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Brønsted sites and structural stabilization effect of acidic low-silica zeolite A prepared by partial ammonium exchange

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ABSTRACT

It is demonstrated for low-silica zeolite 25NH$_4$,Na-A ($n_{Si}/n_{Al} = 1.0$) with an ammonium exchange degree of 25% that the formation of acidic bridging OH groups (Si(OH)Al) after thermal deammoniation is accompanied by a weak dealumination of the framework. As the extra-framework aluminum species mainly exist predominantly in the form of Al^{3+} cations, they partially neutralize negative framework charges. The remaining framework charges are compensated by Na$^+$ cations and hydroxyl protons of Si(OH)Al groups. Therefore, a lower number of Si(OH)Al groups is formed than expected by the stoichiometry of the ammonium exchange. For zeolite 25NH$_4$,Na-A, only 17% of the introduced ammonium ions form Si(OH)Al groups after thermal deammoniation. A benefit of the cationic extra-framework aluminum species (Al^{3+}) is their stabilizing effect exerted on the remaining framework aluminum atoms and the whole structure of the obtained zeolite 25H,Na-A. ^{1}H MAS NMR signals of acidic OH groups were observed at 3.6 and 4.8 ppm and assigned to Si(OH)Al groups in the α- and β-cages, respectively. A low-field signal at 13.3 ppm is probably due to Si(OH)Al groups, however, involved in H-bondings (Si(OH···O)Al) with hydroxyl protons directed to very near oxygen atoms, such as expected in double 4-rings of the LTA structure.

1. Introduction

Low-silica zeolite A ($n_{Si}/n_{Al} = 1$) is one of the first zeolitic materials, which could be obtained by a large-scale industrial synthesis procedure. Due to the high framework aluminum content and the correspondingly large number of negative framework charges, zeolite A rapidly found a broad application as component of detergents to decrease the water hardness by exchanging Ca^{2+} and Mg^{2+} ions for Na$^+$ [1].

Zeolite A, also called Linde Type A, has a unit cell (u.c.) consisting of $|Na_{12}(H_2O)_{27}|_8[Al_{12}Si_{12}O_{48}]_8$ and an LTA structure with a 3-dimensional pore system. These pores are running perpendicular to each other and are formed by 8-membered rings with a diameter of 0.42 nm. The 8-membered rings are windows to large cavities, the so-called α-cages, with a minimum free diameter of 1.14 nm. Each α-cage is surrounded by eight sodalite cages (β-cages) connected via double 4-rings. The Na$^+$-form of low-silica zeolite A (Na-A) with $n_{Si}/n_{Al} = 1.0$ is thermally stable up to ca. 973 K [1–3]. On the other hand, it is well-known that low-silica zeolite Na-A cannot be transformed into a pure H-form zeolites because this leads to a collapse of the crystalline structure.

Recent research was focused on the preparation and application of zeolites Na-A and Ca-A in membrane systems for the separation of H$_2$/CH$_4$, H$_2$/CO$_2$, and H$_2$/O$_2$ mixtures [4,5] and in shape-selective zeolite films on microsensors [6]. Similarly, the high selectivity of zeolite A is utilized for the adsorption of CO$_2$ and the adsorptive separation of CO$_2$/CH$_4$ mixtures [7,8]. Application of zeolite A for the molecular sieving of hydrocarbons, such as mixtures of n-hexane and 3-methylpentane, is well known [9]. Due to its regular pore system, zeolite A is also interesting as catalyst material in the shape-selective heterogenous catalysis [10]. The α-cages of zeolite A are large enough for the cracking and isomerization of hydrocarbons, while the narrow pores restrict the entering and diffusion to small molecules, i.e. normal alkanes. A typical example is the application of noble metal-containing zeolite A for the selective hydrocracking of normal alkanes in the presence of

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branched alkanes [11]. However, until now only little knowledge exists on the nature and properties of catalytically active Brønsted acid sites in zeolite A [12–14].

The objective of this work was to monitor the formation of different hydroxyl species in zeolite Na-A upon different modifications, such as partial ammonium exchange and thermal deammoniation. Due to the high aluminum content of zeolite A, the framework stability is a critical topic in this procedure. Therefore, the effect of the partial decationization of zeolite A on its crystallinity and the local structure of framework atoms has been investigated.

2. Experimental

2.1. Preparation of the materials

Parent zeolite Na-A ($n_{Si}/n_{Al} = 1.0$) was purchased from Henkel KGaA, Düsseldorf, Germany. Zeolites $10NH_4$,Na-A and $25NH_4$,Na-A (ammonium exchange degrees of 10% and 25%, respectively) were prepared by a one-fold exchange of the parent zeolite Na-A with a stoichiometric amount of a 0.1 M aqueous solution of $NH_4(NO_3)_3$ at 353 K. Zeolite 10Al,Na-A was obtained by a threefold ion exchange of zeolite Na-A under the same conditions, but with a 0.1 M aqueous solution of $Al(NO_3)_3$, leading to the maximum exchange of 10% of the sodium cations by aluminum cations. Subsequently, the materials were washed with demineralized water and dried in air. The chemical compositions of the parent NH_4- and Al-exchanged zeolites were determined by optical emission spectroscopy with inductively coupled plasma (ICP-OES, Varian VISTA-MPX). Prior to the solid-state NMR spectroscopic studies, the zeolite samples were dehydrated and deammoniated according to the following procedure: Heating with a rate of 20 K/h up to the temperatures of 473 or 673 K, evacuation at a pressure of $p < 10^{-2}$ mbar for 12 h, and sealing in glass ampoules. Crystallinity of the zeolite samples after the above-mentioned treatments was studied by X-ray diffraction (XRD). The XRD patterns were recorded on a Bruker D8 diffractometer with CuKα radiation ($\lambda = 1.5418$ Å) in the range of $2\theta = 5–50°$ with a scan rate of 6.0°/min.

Using a vacuum line, a surplus of ammonia (NH_3) and acetonitrile-d_3 (CD_3CN, 99.9% deuterated, Sigma–Aldrich) was loaded on dehydrated zeolite 25H,Na-A, i.e. 100 mbar of NH_3 and CD_3CN, subsequently evacuated at 453 K for 2 h and at room temperature for 1 h, respectively, and sealed. For excluding contact with air, the transfer of the pretreated sample materials into the MAS rotors was performed inside a glove box purged with dry nitrogen gas.

2.2. Spectroscopic characterization

Solid-state MAS NMR spectra were recorded using a Bruker Avance III 400WB spectrometer at resonance frequencies of 400.1 MHz for ^{1}H, 104.3 MHz for ^{27}Al, and 79.5 MHz for ^{29}Si nuclei. For the ^{1}H and ^{27}Al MAS NMR studies, a standard 4 mm double-bearing Bruker MAS NMR probe with a sample spinning rate of 8 kHz, single-pulse excitation corresponding to $\pi/2$ (^{1}H) and $\pi/6$ (^{27}Al) flip angles, and with repetition times of 10 s (^{1}H) and 500 ms (^{27}Al), respectively, was used. For the ^{29}Si MAS NMR investigations, a 7 mm double-bearing Bruker MAS standard probe with a single-pulse excitation corresponding to $\pi/4$, a rotation frequency of ca. 3.5 kHz, and a recycle delay of 20 s was applied. The ^{1}H{^{27}Al} TRAPDOR MAS NMR experiment was carried out by irradiating ^{27}Al pulses with an rf field of 50 kHz in the pulse delays τ of the $\pi/2-\tau-\pi-\tau$ pulse sequence applied to the ^{1}H nuclei ($\nu_{rot} = 6$ kHz and $\tau = 996$ μs) [15,16]. The decomposition and simulation of the NMR spectra were performed using the Bruker software WINNMR and WINFIT.

Before the ^{1}H MAS NMR experiments, the dehydrated samples were filled into 4 mm MAS rotors inside a glove box purged with dry nitrogen. Quantitative ^{1}H MAS NMR measurements were performed by comparing 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. If indicated, the zeolite samples were fully hydrated in a desiccator over saturated calcium nitrate solution for at least 12 h.

3. Results and discussion

3.1. Structural changes of zeolite A upon partial decationization and calcination

The X-ray pattern of the non-modified parent zeolite Na-A, shown in Fig. 1a, agrees very well with that of a highly crystalline material with structure type LTA [17]. Since the strongest structural damages were expected for the material with the highest degree of decationization studied in the present work, the pattern of the parent material was compared with those of the 25% decationized material (25H,Na-A) before (Fig. 1b) and after calcination at 673 K and rehydration (Fig. 1c). According to Fig. 1, neither the ammonium exchange, leading to zeolite $25NH_4$,Na-A, nor the deammoniation (673 K), delivering zeolite 25H,Na-A, have a significant influence on the long-range order of the LTA structure of zeolite A.

For clarifying the effect of the ammonium exchange and calcination of zeolite A on the short-range order and local structure of the framework silicon and aluminum atoms, ^{29}Si and ^{27}Al MAS NMR spectroscopic studies, respectively, were performed (Fig. 2). In agreement with literature [18,19], the ^{29}Si MAS NMR spectrum of the parent zeolite Na-A in the hydrated state consists of a single signal at −89.6 ppm (Fig. 2a, left) caused by Si(4Al) species. No additional signals of SiO_2 phases or Si(3Al) species occurred. Correspondingly, the ^{27}Al MAS NMR spectrum of this material consists of a single signal at 59 ppm due to tetrahedrally coordinated aluminum atoms (Al^{IV}) at framework positions (Fig. 2a, right) [19].

Upon exchange of 25% of the Na^+ cations by ammonium ions leading to zeolite $25NH_4$,Na-A, no significant change of the ^{29}Si MAS NMR spectrum occurred (Fig. 2b, left). In the ^{27}Al MAS NMR spectrum (Fig. 2b, right), the signal of Al^{IV} species is slightly shifted to 56 ppm and a very weak hump of hexagonally

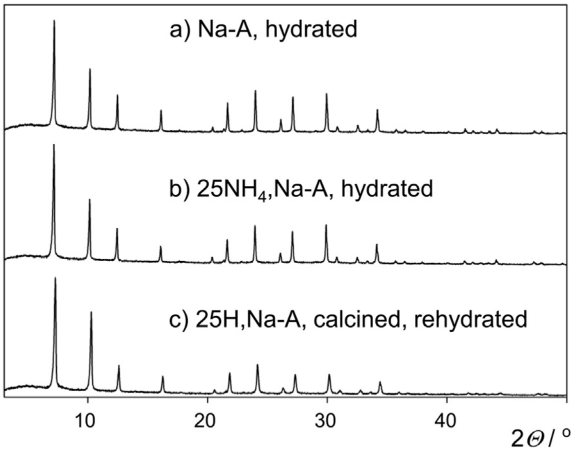

Fig. 1. XRD patterns of parent zeolite Na-A (a), zeolite $25NH_4$,Na-A (ammonium exchange degree of 25%) before first calcination (b), and zeolite 25H,Na-A upon calcination at 673 K and rehydration (c).