Characterization of boron-containing catalysts by ^{11}B solid-state NMR

Spectroscopic background: ^{11}B nuclei have a spin of $I = 3/2$ and a quadrupole moment of $Q = 4.059 \times 10^{-30}$ m^2. Therefore, ^{11}B NMR signals of boron atoms in solids are affected by quadrupolar interactions leading to broad ^{11}B MAS NMR signals and quadrupole patterns. The ^{11}B isotope has a natural abundance of 80.1 % and a sensitivity of 0.13 in comparison with ^{1}H nuclei (1.0), making this isotope a very suitable candidate for NMR studies of solids. For basic principles of solid-state NMR, see lectures “Solid-State NMR Spectroscopy” for Bachelor students or PhD seminars, accessible via the link “Lectures for Students”.

The ^{11}B NMR spectroscopic parameters of boron incorporated in solids depend on the electric field gradient caused by the local structure and the presence or absence of adsorbate molecules, such as water. For framework boron in water-free zeolites, the coordination number of boron depends on the counterions in the local structure [1-8]. Tetrahedral boron, BO_4, is mostly located near extra-framework cations, such as Na^+ or quaternary ammonium cations. Trigonal boron, BO_3, have hydroxyl groups in their vicinity.

Tetrahedral BO_4 units in **water-free boron-containing zeolites** yield **narrow ^{11}B MAS NMR signals** with a symmetric line shape. Since the local structures of **trigonal BO_3** units are accompanied by large electric field gradients, they cause **broad quadrupole patterns** in the absence of water [1-8].

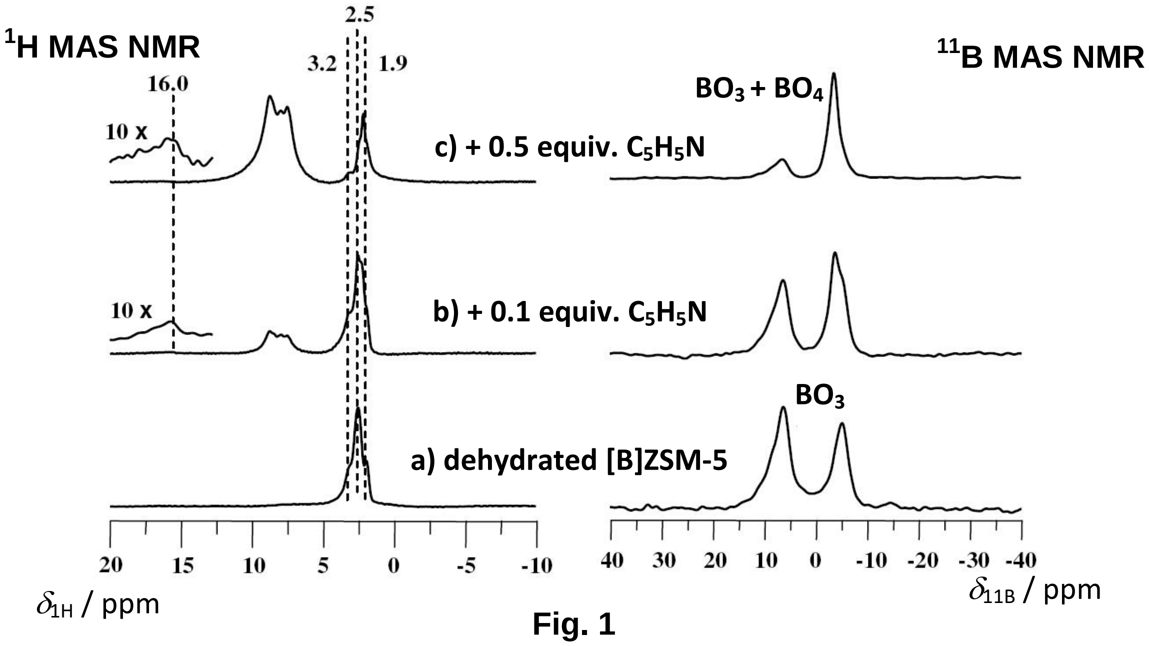

Fig. 1

The narrow **BO_4 signal** of water-free boron-containing zeolite [B]ZSM-5 has a chemical shift of **δ_{11B} = -3 ppm** and a line width **$\Delta\nu_{1/2}$ of ca. 1 ppm**. The latter corresponds to very small C_Q value. At the Larmor frequency of ν_0 = 96.2 MHz, the singularities of the **BO_3 quadrupole patterns** have a **peak-peak distance of ca. 20 ppm** corresponding to a C_Q value of ca. 2.5 MHz (**Fig.1a**) [9]. This peak-peak distance becomes smaller for higher Larmor frequencies. In the ^{11}B MAS NMR spectra of water-free zeolite [B]ZSM-5, the broad BO_3 pattern predominates and, in some cases, is superimposed by the narrow signal of few BO_4 units.

Hydration causes an increase of the narrow BO_4 signal due to a **transformation of BO_3 units into BO_4 units** [1-4]. Similarly, adsorption of basic molecules, such as pyridine or ammonia, on dehydrated boron-containing zeolite [B]ZSM-5 is accompanied by a deprotonation of the zeolite framework in the local structure of the BO_3 units. This deprotonation leads to a transformation of BO_3 into BO_4 units and a corresponding change of the ^{11}B MAS NMR spectrum (**Figs. 1b and 1c**, right, and **Fig. 2**) [9].

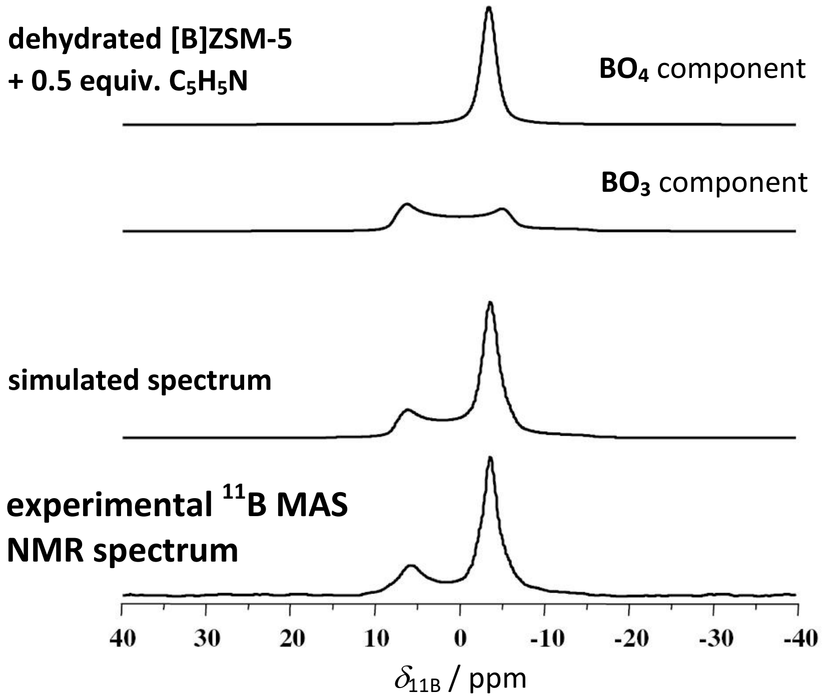

Fig. 2

A more complicated situation exists for boron in zeolite [B]Beta with a high content of SiOH groups (**Fig. 3**) [10]. The ^{11}B MAS NMR spectrum of dehydrated zeolite [B]Beta with the n_{Si}/n_B ratio of 15.4, recorded at ν_0 = 160.5 MHz, consists of three signal components BO_4 ($\delta_{11B,iso}$ = -4 ppm) with neighbouring Na^+ cations, BO_3 (C_Q = 2.56 MHz, η = 0.14, $\delta_{11B,iso}$ = 10.1 ppm), and BO_3^* (C_Q = 2.46 MHz, η = 0.29, $\delta_{11B,iso}$ = 14.6 ppm) [10]. The assignment of these three signals was supported by the 2D ^{11}B MQMAS NMR spectrum of dehydrated zeolite [B]Beta-15.4 in **Fig. 4**, recorded at the same Larmor frequency [10]. For the basic principles of 2D MAS NMR, see e.g. Refs. [11] and [12].

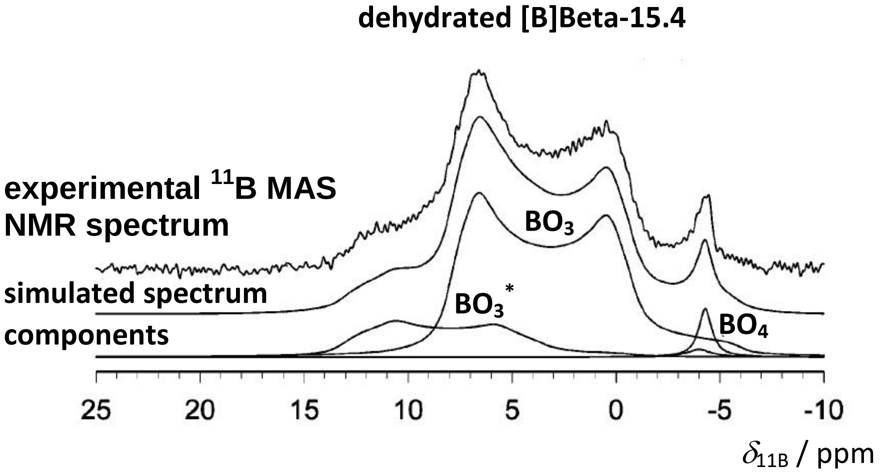

Fig. 3

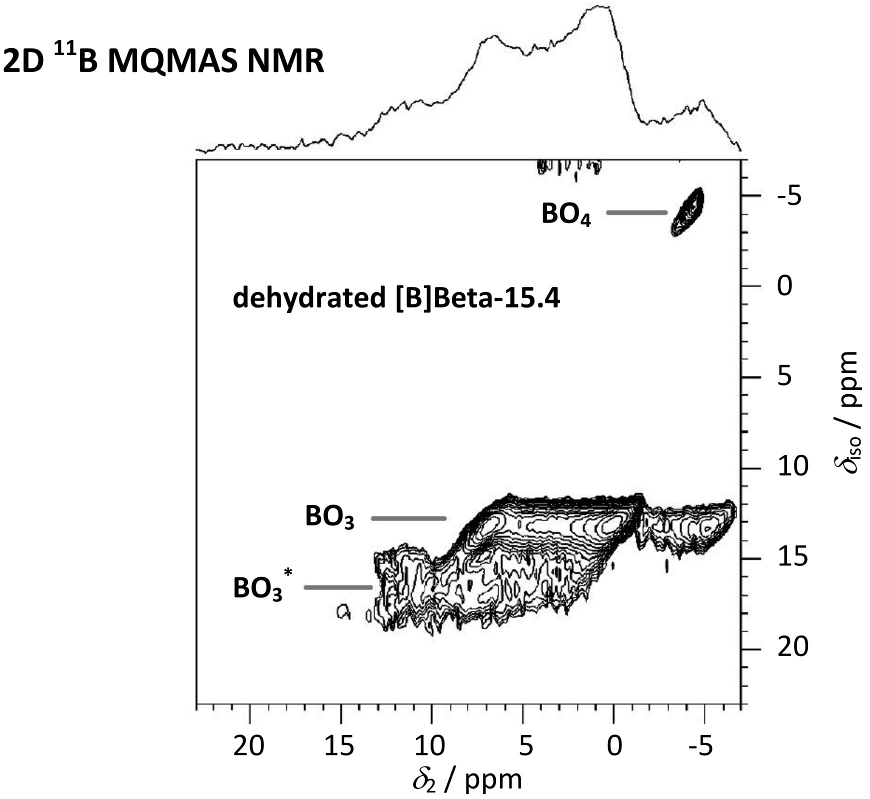

Fig. 4

2D $^{1}H/^{11}B$ HETCOR (Heteronuclear Correlation) spectra of this material showed a cross peak for ^{1}H MAS NMR signals of OH groups at δ_{1H} = 4 to 6 ppm and the ^{11}B MAS NMR signal of the BO_3* species. Therefore, the BO_3* species the ^{11}B MAS NMR spectra of dehydrated zeolite [B]Beta-15.4 were explained by trigonal boron bearing various hydroxyl groups (see Scheme 3 in Ref. [10]).

Trigonal boron atoms, which are partially extracted from the zeolite framework, have distinct ^{11}B chemical shifts of **δ_{11B} ca. 12 ppm ($B(OSi)_2(OH)$), ca. 15 ppm ($B(OSi)(OH)_2$),** and **ca. 18 ppm ($B(OH)_3$)**, while the signal of **$B(OSi)_3$** species occurs at **ca. 10 ppm** [13, 14].

Catalyst preparation: In the most cases, the observation of the quadrupole patterns of BO_3 units require a dehydration of the powder samples at temperatures of at least 393 K or higher. For this purpose, the dehydration of the solid catalyst inside a „sample tube system 1“ at „vacuum line 1“ (see link “*In Situ* Solid-State NMR Techniques”) is performed. The activation starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature ramp from room temperature to 393 K within 2 hours. At this temperature, the sample is dehydrated for 2 hours. Subsequently, the temperature is increased up to 723 K within 3 hours and evacuated at this temperature for 12 hours. After this treatment, the sample tube system is closed via the vacuum valve and disconnected from „vacuum line 1“ after this line was ventilated with air. Finally, the transfer of the dehydrated sample into the MAS NMR rotor is performed without air contact, e.g. in a mini glove box (see Section “mini glove box”, accessible via the link “*In Situ* Solid-State NMR Techniques”).

^{11}B solid-state NMR studies: Due to the quadrupolar interactions of ^{11}B nuclei (I = 3/2), their single pulse excitation should be performed by less than $\pi/4$ and most suitable by $\pi/8$ pulses. Often, repetition times of 1 to 2 s are suitable. For reaching a high resolution of the ^{11}B MAS NMR spectra, the sample spinning rate has to be as high as possible and at least 10 kHz. The 2D ^{11}B MQMAS NMR experiments were performed using the standard z-filtered pulse sequence [12] and at a sample spinning frequency of 13 kHz. Referencing of the chemical shift is performed to BF_3-$O(C_2H_5)_2$ (δ_{11B} = 0 ppm).

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