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^{29}Si and ^{27}Al MAS NMR characterization of non-hydrated zeolites Y upon adsorption of ammonia

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Dedicated to the late Denise Barthomeuf, George Kokotailo and Sergey P. Zhdanov in appreciation of their outstanding contributions to zeolite science

Abstract

Solid-state NMR characterization of zeolite catalysts in the hydrated state is often accompanied by an uncontrolled hydrolysis of the framework. In the present work it is demonstrated that the limitations occurring for ^{29}Si and ^{27}Al MAS NMR spectroscopy of non-hydrated zeolites Y, such as strong decrease of resolution and significant line broadening, can be overcome by loading these materials with ammonia. In the ^{29}Si MAS NMR spectra of non-hydrated and ammonia-loaded zeolites Y, no dehydration-induced high-field shift of Si(nAl) signals ($n = 3$, 2, 1) occurs, which is generally responsible for the loss of resolution in the spectra of non-hydrated materials. The ^{27}Al MAS NMR spectra of the non-hydrated and ammonia-loaded zeolites Y consist exclusively of signals of the tetrahedrally coordinated framework aluminum atoms with spectroscopic parameters similar to those of framework aluminum atoms in hydrated samples. The framework n_{Si}/n_{Al} ratios of the *non-hydrated* zeolites Y obtained by both ^{29}Si and ^{27}Al MAS NMR spectroscopy upon ammonia-loading agree well with each other.
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Keywords: Zeolites; Framework composition; Non-hydrated samples; Solid-state NMR spectroscopy; Ammonia adsorption

1. Introduction

During the past decades, most of the solid-state NMR investigations of zeolite catalysts were performed on hydrated materials [1–12]. The characterization of solid catalysts in a state comparable to their application in industrial processes, however, requires the investigation of calcined and non-hydrated materials. Hydration of calcined zeolite catalysts before the spectroscopic characterization is often accompanied by an uncontrolled hydrolysis of framework aluminum atoms and a change of the nature of extra-framework aluminum species.

van Bokhoven et al. [13] applied XANES (X-ray absorption near-edge spectroscopy) for the study of non-hydrated zeolites H-Beta under vacuum and found three-coordinated aluminum atoms at high temperatures and distorted tetrahedral aluminum atoms at ambient temperature [13]. In addition, they observed that the distorted tetrahedral aluminum atoms can be converted to the regular tetrahedral aluminum just upon rehydration [14]. Solid-state ^{27}Al NMR studies of hydrated and non-hydrated zeolites Y and ZSM-5 indicated a significant increase of the quadrapolar coupling constant C_{QCC} of the framework aluminum atoms from ca. 3 to 16 MHz, in the vicinity of bridging hydroxyl protons upon dehydration, which corresponds to a strong decrease of the local symmetry of the oxygen coordination of these aluminum species [15,16]. While framework aluminum atoms in the vicinity of bridging hydroxyl protons in hydrated zeolite catalysts are tetrahedrally coordinated, it was suggested that they exist in dehydrated materials in a semi-threefold oxygen coordination [15,16].

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Generally, the dehydration-induced coordination change of the framework aluminum atoms in the vicinity of bridging hydroxyl protons in zeolite catalysts affects the ^{29}Si NMR parameters of silicon atoms in their local structure. Very recently, the aluminum distribution in steamed and non-hydrated zeolites H–Y was investigated by solid-state ^{1}H, ^{27}Al and ^{29}Si NMR spectroscopy [17,18]. For these materials, a significant dehydration-induced high-field shift of Si(nAl) signals ($n = 3$, 2, 1) in the ^{29}Si MAS NMR spectra of the non-hydrated materials was found. It has been suggested that the origin of this effect lies in the change of the bonding geometry of framework aluminum atoms in the vicinity of bridging OH groups in the non-hydrated zeolites [17,18]. In addition, it was observed that the high-field shift of Si(nAl) signals does not occur, if the negative charges of framework aluminum atoms are compensated by extra-framework cations, such as sodium cations [18]. Due to the high-field shifts of Si(nAl) signals, the resolution of the ^{29}Si MAS NMR spectra decreases considerably, and, therefore, the determination of the framework n_{Si}/n_{Al} ratio becomes impossible.

Already in 1991, Bourgeat-Lami et al. [19] investigated the effect of ammonia and pyridine on the coordination of aluminum atoms occurring as octahedrally coordinated species in calcined and rehydrated zeolites Beta and found an ammonia-induced Al^{IV}–Al^{VI} transformation. Also in the case of zeolite Beta, the effect of ammonia on the stabilization of framework aluminum atoms during the steaming of this material was demonstrated [20]. Wichterlová and coworkers [21] published quantitative ^{27}Al MAS NMR studies of various ammonia-loaded zeolites containing Al and Fe on isomorphously substituted silicon sites in their framework. However, all the above-mentioned solid-state ^{27}Al NMR investigations of ammonia-loaded zeolites were performed with samples in the hydrated state.

In the present work, the effect of the adsorption of ammonia on non-hydrated zeolites Y was studied by ^{29}Si and ^{27}Al MAS NMR spectroscopy. The zeolite catalysts under study were parent H-form and steamed materials. It is demonstrated that solid-state NMR spectroscopy of ammonia-loaded samples can be utilized as a tool for the quantitative characterization of the framework composition of zeolites in the non-hydrated state.

2. Experimental part

Zeolite Na-Y ($n_{Si}/n_{Al} = 2.7$) of Degussa AG, Hanau, Germany, was sixfold exchanged in a 1.0 M aqueous solution of NH_4NO_3 at 353 K for 12 h. The obtained zeolite NH_4-Y was washed with demineralized water until no nitrate ions were detected any more. Subsequently, the powder material was dried in air at 353 K for 12 h. After this treatment, a cation-exchange degree of 93.3% was reached, as determined by atomic emission spectroscopy (AES-ICP, Perkin Elmer Plasma 400). X-ray diffraction (Siemens D5000, CuKα radiation) and solid-state NMR spectroscopy were applied in tandem to exclude the presence of framework defects and extra-framework aluminum in the zeolite NH_4-Y sample. For dealumination by steaming, ca. 2 g of zeolite NH_4-Y were placed in a horizontal quartz glass tube under flowing nitrogen (200 cm^3/min). Subsequently, the material was heated at a rate of 1.6 K/min up to 748 K, followed by calcination at 748 K for 10 h. Steaming of the zeolite materials was performed at 748 K for 2 h, after switching from a flow of dry nitrogen to a flow of nitrogen saturated with water vapor. The water vapor pressure was 0 (zeolite H,Na-Y), 31.1 (zeolite deH,Na-Y/31.1), and 81.5 kPa (zeolite deH,Na-Y/81.5). This was achieved by directing the flow of nitrogen through a water bath at temperatures of 343 K (zeolite deH,Na-Y/31.1) and 367 K (zeolite deH,Na-Y/81.5). To exclude an uncontrolled modification of the resulting materials by rehydration of the calcined or steamed zeolites Y, these materials were transferred into glass containers under dry nitrogen in an air-lock. Prior to the NMR investigations of the non-hydrated samples, some of these were rehydrated for 12 h in a desiccator (hydrated samples) or loaded with ammonia at a pressure of 20 kPa for 4 h at 300 K (non-hydrated/ammonia-loaded samples). The non-hydrated and non-hydrated/ammoniated materials were filled into MAS NMR rotors under dry nitrogen using a glove box.

^{27}Al and ^{29}Si MAS NMR studies were carried out on a Bruker MSL 400 spectrometer at resonance frequencies of 104.26 and 79.49 MHz, respectively. ^{29}Si MAS NMR spectra were recorded with a 7 mm MAS rotor system, a sample spinning rate of 3.5 kHz, and after a $\pi/2$ single-pulse excitation of 6.0 μs. Repetition times of 50 s for non-hydrated samples, 10 s for rehydrated samples, and 90 s for non-hydrated/ammonia-loaded samples were used. To decrease the longitudinal relaxation time of silicon atoms in the non-hydrated zeolite Y, these samples were loaded with synthetic air ($p = 100$ kPa) consisting of 20 vol.% oxygen and 80 vol.% nitrogen. By comparison of the ^{29}Si MAS NMR spectra of oxygen-loaded and unloaded samples it was ensured that the gaseous oxygen had no influence on the shape of spectra. ^{27}Al MAS NMR measurements were carried out with a 4 mm MAS rotor system, a sample spinning rate of 10 kHz, $\pi/6$ single-pulse excitation of 0.61 μs, and repetition times of 500 ms for hydrated samples and 2 s for non-hydrated/ammonia-loaded samples. A fully hydrated zeolite NH_4-Y was used as the external intensity standard for the ^{27}Al MAS NMR studies. The decomposition and simulation of NMR spectra were performed using the Bruker software WINNMR and WINFIT. All steamed zeolites Y were investigated by atomic emission spectroscopy (AES-ICP) to determine the total (bulk) amount of aluminum.

3. Results and discussion

3.1. Characterization of non-hydrated zeolites by ^{29}Si MAS NMR spectroscopy

In the present work, a series of calcined and steamed zeolites Y were investigated by ^{29}Si MAS NMR spectroscopy

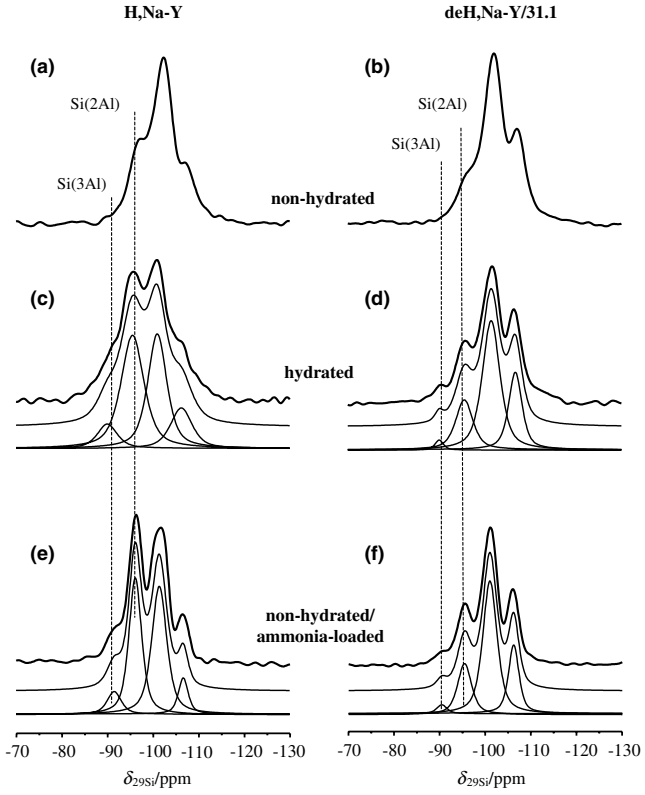

Fig. 1. ^{29}Si MAS NMR spectra of non-hydrated (a, b), rehydrated (c, d), and non-hydrated/ammonia-loaded (e, f) zeolites H,Na-Y (left) and deH,Na-Y/31.1 (right).

using (i) samples, which were not rehydrated upon calcination and steaming, (ii) rehydrated samples, and (iii) non-hydrated samples loaded with ammonia. As an example, Fig. 1 shows the ^{29}Si MAS NMR spectra of zeolites H,Na-Y and deH,Na-Y/31.1 treated in the above-described manner. Spectra (a) and (b) are those of the non-hydrated materials. As shown in previous papers [17,18], in these spectra the ^{29}Si MAS NMR signals of Si(nAl) species ($n = 3$, 2, 1) are high-field shifted by 2–5 ppm (Fig. 1, top). Therefore, the signals in the spectra of non-hydrated zeolites Y have an intensity distribution characteristic for materials with low framework aluminum content. Upon full rehydration of the calcined and steamed materials, no high-field shift of Si(nAl) signals occurs and the ^{29}Si MAS NMR spectra obtained are comparable with those described in the literature [1–12] (Fig. 1, middle trace). The framework n_{Si}/n_{Al} ratio of the rehydrated zeolites H,Na-Y and deH,Na-Y calculated from the relative intensities of Si(nAl) signals are given in Table 1, second column.

In earlier solid-state ^{27}Al NMR investigations of non-hydrated zeolites Y and ZSM-5 it was found that ammonia adsorption leads to a strong decrease of the quadrapolar interactions of framework aluminum atoms in the vicinity of bridging hydroxyl protons in these materials [22,23]. The effect is accompanied by a change of the oxygen coordination of these framework aluminum atoms. If the high-field shift of Si(nAl) signals in the ^{29}Si MAS NMR spectra of the non-hydrated zeolites is caused by a strain of the local structure of framework aluminum atoms, a decrease of these high-field shifts can be expected upon adsorption of ammonia. As an example, Fig. 1, bottom, shows the ^{29}Si MAS NMR spectra of non-hydrated/ammonia-loaded zeolites H,Na-Y and deH,Na-Y/31.1. These spectra consist of well resolved Si(nAl) lines with relative intensities comparable to those of the hydrated materials. No high-field shift of the Si(3Al) and Si(2Al) signals occurs. The framework n_{Si}/n_{Al} ratios calculated from the relative intensities of Si(nAl) signals are given in Table 1, second column. A comparison of the framework n_{Si}/n_{Al} ratios obtained for non-hydrated/ammonia-loaded zeolites Y with those of the rehydrated samples shows that the latter values are systematically higher, which indicates a slightly lower framework aluminum content. This finding indicates a weak hydrolysis of framework aluminum atoms in the rehydrated materials.

Table 1
Framework n_{Si}/n_{Al} ratios of zeolites H,Na-Y, deH,Na-Y/31.1, and deH,Na-Y/81.5 determined by ^{29}Si and ^{27}Al MAS NMR spectroscopy of samples in the rehydrated state and of non-hydrated samples, which were loaded with ammonia

Samples	Framework n_{Si}/n_{Al} ratio	
	^{29}Si MAS NMR	^{27}Al MAS NMR
H,Na-Y, rehydrated	2.8	3.6
H,Na-Y, non-hydrated/ammonia-loaded	2.7	2.6
deH,Na-Y/31.1, rehydrated	4.0	3.5
deH,Na-Y/31.1, non-hydrated/ammonia-loaded	3.8	3.8
deH,Na-Y/81.5, rehydrated	5.9	3.8
deH,Na-Y/81.5, non-hydrated/ammonia-loaded	5.8	6.1

3.2. Characterization of non-hydrated zeolites by ^{27}Al MAS NMR spectroscopy

Due to the strong quadrapolar interactions of framework aluminum atoms in the vicinity of bridging hydroxyl protons in non-hydrated zeolites (C_{QCC} ca. 16 MHz), these ^{27}Al NMR signals have a line broadening of the order of 500 ppm [24]. In the case of ^{27}Al MAS NMR spectroscopy in magnetic fields of 7.0–11.7 T, therefore, the above-mentioned signal is much broader than the commonly used spectral windows of ca. 200 ppm. As an example, the ^{27}Al MAS NMR spectra of non-hydrated zeolites H, Na-Y and deH,Na-Y/81.5 (Fig. 2, top) consist of very weak signals due to framework aluminum atoms only, the negative charges of which are compensated by residual sodium cations and cationic extra-framework aluminum species. Upon rehydration of the calcined and steamed zeolites Y, the C_{QCC} value of framework aluminum atoms in the vicinity of bridging hydroxyl protons is strongly decreased from 16 MHz to a value of 3–6 MHz leading to

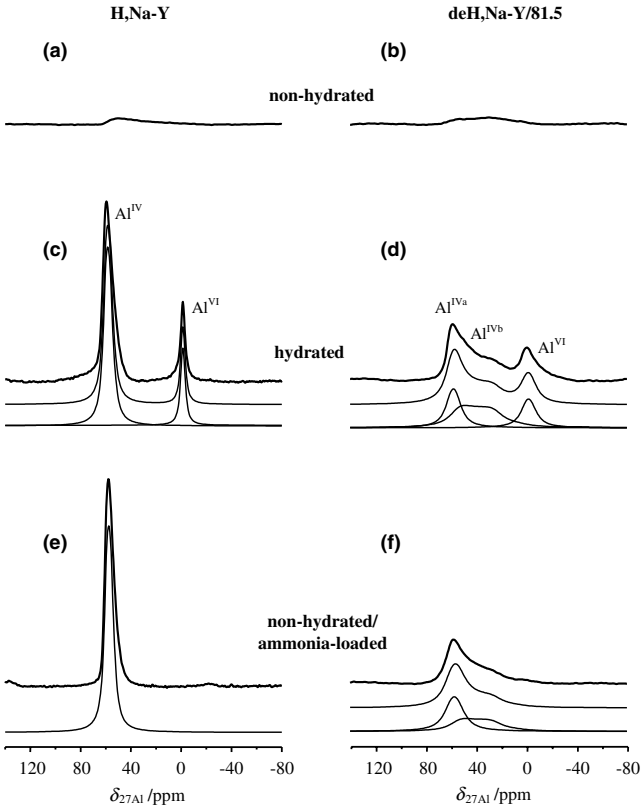

Fig. 2. ^{27}Al MAS NMR spectra of non-hydrated (a, b), rehydrated (c, d), and non-hydrated/ammonia-loaded (e, f) zeolites H,Na-Y (left) and deH,Na-Y/81.5 (right).

^{27}Al MAS NMR signals at ca. 60 ppm (Al^{IVa} and Al^{IVb}) [23]. The signals at ca. 0 ppm are due to octahedrally coordinated aluminum species (Al^{VI}). The spectra of the rehydrated materials in Fig. 2, middle, were simulated using the quadrapolar parameters determined by ^{27}Al MQMAS NMR spectroscopy in an earlier study [25]. The signals of tetrahedrally coordinated framework aluminum atoms are described by the two components with C_{QCC} values of 2.2 (Al^{IVa}) and 6.7 MHz (Al^{IVb}) [25]. The quantitative comparison of the intensities of the signals Al^{IVa} and Al^{IVb} with that of an external intensity standard gives the framework n_{Si}/n_{Al} ratios summarized in Table 1, last column.

A comparison of the framework n_{Si}/n_{Al} ratios in columns 2 and 3 indicates that the values determined by ^{27}Al MAS NMR spectroscopy deviate from those obtained by ^{29}Si MAS NMR spectroscopy. In the case of zeolite H,Na-Y, this deviation is caused by a partial hydrolysis of framework aluminum atoms leading to the ^{27}Al MAS NMR signal at 0 ppm. In the case of steamed and rehydrated zeolites Y, signals of extra-framework aluminum species may contribute to the signal Al^{IVb} thus leading to an incorrect quantification of the framework aluminum atoms.

A more selective ^{27}Al MAS NMR investigation of framework aluminum atoms without uncontrolled hydrolysis of these species was performed by loading the non-hydrated materials with ammonia. Fig. 2, bottom, shows the ^{27}Al MAS NMR spectra obtained for the non-hydrated/ammonia-loaded zeolites H,Na-Y and deH,Na-Y/81.5. In contrast to the spectrum of the rehydrated material, the ^{27}Al MAS NMR spectrum of the non-hydrated/ammonia-loaded zeolite H,Na-Y gives only a signal of the tetrahedrally coordinated framework aluminum atoms at ca. 60 ppm. The quantitative evaluation of this signal gives a framework n_{Si}/n_{Al} ratio of 2.6, which agrees very well with the value of 2.7 determined by ^{29}Si MAS NMR spectroscopy. Similar results were obtained for steamed zeolite Y samples. As an example, the ^{27}Al MAS NMR spectrum of the non-hydrated/ammonia-loaded zeolite deH,Na-Y/81.5 consists exclusively of the signals due to the tetrahedrally coordinated framework aluminum atoms. The comparison of the intensities of these signals with that of the external intensity standard leads to a framework n_{Si}/n_{Al} ratio of 6.1, which agrees reasonably well with the value of 5.8 determined by ^{29}Si MAS NMR spectroscopy.

4. Conclusions

Generally, the determination of the framework aluminum content of non-hydrated zeolite catalysts is hampered by high-field shifts of Si(nAl) signals in ^{29}Si MAS NMR spectroscopy and a strong broadening of the ^{27}Al MAS NMR signals of the framework aluminum atoms in the vicinity of the bridging hydroxyl protons. The rehydration of calcined and steamed materials, however, is often accompanied by an uncontrolled hydrolysis of framework aluminum species. A suitable approach to overcome these problems is the adsorption of ammonia on the non-hydrated zeolite catalysts under study.

The ^{29}Si MAS NMR spectra obtained for the non-hydrated and ammonia-loaded zeolites Y show well resolved Si(nAl) signals suitable for the determination of the framework n_{Si}/n_{Al} ratio using the known formula. The ^{27}Al MAS NMR spectra of the non-hydrated and ammonia-loaded materials give exclusively rise to the signals of tetrahedrally coordinated framework aluminum atoms, the negative charges of which are compensated by extra-framework cations, such as ammonium ions and residual sodium cations. The quantitative evaluation of these signals by comparison with the external intensity standard gives framework n_{Si}/n_{Al} ratios being in good agreement with those obtained by ^{29}Si MAS NMR spectroscopy. ^{29}Si and ^{27}Al MAS NMR spectroscopy of the ammonia-loaded samples is therefore suggested as a standard tool for characterization of the framework composition of non-hydrated zeolite catalysts.

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