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Effect of probe molecules with different proton affinities on the coordination of boron atoms in dehydrated zeolite H-[B]ZSM-5

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Abstract

The influence of probe molecules with proton affinities of PA = 812–930 kJ mol^{-1} adsorbed at Brønsted acid sites in boron-substituted zeolite ZSM-5 on the coordination of boron atoms in this material has been studied by ^{1}H and ^{11}B MAS NMR spectroscopy. The probe molecules are, in the sequence of their PA values, acetone (PA = 812 kJ mol^{-1}), tetrahydrothiophene (PA = 849 kJ mol^{-1}), ammonia (PA = 854 kJ mol^{-1}), acetamide (PA = 864 kJ mol^{-1}), dimethyl sulfoxide (PA = 884 kJ mol^{-1}) and pyridine (PA = 930 kJ mol^{-1}). By ^{11}B MAS NMR spectroscopy, it has been found that loading of zeolite H-[B]ZSM-5 with probe molecules characterized by proton affinities of PA $\geqslant$ 854 kJ mol^{-1} leads to a transformation of trigonally coordinated boron species (B$^{[3]}$) into tetrahedrally coordinated boron species (B$^{[4]}$). This coordination change is accompanied by a decrease of the ^{11}B quadrupole coupling constant from $C_{\mathrm{QCC}} = 2.7 \pm 0.1$ MHz for B$^{[3]}$ species to $C_{\mathrm{QCC}} \leqslant 0.85$ MHz for B$^{[4]}$ species. In addition, a proton transfer from the SiOH[B] groups in the vicinity of framework boron atoms in zeolite H-[B]ZSM-5 to probe molecules with a proton affinity of PA $\geqslant$ 854 kJ mol^{-1} occurs. This PA value is ca. 30 kJ mol^{-1} higher in comparison with the proton affinity required for a protonation of probe molecules adsorbed at Brønsted acid sites in aluminosilicate-type zeolites (PA = 821 kJ mol^{-1}).

Keywords: Zeolite H-[B]ZSM-5; Coordination of boron atoms; Probe molecules; Proton affinity; Solid-state NMR spectroscopy

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1. Introduction

Boron-substituted zeolites, especially zeolite H-[B]ZSM-5, have extensively been studied and used in the vapor phase Beckmann rearrangement reaction due to their weaker Brønsted acid sites in comparison with those in aluminosilicate-type zeolites [1,2]. According to the bond order conservation principle and quantum-chemical calculations [3–7], the weaker Brønsted acid sites in boron-substituted zeolites are attributed to the longer bond distance between the framework boron atom and the framework oxygen atom bound to the hydroxyl proton. The bond between framework boron and oxygen atoms in boron-substituted zeolites can effectively be formed and broken upon the hydration and dehydration, respectively [9–11]. Therefore, boron exists in a tetrahedral (B$^{[4]}$) coordination in the hydrated state and in a trigonal (B$^{[3]}$) coordination in the dehydrated state of boron-substituted zeolites [7–12]. In addition, both kinds of boron species can occur in these materials depending on the hydration state and the presence of counter ions, such as template molecules [7,8,12].

In 1985, Scholle and Veeman [9] applied solid-state ^{11}B NMR spectroscopy to study the coordination change of boron atoms in H-boralite upon dehydration and rehydration. The coordination change of boron species was found to be accompanied by a variation of the ^{11}B quadrupole

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coupling constant C_{QCC} of framework boron atoms from $C_{QCC} = 2.55 \pm 0.02$ MHz for $B^{[3]}$ species to a very small C_{QCC} value for $B^{[4]}$ species. Generally, the quadrupole coupling constant C_{QCC} is a measure of the strength of the quadrupolar interaction between the electric quadrupole moment of nuclei characterized by a spin $I > 1/2$ (^{11}B: spin $I = 3/2$) and the electric field gradient at their sites.

Axon and Klinowski [10] reported the coordination change of boron upon the adsorption and desorption of polar organic molecules, such as anhydrous methanol and ethanol, on zeolite [Si,B]ZSM-5. In addition, it was found that the non-polar solvents like anhydrous benzene could not induce a coordination change of boron [10]. Recently, Hwang et al. [11] investigated the boron coordination in zeolites [B]Beta, [B]SSZ-33 and [B]SSZ-42 and revealed an intermediate stage referred as defective trigonal boron species ($B^{[3]}$-*I*) upon the hydration of dehydrated samples characterized by a ^{11}B quadrupole coupling constant of $C_{QCC} = 2.46$ MHz. Koller et al. [12] studied the boron coordination in dehydrated zeolites H-[B]Beta and H,Na-[B]Beta. While the ^{11}B MAS NMR spectra of dehydrated zeolite H-[B]Beta consist only of signals of trigonal boron species, both trigonal and tetragonal boron species were observed for dehydrated zeolite H,Na-[B]Beta with alkaline counter ions [12].

The present work is a systematic investigation of the effect of probe molecules with proton affinities in the range of PA = 812–930 kJ mol^{-1} on the local structure of boron atoms in dehydrated zeolite H-[B]ZSM-5. Since the coordination change of $B^{[3]}$ into $B^{[4]}$ species can be accompanied by a proton transfer from the zeolite framework to the probe molecules, simultaneous ^{11}B and ^{1}H MAS NMR studies have been performed. The results obtained help to understand the role of framework boron atoms in zeolites H-[B]ZSM-5 for their application as solid acid catalysts.

2. Experimental section

Zeolite [B]ZSM-5 was synthesized according to Ref. [7] using a molar gel ratio of 1 SiO_2: 0.042 B_2O_3: 0.1 TPAOH: 36H_2O. The typical synthesis procedure is as follows: 12.4 g of tetrapropylammonium hydroxide (TPAOH) was added to a beaker containing 71.0 g of distilled water and stirred for 10 min. To this mixture, 0.7 g of H_3BO_3 were added and stirred for 30 min. Finally, 7.6 g of Cabosil were slowly added under stirring. This synthesis mixture was stirred for 1 h, transferred into a 0.3 l stainless steel autoclave containing a Teflon insert and heated at 423 K for 5 days. The obtained product was recovered by filtration, washed thoroughly with demineralized water, dried at 353 K and calcined at 823 K for 6 h in synthetic air (20 vol.% oxygen, 60 l/h). As determined by ICP/AES, the calcined material has an n_{Si}/n_B ratio of 38. In order to obtain zeolite H-[B]ZSM-5, the calcined [B]ZSM-5 material was ion-exchanged in an aqueous solution of 1.0 M ammonium acetate for 12 h at 353 K. After ion-exchange, the material was recalcined at 773 K in synthetic air. Prior to adsorption of probe molecules and solid-state NMR investigations, the zeolite H-[B]ZSM-5 was dehydrated under vacuum ($p < 10^{-2}$ mbar) at 723 K for 12 h and sealed in glass tubes.

Pyridine, ammonia and acetone were loaded using the *in situ* injection equipment described elsewhere [13,14]. Before these *in situ* NMR investigations, the catalyst was filled into a 4 mm rotor inside a glove box purged with dry nitrogen. The amounts of adsorbed molecules were controlled by the flow of carrier gas (dry nitrogen) via a mass flow controller and the duration of the flow. Probe molecules with low vapor pressures, such as dimethyl sulfoxide, tetrahydrothiophene and acetamide, were *ex situ* loaded. In this case, the dehydrated zeolite H-[B]ZSM-5 and the probe molecule were quantitatively mixed in a glass bottle and then transferred into a glass tube and sealed. To reach a proper distribution of the probe molecule over the H-[B]ZSM-5 particles, the mixtures in the sealed glass tubes were heated at 323 K (dimethyl sulfoxide, tetrahydrothiophene) or 352 K (acetamide) for 1 h. To describe the coverage of hydroxyl groups with probe molecules, the equivalent number *equiv.* is used. This is the ratio of the number of adsorbed molecules n_{ad} and the number of SiOH groups n_{OH}, both determined by ^{1}H MAS NMR spectroscopy. For the quantitative evaluation of ^{1}H MAS NMR signals, dehydrated zeolite H,Na-Y with a cation exchange degree of 35% was used as an external intensity standard.

The ^{1}H and ^{11}B MAS NMR spectra were acquired on a Bruker MSL 400 spectrometer using a 4 mm MAS probe with a sample spinning rate of ca. 9.0 kHz and at resonance frequencies of 400.1 and 128.3 MHz, respectively. The spectra were recorded after single pulse excitation with pulse lengths of 2.2 and 1.0 μs, repetition times of 10 and 2 s and accumulation numbers 48 and 800 for ^{1}H and ^{11}B nuclei, respectively.

3. Results and discussion

3.1. *In situ MAS NMR investigations of dehydrated zeolite H-[B]ZSM-5 upon the adsorption of pyridine*

Fig. 1, left, shows the ^{1}H MAS NMR spectra of unloaded zeolite H-[B]ZSM-5 and zeolite H-[B]ZSM-5 loaded with pyridine (PA = 930 kJ mol^{-1}). The ^{1}H MAS NMR spectrum of unloaded zeolite H-[B]ZSM-5 consists of signals at 1.9, 2.5 and 3.2 ppm due to silanol groups at defect sites and SiOH[B] groups in the vicinity of framework boron species [7,8]. The quantitative evaluation of the ^{1}H MAS NMR signals at 1.9, 2.5 and 3.2 ppm gave concentrations of 0.062 ± 0.01, 0.402 ± 0.02 and 0.155 ± 0.01 mmol/g, respectively. Upon adsorption of pyridine, three new signals occurred at ca. 7.4, 7.9 and 8.7 ppm (Fig. 1b to e, left), which are explained by hydrogen atoms bound to the rings of pyridine molecules [15]. A weak signal at ca. 16 ppm (inserts in Fig. 1b and c) indicates that proton transfer occurs from the acid sites of