NMR STUDIES CONCERNING THE DEHYDROXYLATION OF ZEOLITES HY

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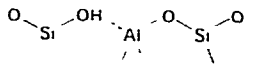
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By applying the magic-angle spinning technique to proton magnetic resonance of zeolites HY two or three different lines could be separated. Measurements of the number of structural OH groups and of lattice aluminium atoms by ^{1}H and ^{27}Al nuclear magnetic resonance show that the dehydroxylation of the zeolite lattice is accompanied in all cases by a corresponding dealumination process. The number of dehydroxylated structural OH groups is always equal to the number of four-fold oxygen-coordinated lattice aluminium atoms released from the framework during dealumination. Since no three-fold oxygen-coordinated aluminium appears in the lattice, all released aluminium must migrate to extra-lattice positions.

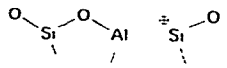
1. Introduction

Aluminosilicates may contain terminal OH groups at the surface of the crystallites and at lattice defects but also hydroxyl groups in a bridged arrangement of the form



(the so-called structural OH groups) in their structure. Hence it is possible to construct an ideal zeolite H without any cation. But during a hydrothermal treatment (activation) of an ammonium-exchanged zeolite, defects of the zeolite framework arise because of the deammoniation and dehydroxylation and a real structure appears which is quite different from the ideal structure of the zeolite. An activated zeolite H contains Brønsted-acid sites as well as Lewis-acid sites as catalytically effective centres.

Ward [1] reviewed several publications devoted to the study of dehydroxylation by IR experiments. A model of the dehydroxylation process was established by Uytterhoeven et al. [2] in 1965. From this model it follows that a three-fold oxygen-coordinated aluminium atom of the form



with Lewis-acid properties arises in the lattice during dehydroxylation. But the existence of the three-fold coordinated lattice aluminium could be excluded by X-ray spectroscopy [3,4] and ^{27}Al NMR [5,6]. Therefore Jacobs and Beyer [7] proposed Al–O species on extra-lattice positions as Lewis-acid sites instead of the three-fold coordinated lattice aluminium.

In the present paper it is shown that a dehydroxylation of zeolites HY is always accompanied by a consistent dealumination of the framework and an extended model of the dehydroxylation process is represented.

2. Experimental

Starting from a zeolite NaY (VEB Chemiekombinat, Bitterfeld, GDR) with a Si/Al ratio of 2.6 the ammonium type was prepared by a cation exchange of $88 \pm 3\%$ in an aqueous solution of NH_4NO_3 according to Chu et al. [8].

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One portion of the samples was prepared under "deep-bed" (DB) conditions: About one gram of the zeolite was heated in an open glass tube (10 mm diameter) under 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 two hours at this temperature it was evacuated for twenty hours and sealed off. During this latter procedure the pressure decreased below 10^{-2} Pa.

For the other portion of the samples "shallow-bed" (SB) conditions were used for preparation: The layer thickness of the zeolite powder was chosen to be less than 3 mm, the sample was heated up in vacuo at a rate of 10 K h^{-1} to the final temperature of activation and sealed off under vacuum.

In what follows, a sample prepared at a final temperature of 400°C under deep-bed conditions is denoted by "400 DB", for example. The ^{1}H NMR intensity measurements for the determination of the number of OH groups were carried out with an NMR pulse spectrometer at 90 MHz. The highly resolved spectra were obtained with an NMR pulse spectrometer working at 270 MHz using the magic angle spinning (mas) technique (rotation frequency 2.2 kHz, cf. ref. [9]; ^{1}H NMR at strong magnetic fields with additional mas yields a reduction of the influence of heteronuclear ^{1}H- and ^{27}Al-dipole–dipole interaction) and the WHH-4 pulse sequence (cf. ref. [10]) with a repetition time of 10 s, a recycle time of the sequence of 24 μs and a pulse width of 1 μs. The zeolite powder for mas was also placed in small glass tubes (4 mm diameter) and sealed off under vacuum. The ^{1}H resonance shifts are referred to TMS, given in ppm and positive to lower field. The accuracy is ±0.5 ppm. Therefore a correction according to Michel et al. [11] considering the susceptibility could be neglected.

The ^{27}Al NMR measurements for the determination of the number of aluminium atoms in the zeolite framework and on extra-lattice positions [5] were carried out with an NMR pulse spectrometer at a resonance frequency of 70.34 MHz.

All values of intensity (calculated by comparison with a standard of known intensity) are referred to one cavity. Because of the proceeding dealumination of the samples during activation accompanied by a migration of silicon [12] the number of cavities decreases. This mechanism is rather complicated, connected with the formation of secondary pores [13], and difficult to comprehend quantitatively. Therefore all intensities are referred to the number of cavities of an *ideal*, 88% ammonium-exchanged zeolite HY. The concentrations of aluminium atoms and OH groups per cavity of a real zeolite HY are greater. But since the factor is the same for aluminium and OH groups, conclusions based on the comparison of the concentration of these two species are not influenced.

3. Results and discussion

The determination of the number of structural OH groups requires both the measurement of the total intensity of all existing OH groups and the separation of their different kinds in the activated zeolite. The highly resolved ^{1}H NMR spectra shown in fig. 1 exhibit lines at (i) 2.0 ppm, (ii) 4.2–5.0 ppm, and (iii) 6.8–8.0 ppm. The separated intensities of these three lines are given in table 1 as a function of the conditions of activation. Residual ammonium which is present especially in the samples activated at low temperatures yields a resonance line at 7.1 ppm (see, e.g. ref. [14]). The exact amount of the residual ammonium was determined by thermodesorption [15] and subtracted from the intensity of line (iii).

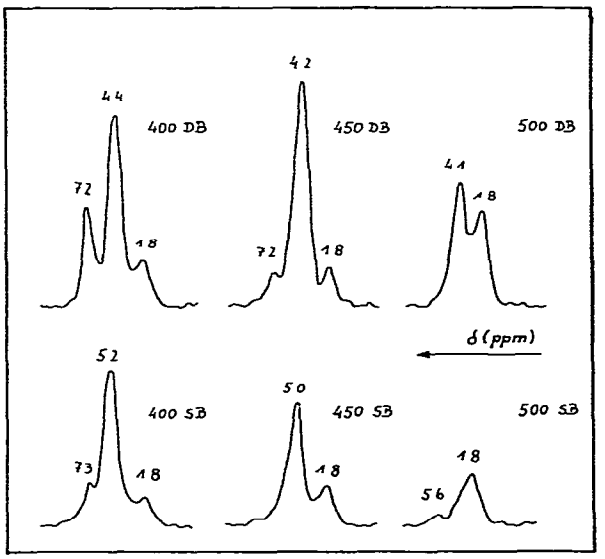


Fig. 1. High-resolution ^{1}H NMR spectra of 270 MHz with mas and WHH-4 pulse sequence of an 88% ammonium-exchanged zeolite HY depending on the activation conditions.

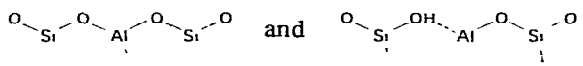
Table 1
Concentration of hydroxyl groups and of the observable aluminium atoms of a 88% ammonium-exchanged zeolite HY in dependence on the activation conditions

Sample	Terminal OH groups, line (i) (OH/cavity)	Structural OH groups		Four-fold coordinated lattice aluminium (Al/cavity)	Rehydrated extra-lattice aluminium (Al/cavity)
		line (ii) (OH/cavity)	line (iii) (OH/cavity)		
NaY 300 DB[a]				6.7 ± 0.4	0.0 ± 0.0
300 DB	0.4 ± 0.2	3.6 ± 0.4	0.7 ± 0.2	4.7 ± 0.4	1.4 ± 0.2
400 DB	0.5 ± 0.2	2.8 ± 0.4	0.4 ± 0.2	3.7 ± 0.4	1.1 ± 0.2
450 DB	0.6 ± 0.2	3.0 ± 0.4	0.3 ± 0.2	b)	b)
500 DB	0.9 ± 0.2	1.9 ± 0.4	0.0 ± 0.1	2.7 ± 0.4	0.4 ± 0.1
600 DB	>0.9 ± 0.2	<0.9 ± 0.4	0.0 ± 0.1	1.1 ± 0.4	0.1 ± 0.1
300 SB	0.5 ± 0.2	5.8 ± 0.4	0.3 ± 0.2	5.5 ± 0.4	1.3 ± 0.2
400 SB	0.5 ± 0.2	5.8 ± 0.4	0.2 ± 0.2	5.8 ± 0.4	1.4 ± 0.2
450 SB	0.9 ± 0.2	5.6 ± 0.4	0.0 ± 0.1	5.9 ± 0.4	1.1 ± 0.2
500 SB	1.5 ± 0.2	0.0 ± 0.1	0.0 ± 0.1	b)	b)
600 SB	0.7 ± 0.3	0.0 ± 0.1	0.0 ± 0.1	1.2 ± 0.4	0.1 ± 0.1

[a] Reference for ^{27}Al intensity measurements. [b] Values not yet measured.

The free induction decay (fid) of all samples is characterized by a component with a transverse relaxation time T_2 from 60 to 75 μs. A comparison with IR measurements [16] shows that these signals must be caused by structural OH groups. Only the 500 SB sample yields a second component of the fid with a much shorter transverse relaxation time (T_2 = 25 μs). Such a short T_2 is characteristic of AlOH groups of γ-Al_2O_3 [17, 18]. The intensity of the sort component of the signal was 40%.

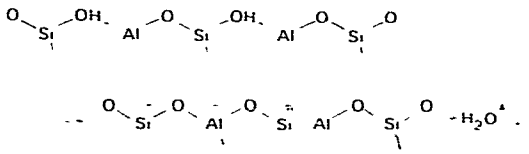
By ^{27}Al NMR it is possible to separate the signals of that extra-lattice aluminium which has formed hexaaquo complexes during rehydration and of the lattice aluminium in a tetrahedral oxygen environment [6]. This four-fold coordinated aluminium can exist in the two forms,



Lattice aluminium in a three-fold coordination of oxygen (if it is available) is not "visible" in the ^{27}Al NMR signal. The concentrations of four-fold lattice aluminium and of the extra-lattice aluminium which can be rehydrated is given in table 1 for the samples activated at different temperatures.

From previous investigations [19] it is evident that both the SiOH groups (terminal OH groups) and the AlOH groups (e.g. at the extra-lattice aluminium) yield chemical shifts from 1.8 to 2.5 ppm. From this it follows that line (i) is caused by SiOH and AlOH groups too. But the latter only appeared in significant amounts in the 500 SB sample (short fid with T_2 = 25 μs).

Measurements of amorphous aluminosilicates [18] showed that OH groups which yield a line at the position (iii) have a great catalytic activity (structural OH groups). But also hydroxyl groups of line (ii) may be identified as structural OH groups, because they show strong interaction with pyridine [19] just like the OH groups of line (iii). Therefore the sum of the intensities of lines (ii) and (iii) gives the total amount of all existing structural OH groups in the zeolite. The well-established model of Uytterhoeven et al. [2] characterizes the dehydroxylation procedure of zeolites as follows



Always two structural OH groups are dehydroxylated forming one water molecule. One of the two four-fold coordinated aluminium atoms in the neighbourhood of these OH groups remains four-fold coordinated, the

other one becomes three-fold coordinated. From this model it follows that for each lattice aluminium atom which becomes three-fold coordinated during dehydroxylation two structural OH groups must be dehydroxylated. However, from table 1 it is evident that the number of structural OH groups is always equal to the number of four-fold coordinated lattice aluminium atoms. This leads to the conclusions that (i) *three-fold coordinated lattice aluminium does not appear during the dehydroxylation of zeolites HY* and that (ii) *the dehydroxylation in the neighbourhood of a lattice aluminium atom is always accompanied by its release from the framework.*

During a deep-bed activation the aluminium atom in the neighbourhood of a structural OH group is released from the framework due to hydrothermal damage, forming extra-lattice aluminium and dehydroxylating that OH group at the same time. The formation of so-called OH nests at the resulting lattice defects can be excluded because no increase of the intensity of line (i) was noticed (cf. ref. [20]). Lohse et al. [13] proposed a healing process of the framework by a migration of silicon atoms accompanied by a formation of secondary pores.

During an ideal shallow-bed activation no hydrothermal damage takes place because ammonia and water are always evacuated. Therefore the framework shows no essential change at temperatures below 450°C (small amounts of extra-lattice aluminium because the SB conditions were not ideal [6]). Since no dealumination and hence no thermal stabilization occurs (e.g. ref. [21]) the lattice breaks down at temperatures above 450°C. This breakdown is confirmed by the appearance of AlOH groups in the 500 SB sample which are similar to those of γ-Al_2O_3.

The difference between the total amount of aluminium atoms (6.7 Al/cavity) which are present in the zeolite used and the sum of the aluminium atoms given in table 1 can be attributed to solid extra-lattice aluminium which cannot be rehydrated and which is deposited as Al_2O_3 clusters inside the secondary pores.

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