

Dissociative adsorption of water in CaNaA zeolites studied by TG, DRIFTS and ^1H and ^{27}Al MAS NMR spectroscopy

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Received 2 July 2004; received in revised form 11 October 2004; accepted 12 October 2004

Available online 8 December 2004

This paper is dedicated to Priv.-Doz. Dr. Heinz Böhlig, Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Leipzig, Germany, on the occasion of his 60th birthday

Abstract

Three CaNaA zeolites, in which, respectively, 49%, 65% and 83% of the Na^+ cations were exchanged with Ca^{2+} ions, along with a NaA sample were studied by thermogravimetry, temperature-programmed DRIFT spectroscopy and MAS NMR. Thermogravimetric desorption profiles of the Ca^{2+} exchanged zeolites show a low-temperature peak between 423 and 508 K as well as two high-temperature peaks at 853 and 973 K, which are missing in case of the NaA sample. Three main bands at 3603–3611, 3495–3510 and 3552–3565 cm^{-1} , of which the first two are due to bridging Si–OH–Al groups located in 8- and 6-rings, respectively, whereas the third corresponds to $\text{Ca}(\text{OH})^+$ groups dominate the DRIFT spectra of zeolite samples exchanged with Ca^{2+} ions. The intensity of the band at 3603–3611 cm^{-1} decreases significantly until it vanishes almost completely at 823 K. A simultaneous decrease of the intensity of the band of $\text{Ca}(\text{OH})^+$ groups is indicative of a low-temperature dehydroxylation process between these two species. The intensity of the other Si–OH–Al group bands at 3495–3510 cm^{-1} shows almost no change up to 823 K, thus suggesting that these groups participate in a high-temperature dehydroxylation process. A weak band in the region 3670–3680 cm^{-1} is attributed to Al–OH groups of extra-framework aluminum species formed during dehydration of the CaNaA zeolites. Peaks at 4.3 and 5.2 ppm in the ^1H MAS NMR spectra are assigned to Si–OH–Al groups in 8- and 6-rings, respectively. ^{27}Al MAS NMR spectra show two main peaks at 57.3 and 78.7 ppm, which are due to tetrahedrally coordinated aluminum and calcium aluminosilicate groups. A weak signal between 12 and 13 ppm ascribed to octahedrally coordinated aluminum disappears at higher temperatures. © 2004 Elsevier Inc. All rights reserved.

Keywords: CaNaA zeolites; H_2O ; Dissociative adsorption; DRIFT spectroscopy; Solid state NMR

1. Introduction

Zeolites are important catalytic materials with a broad spectrum of industrial applications. They are also extensively used as adsorbents and in separation pro-

cesses. Type A molecular sieves were amongst the first synthetic zeolites to be used for industrial catalysis, separation and ion exchange. Intensive studies by Breck et al. [1,2], Barrer et al. [3,4] and Zhdanov et al. [5,6] contributed significantly to the elucidation of the zeolite A formation mechanism during hydrothermal synthesis. Because water is encountered in almost all industrial processes its adsorption in type A zeolites is of special interest and has been extensively studied by many

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authors [7–23]. Methods used vary from thermal analysis to infrared and NMR spectroscopy. It has been widely accepted that dissociative adsorption of water takes place in zeolites exchanged with doubly charged cations according to Plank's mechanism [24]. Bridged Si–OH–Al groups in zeolites can be studied by means of several experimental methods. Thermal analysis studies relate desorption peaks of water observed at temperatures above 800 K to dehydroxylation processes [25], while infrared and near infrared studies assign several bands in the OH stretching region to the stretchings of bridging Si–OH–Al groups and OH groups, which are bonded to the doubly charged cation (see, e.g. [26]). In ^1H MAS NMR spectra, Si–OH–Al groups show a chemical shift in the range of 3.8–5.2 ppm [27].

In this study we used temperature-programmed diffuse reflectance infrared spectroscopy (TP-DRIFTS) alongside thermogravimetry (TG) and MAS NMR to shed more light into the formation and positions of OH groups formed by dissociative adsorption of water in three CaNaA zeolites with different exchange degrees of Ca^{2+} ions. The advantage of TP-DRIFT over earlier infrared techniques is that we can easily monitor spectral changes as water is being desorbed, thus being able to obtain information about different absorbed species. We also used both ^1H and ^{27}Al NMR to study bridging Si–OH–Al groups directly as well as to obtain information about their environment and the occurrence of Al–OH groups and Si–OH groups which could be formed under our experimental conditions.

2. Experimental

2.1. Zeolites

Three CaNaA samples in which, respectively, 49%, 65% and 83% of the Na^+ cations were exchanged with Ca^{2+} ions, denoted as CaNaA-49, CaNaA-65 and CaNaA-83, were prepared from the batch of a commercial NaA zeolite. The cation exchange was performed in a solution of $\text{CaCl}_2 \times 6\text{H}_2\text{O}$ maintained at 343 K during 6 h. After the exchange was complete, samples were dried at 398 K overnight. It was checked by ^{27}Al NMR and X-ray diffraction that no dealumination or loss of crystallinity occurred during the exchange process.

2.2. Thermogravimetric measurements

Thermogravimetric measurements were performed from room temperature to 1073 K using two heating rates of 1 and 10K min^{-1} , respectively. Two carrier gases were employed: dried helium or helium saturated with water to perform the experiment under equilibrium conditions. The influence of the sample mass was exam-

ined on samples saturated with water. The experimental setup for the thermogravimetric measurements consists of a Setaram balance coupled with a Balzer mass spectrometer.

2.3. TP-DRIFT measurements

The TP-DRIFT experiments were carried out with a System 2000R spectrometer (Perkin-Elmer) using a Praying Mantis diffuse reflection attachment equipped with a stainless steel reaction chamber (Harrick), which allows temperature-programmed investigations between room temperature and 823 K in a carrier gas flow (helium, $50\text{ cm}^3\text{ min}^{-1}$). The zeolites were equilibrated with water vapor over a saturated $\text{Ca}(\text{NO}_3)_2$ solution in a desiccator. For each experiment, about 50 mg of the water loaded zeolite (granulated, 0.2–0.4 mm) were used. At first the samples were flushed with helium at room temperature for one hour and then the linear temperature program (5 K min^{-1}) was started. The spectra were continuously recorded at a resolution of 4 cm^{-1} with 32 scans being averaged. KBr was used as standard (background). The spectra were recorded every 10 K, this means that a full measurement consists of a set of about 50 spectra.

2.4. NMR measurements

Samples of the CaNaA-83 and a NaA zeolite were filled in a glass tube of 4.2 mm inner diameter and then dehydrated under permanent vacuum at temperatures of 373 K, 473 K, 573 K, 673 K, 773 K, and 1023 K for 48 h, respectively. After the treatment the samples were sealed. The ^1H and ^{27}Al MAS NMR spectra were recorded on a Bruker MSL 500 spectrometer operating at resonance frequencies of 500.13 and 130.31 MHz, respectively. The sealed samples were spun at a rotation frequency of 4.5 kHz. ^1H MAS NMR spectra were obtained using a 90° pulse of $5.3\ \mu\text{s}$ and a recycle delay of 10 s. Typically, 32 scans were accumulated to obtain a good signal to noise ratio. ^{27}Al MAS NMR spectra were recorded applying a $\pi/6$ pulse of $2.1\ \mu\text{s}$, a recycle delay of 200 ms and 1024 scans. The ^{27}Al chemical shifts were referenced to external aluminum chloride (0 ppm).

3. Results and discussion

3.1. TP-DRIFT spectra

DRIFT spectra of all studied zeolite samples at relatively low temperatures show a broad, rather featureless band in the OH stretching region. These low temperature spectra are, however, almost irrelevant for the purpose of investigating the dissociative adsorption of water in CaNaA zeolites, because spectral features of

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