

LATTICE DEFECTS AND SURFACE BARRIERS
IN THERMALLY TREATED ZEOLITE Ca A

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ABSTRACT

Novel NMR techniques are applied to study the molecular transport and lattice defects in thermally treated zeolite $\text{Na}_{3.2}\text{Ca}_{4.4}\text{A}$. Mechanisms for the formation of lattice defects and surface barriers are discussed.

INTRODUCTION

With the development of the NMR tracer desorption technique for the first time a method has been found which provides unequivocal information about the existence and the intensity of transport resistances at the surface of molecular sieve crystallites [1,2]. Combining this technique with traditional NMR self-diffusion measurements, it could be demonstrated [2] that in zeolite Na Ca A after different pretreatments, molecular transport of paraffins may significantly be influenced by such surface barriers. However, until now the nature of these barriers and the extend of lattice distortion connected with it are unclear. In the last few years MAS NMR has successfully been applied to the investigation of the lattice structure and of lattice defects in zeolites [3]. Applying these novel techniques and traditional NMR intensity and relaxation measurements, in the present work possible mechanisms for the formation of lattice defects and surface barriers on thermally treated zeolites Na Ca A are discussed.

EXPERIMENTAL

The basic material of all samples is Zeosorb 5 AZ ($\text{Na}_{3.2}\text{Ca}_{4.4}^{\text{A}}$) type zeolite powder with a mean crystallite diameter of about 4 μm purchased from VEB Chemiekombinat Bitterfeld, GDR. For sample preparation either "deep bed" (DB) or "shallow bed" (SB) conditions have been chosen: Under deep bed conditions the powder is heated in an open glass tube of about 30 mm length at atmospheric pressure by raising the temperature at a rate of 100 K h^{-1} up to the chosen temperature of activation. After keeping the sample for two hours at this temperature, it is evacuated for twenty hours. Under shallow bed conditions the layer thickness of the zeolite powder is less than 3 mm and the sample is heated in vacuo at a rate of 10 K h^{-1} up to the final temperature of activation.

In what follows, a sample prepared with a final temperature of 400°C under deep bed conditions is denoted by "400 DB", for example. The samples sealed off under vacuum after the procedures described above are denoted as "dehydrated". One portion was slowly "rehydrated" at room temperature up to about 95% of the saturation value of the adsorption capacity by keeping it for three days in a desiccator over an aqueous NH_4Cl solution. For the self-diffusion and tracer desorption experiments before sealing the adsorbate has been introduced (ethane, about 4 molecules per cavity).

Details of the NMR self-diffusion as well as of the NMR intensity, relaxation and MAS experiments are described in references [2] and [4], respectively.

RESULTS

Tab. 1 shows values for the intracrystalline self-diffusion coefficients D_{intra} and mean life-times τ_{intra} of ethane in different $\text{Na}_{3.2}\text{Ca}_{4.4}^{\text{A}}$ specimens. If molecular desorption is exclusively determined by intracrystalline self-diffusion (i.e. if there is a negligible small transport resistance at the crystallite surface), the intracrystalline molecular mean life time is given by the relation [1,2]

$$\tau_{\text{intra}}^{\text{model}} = \langle R^2 \rangle / 15 \cdot D_{\text{intra}}$$

and may straightforwardly be determined therefore from the mean square crystallite radius $\langle R^2 \rangle$ and D_{intra} (4th column of Tab. 1).

As can be seen from Table 1 the values of τ_{intra} and $\tau_{\text{intra}}^{\text{model}}$ agree reasonably well for the samples 400SB and 200DB so that a significant influence of surface barriers may be excluded. By contrast, for the samples 400DB and 600DB the values of τ_{intra} distinctly exceed that of $\tau_{\text{intra}}^{\text{model}}$, which clearly indicates the existence of surface barriers.

Table 1

Intracrystalline self-diffusion coefficients D_{intra} , mean life times τ_{intra} and $\tau_{\text{intra}}^{\text{model}}$ for ethane in $\text{Na}_{3.2}\text{Ca}_{4.4}\text{A}$ at 293 K in dependence on the activation procedure of the zeolite

activation procedure	$\tau_{\text{intra}}/\text{ms}$	$D_{\text{intra}}/\text{m}^2\text{s}^{-1}$	$\tau_{\text{intra}}^{\text{model}}/\text{ms}$
400SB	1.5 ± 0.3	$(2.0 \pm 0.6) \cdot 10^{-10}$	1.3 ± 0.4
200DB	3.0 ± 0.6	$(1.0 \pm 0.3) \cdot 10^{-10}$	2.7 ± 0.8
400DB	8.0 ± 1.6	$(1.0 \pm 0.3) \cdot 10^{-10}$	2.7 ± 0.8
600DB	8.0 ± 1.6	$(1.0 \pm 0.3) \cdot 10^{-10}$	2.7 ± 0.8

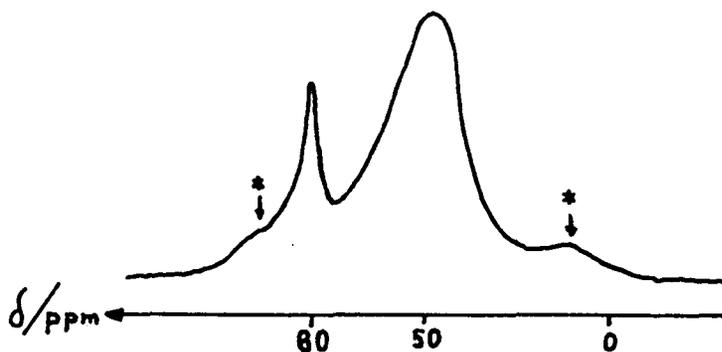


Fig. 1. ^{27}Al MAS NMR spectrum of the 300DB-sample, partially rehydrated, measured at 70 MHz, * denotes spinning side bands.

Fig. 1 shows the ^{27}Al MAS NMR spectrum of the partially rehydrated (6 H_2O per cavity) 300DB sample measured at 70 MHz with a rotational frequency of 3 kHz. The signal of the lattice aluminium atoms with a resonance shift of about 50 ppm referred to $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is in a good agreement with values given in [3]. A signal at 0 ppm corresponding to $\text{Al}(\text{H}_2\text{O})_6^{3+}$ -cations which has been observed in the ^{27}Al MAS NMR spectra of rehydrated zeolites HY [5] could not be found here. However, an additional signal appears with a resonance shift of 79 ± 1 ppm. According to [6] a signal at 80 ppm must be ascribed to the anion $\text{Al}(\text{OH})_4^-$ of aluminates. From the intensity of the signal at 79 ± 1 ppm a concentration of 1.7 aluminate anions per cavity would be determined. This means that after a 300°C deep bed activation at least 1.7 aluminium atoms per cavity are released from the zeolite lattice. The maximum number of extra-lattice aluminium cannot exceed a value of two aluminium atoms per cavity since a greater deficiency of lattice aluminium should be observable by a decrease of the intensity of the line at 50 ppm.

The experimental results of the ^{27}Al MAS NMR measurements can be explained as follows: Extra-lattice aluminium forms $\text{Al}(\text{OH})_4^-$ -anions and $\text{Al}(\text{H}_2\text{O})_6^{3+}$ -cations if it is solved in a basic (e.g. zeolite Ca A) or in an acidic environment (e.g. zeolite HY), respectively.

The signal of the aluminate anion could only be observed in Ca A samples activated at temperatures from 200°C up to 600°C under deep bed conditions followed by a rehydration. Samples prepared under shallow bed conditions or deep bed treated dehydrated zeolites did not show any signal at this position. In Table 2, column 4, values for the number of aluminate anions per cavity are given for fully rehydrated samples. The fact that in these cases the concentration does not attain the value of 1.7 measured for the partially rehydrated sample (as described above) may be explained by the lower pH-value in the fully hydrated samples.

The ^1H NMR spectra of the hydrated samples measured at $T_M < 150\text{K}$ are characterised by a superposition of a singlet due to hydroxyl protons and a doublet due to water protons. By a separation process both intensities can be determined [7]. The concentration of water in the rehydrated samples has been found thus to be about 25 molecules per cavity. After dehydration this value decreases to a concentration of ca. 10 for the samples 20DB, 20SB and 100DB, to about 4 for the sample 100SB and to less than 1/3 for the samples dehydrated at 200°C and above. Values for the concentration of hydroxylgroups are given in Tab. 2.

Table 2

Concentration of OH groups and of aluminate anions in dependence on the sample preparation.

sample preparation	dehydrated samples, OH groups per cavity	rehydrated samples		
		OH groups per cavity	$\text{Al}(\text{OH})_4^-$ per cavity	non-aluminate OH groups per cavity
20DB	1.6 ± 0.6	0.9 ± 0.4	0.0	0.9 ± 0.4
100DB	2.3 ± 0.6	0.9 ± 0.4	0.0	0.9 ± 0.4
200DB	4.7 ± 0.4	3.6 ± 0.4	0.55 ± 0.05	1.4 ± 0.6
300DB	4.4 ± 0.4	3.9 ± 0.4	0.35 ± 0.05	1.5 ± 0.6
400DB	3.0 ± 0.3	3.4 ± 0.4	0.20 ± 0.05	2.6 ± 0.6
500DB	2.1 ± 0.3	2.5 ± 0.4	0.16 ± 0.05	1.9 ± 0.6
600DB	0.8 ± 0.3	3.2 ± 0.4	0.13 ± 0.05	2.7 ± 0.6
20SB	1.5 ± 0.6	0.9 ± 0.4		
100SB	2.6 ± 0.6	1.0 ± 0.4		
200SB	2.0 ± 0.3	1.1 ± 0.4		
300SB	1.5 ± 0.3	1.1 ± 0.4		
400SB	1.1 ± 0.3	1.2 ± 0.4		
500SB	0.6 ± 0.3	1.2 ± 0.4		

The free induction decay (FID) of the dehydrated samples measured at room temperature can be described by a single transverse relaxation time T_2^{FID} . Its value is 70 μs and 50 μs for the 400DB and 400SB samples, respectively. The envelope of Hahn's spin echoes decays with the relaxation times of $T_2^{\text{Hahn}} = 340 \mu\text{s}$ and 170 μs for the 400DB and 400SB samples, respectively.

Fig. 2 shows the ^1H MAS NMR spectra of the 300DB and 300SB samples measured at 270 MHz. According to [8] a signal with a chemical shift of 1.8 ppm must be ascribed to isolated SiOH or AlOH groups similar to OH groups at the surface of silica gel or $\gamma\text{-Al}_2\text{O}_3$. A signal at 3.9 ... 5.6 ppm corresponding to bridging OH groups [8] could not be found. However, a signal appears at about 3 ppm, which is weak for shallow bed and strong for deep bed pretreatment.

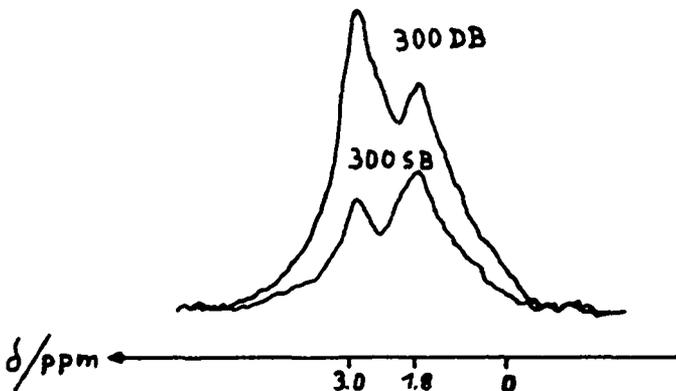


Fig. 2. ^1H MAS NMR spectra of dehydrated 300DB and 300SB samples; measured at 270 MHz

DISCUSSION

Combination of the NMR self-diffusion and tracer desorption experiments (cf. tab.1) clearly indicates the formation of surface barriers during the deep bed activation. We shall discuss the following three possibilities of their structural origin:

(i) transformation of the crystallite in the vicinity of the surface from a 5 A- to a 4 A-type structure as a consequence of the formation of monovalent CaOH^+ cations,

(ii) formation of an amorphous surface layer due to lattice destruction in the vicinity of the surface,

(iii) deposition of extra-lattice species in the cavities in the vicinity of the surface.

Since the surface barrier is resistant to temperatures as high as 600°C (cf. Tab. 1) and since at these temperatures the final stage of dehydroxilation (cf. Tab. 2) will be reached which as well should comprise the reaction $2 \text{CaOH}^+ \longrightarrow \text{Ca}^{2+} + \text{CaO} + \text{H}_2\text{O}$ explanation (i) must be excluded.

The second model presupposes a destruction of the lattice structure at least for a part of the crystallite surface. This implies that a part of the surface is closed for the molecular transport. However, measurements of the activation energy E of τ_{intra} according to the equation $\tau_{\text{intra}} = \tau_0 \exp \{E/RT\}$ yields an increase of E , whereas for a partially closed surface only an increase of τ_0 with E remaining constant would be expected [9]. Therefore we shall confine

ourselves to the discussion of model (iii).

Evidently we have to assume that the deposition of the extra-lattice species predominantly occurs in the surface layer of the crystallites. The blockade of the cavities (or of the windows between them) will then straightforwardly lead to the formation of a surface barrier. It is well-known [10], that during the process of NaY dealumination extra-lattice aluminium is deposited on the surface. In CaA, the existence of extra-lattice aluminium has been proved by both X-ray [11] and ^{27}Al MAS NMR [12,13] measurements.

We could observe in numerous investigations of A-type zeolites with bivalent cations, a remarkable correlation between the formation of surface barriers and an enhancement of the OH groups concentration. For example, in dehydrated 400DB samples a number of 3.0 ± 0.3 OH groups per cavity could be determined, while for dehydrated 400SB samples (which are characterized by a negligibly small surface resistance - cf. Tab. 1) the value is only 1.1 ± 0.3 . On the other hand the value of $T_2^{\text{Hahn}} = 340 \mu\text{s}$ as obtained for the 400DB samples is in satisfactory agreement with a theoretical value of $316 \mu\text{s}$ calculated under the assumption of a statistical distribution of the OH groups (3 per cavity) over the whole crystallite [14]. Therefore it is most likely that the formation of a surface barrier is correlated with a bulk phase process which as well tends to enhance the OH group concentration.

OH groups arise in the process of water dissociation initiated by a temperature enhancement under the influence of the bivalent cations of the zeolite lattice. We shall consider the following models of their formation:

(*) hydration of aluminium oxide species deposited statistically within the zeolite crystals as a consequence of Al_2O_3 excess during zeolite synthesis,

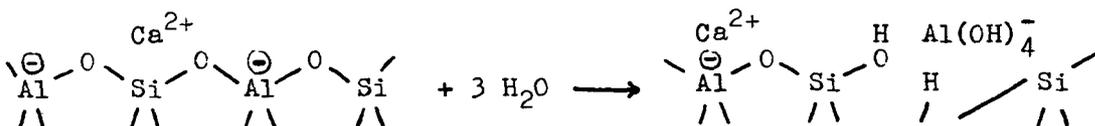
(**) hydroxylation of aluminium atoms released from lattice positions,

(***) formation of CaOH^+ cations and bridging OH groups.

Model (*) is based on the fact that chemical analysis of the NaA zeolite after synthesis yields a ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 1.91 \pm 0.02$ which is not affected by the cation exchange. Since according to the ^{27}Al MAS NMR measurements of the dehydrated samples there are no Al-O-Al bonds in the lattice, the aluminium excess of 4.7 % must be explained by an amount of 0.57 aluminium atoms per cavity on extra-lattice posi-

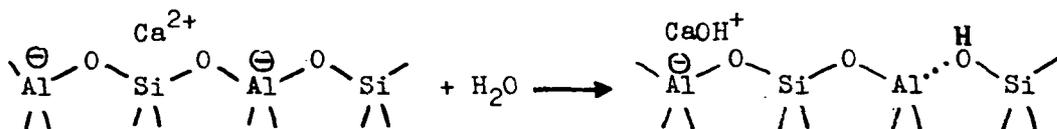
tions. It may be deposited as aluminium oxide or aluminium hydroxide species. Both in the hydrated NaA 400DB and the Na Ca A SB samples no aluminate could be found. If we assume that under the influence of Ca^{2+} these possibly highly condensed compounds may be transformed into small mobile aluminium hydroxide complexes (e.g. $\text{Al}_2\text{O}_3 + 3 \text{H}_2\text{O} \rightarrow 2 \text{Al}(\text{OH})_3$), these species partially may be concentrated at the surface. With a further temperature enhancement or a decrease of the water pressure these species again may condensate leading to the formation of a surface barrier.

Reaction (***) may be described as follows:



where an aluminium atom is released from its lattice position. After the release of an aluminium from its lattice position in zeolite HY, the site is occupied by a silicon atom and hence the crystal structure is preserved even under the process of dealumination [3]. An analogous reaction in zeolites A would lead to the formation of Si-O-Si bonds. Since in the ^{29}Si MAS NMR spectra of the investigated samples no lines corresponding to Si-O-Si bonds did occur [15], any healing of aluminium defects can be excluded. In the course of the above mentioned reaction also an oxygen atom is released from the lattice, which leads to a distortion of the lattice structure. Via the reaction $\text{Ca}^{2+} + \text{Al}(\text{OH})_4^- \longrightarrow \text{CaOH}^+ + \text{Al}(\text{OH})_3$, the aluminate anion may be transformed into aluminium hydroxide. Being uncharged, it has a higher mobility which may lead to the formation of a surface barrier as described above.

According to Planck [16], model (***) might proceed according to the following reaction:



With zeolites CaX and CaY this mechanism could be verified by IR investigations. While two IR bands may be unambiguously attributed to the bridging OH groups, this is not the case for the attribution of the other IR bands to the CaOH^+ cations [17,18]. By contrast, in IR investigations of zeolite CaA no IR band is observed which might be attributed to bridging OH groups [19]. Analogously, also in the ^1H NMR spectra (cf. Fig. 2) no acidic OH groups are detected. This experimental finding is in complete agreement with the above stated basic behaviour of zeolite CaA, containing basic aluminates rather than acidic Al^{3+} in $\text{Al}(\text{H}_2\text{O})_6^{3+}$ complexes. The above reaction cannot be accepted therefore as an explanation for the observed hydroxyl groups and extra-lattice aluminium in zeolite CaA.

Therefore we only have to consider mechanisms (*) and (**). Since the first mechanism permits an amount of extra lattice aluminium of not more than 0.57 per cavity, it must be accompanied by reaction (**). The latter may be considered as a first step of a lattice transformation which may be observed after intense hydrothermal treatment [20]. An unequivocal interpretation of the signal at 3 ppm in Fig. 2 is not yet possible. Perhaps this signal may be attributed to OH groups interacting with additional oxygen atoms. It shall be the task of further investigations, esp. by MAS NMR, to accomplish the proposed model of structural defects in zeolite CaA.

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