before (top) and after (bottom) loading with deuterated pyridine ( $\text{C}_5\text{D}_5\text{N}$ ).

Fig. 3 shows:

❖ After adsorption of  $\text{C}_5\text{D}_5\text{N}$ , the signals occurring at 2.5 ppm and 3.6 ppm are affected by the probe molecules.

❖ Deuterated pyridine ( $\text{C}_5\text{D}_5\text{N}$ ) is often used to investigate the accessibility of hydroxyl groups in acidic zeolites.

❖ Due to the high acid strength of  $\text{SiOHAl}$  groups in zeolite La,Na-X, a protonation of the basic probe molecules occurs leading to the signal of pyridinium ions ( $\text{C}_5\text{D}_5\text{NH}^+$ ) at 16 ppm.

❖ This finding supports the assignment of the above-mentioned LaOH and SiOHAl groups to hydroxyl protons located in the supercages.

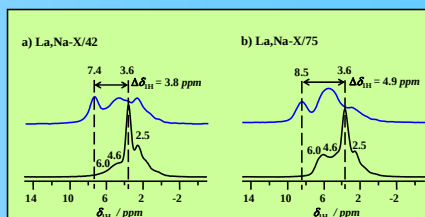


Fig. 4.  $^1\text{H}$  MAS NMR spectra of dehydrated (473 K) zeolites La,Na-X/42 (a) and La,Na-X/75 (b) recorded before (top) and after (bottom) loading with deuterated acetonitrile ( $\text{CD}_3\text{CN}$ ).

## Experimental Section

Zeolites La,Na-X/42 and La,Na-X/75 ( $n_{\text{Si}}/n_{\text{Al}} = 1.3$ ,  $\text{La}^{3+}$ -exchange degrees of 42.5 % and 75.4 %) were prepared by exchange of Na-X with a 0.1 M solution of  $\text{La}(\text{NO}_3)_3$ . All samples were dehydrated at temperatures of 393 to 673 K at  $p < 10^{-2}$  Pa for 12 h. Acetonitrile- $d_3$  and pyridine- $d_5$  were loaded on dehydrated zeolites La,Na-X using a vacuum line. Before the  $^1\text{H}$  MAS NMR measurements, the dehydrated and loaded samples were transferred into a 4 mm MAS NMR rotor inside a glove box under dry nitrogen. The  $^1\text{H}$  MAS NMR investigations were performed on a Bruker MSL-400 spectrometer at a resonance frequency of 400.1 MHz.

## Conclusions

The concentration of bridging OH groups reaches a maximum at dehydration temperature of 423 K. A further raise of the dehydration temperature leads to a dehydroxylation of the above-mentioned zeolites and a negligible dealumination of the framework only. The number of maximum bridging OH groups formed on zeolite La,Na-X via the Hirschler-Plank mechanism correlates well with the lanthanum exchange degree. The acid strength of bridging OH groups was found to increase with increasing lanthanum exchange degree. The polarizing effect of lanthanum cations may be the reason of the different acid strengths.

## Acknowledgements

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