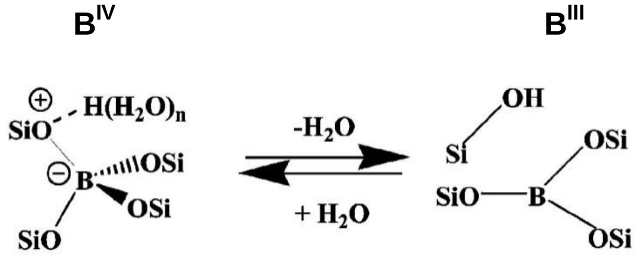
Characterization of boron-containing catalysts by ^{11}B solid-state NMR

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, in this state, 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 zeotype materials depend on the electric field gradient caused by the local structure and the presence or absence of structure-directing agents (SDA) or adsorbate molecules. The coordination number of boron in the zeolite framework depends on the counterions in the local structure [1-10]. **Tetrahedral boron atoms (B^{IV})** are mostly located near extra-framework cations, such as Na$^+$ or quaternary ammonium cations. **Trigonal boron atoms (B^{III}) have silanol groups** in their vicinity. After removal of the SDAs, e.g. by calcination, desorption and adsorption of water molecules lead to a conversion of B^{IV} in to B^{III} species and *vice versa* (**Scheme 1**) [10}.



Scheme 1

Tetrahedral B^{IV} atoms in boron-containing zeolites yield **narrow ^{11}B MAS NMR signals** with a symmetric line shape. Since the local structures of **trigonal BI^{III}** atoms are accompanied by large electric field gradients, they cause **broad quadrupole patterns** in the absence of water [1-10]. The narrow **B^{IV} signal** of boron-containing zeolite [B]ZSM-5 has a ^{11}B 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 values of less than 850 kHz [9].

The **B^{IV} signal** recorded at the Larmor frequency of ν_0 = 96.2 MHz shows singularities of **quadrupole patterns** with a peak-peak distance of ca. 20 ppm corresponding to a **C_Q value of ca. 2.7 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 B^{III} pattern predominates and may be superimposed by a narrow signal of few B^{IV} species.

Like hydration of B^{III} species (**Scheme 1**), adsorption of basic molecules, such as pyridine or ammonia, on dehydrated boron-containing zeolite [B]ZSM-5 is accompanied by a transformation of framework B^{III} species into framework B^{IV} species, due to the deprotonation of the zeolite framework in the local structure of the B^{III} species. This deprotonation is accompanied by a decrease of the B^{III} signal and increase of the B^{IV} signal (**Figs. 1b and 1c, right**, and **Fig. 2**) [9]. The adsorption of probe molecules with different proton affinities PA demonstrated that the deprotonation of hydroxyl groups of zeolite [B]ZSM-5 requires a PA value of ≥ 854 kJ/mol [9]. This PA value is ca. 30 kJ/mol higher in comparison with the proton affinity required for a deprotonation of Brønsted acid sites in aluminosilicate-type zeolites (PA = 821 kJ/mol) [9].

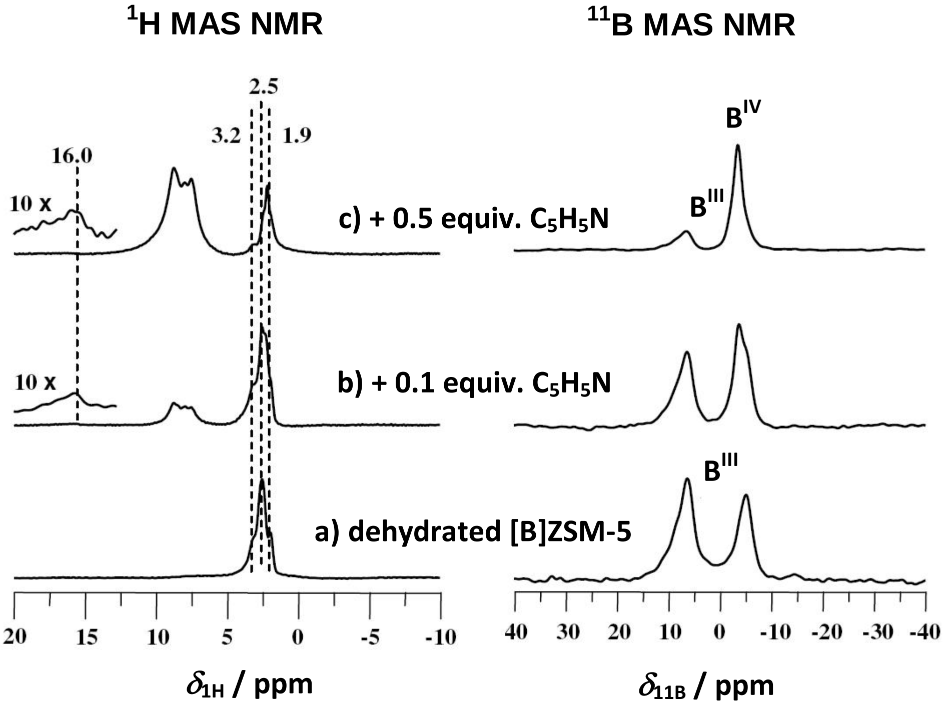


Fig. 1

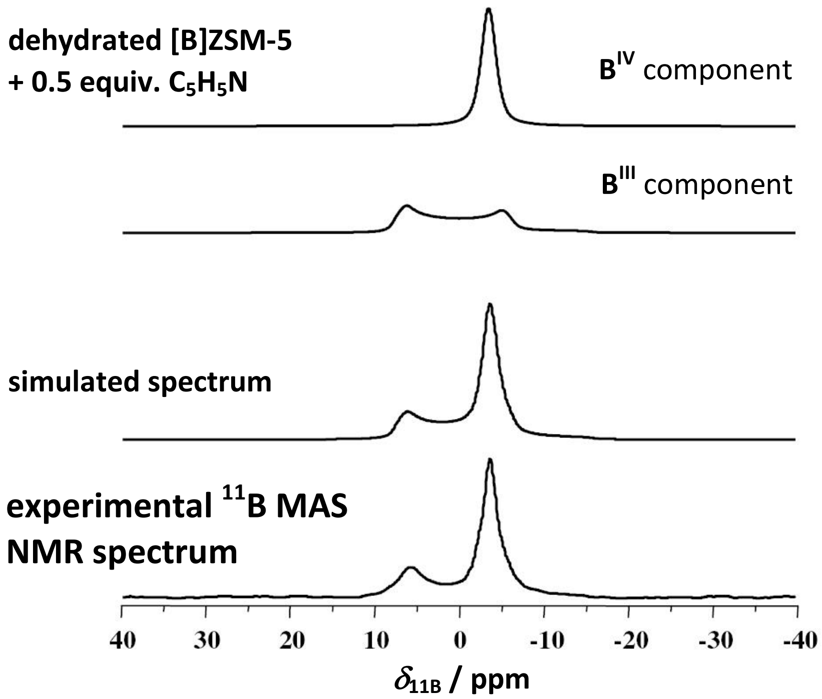


Fig. 2

Boron-containing zeolite [B]Beta is characterized by a significantly higher content of SiOH groups compared to zeolite [B]ZSM-5, which has an influence on the number of signals occurring in the ^{11}B MAS NMR spectra of the former zeolites. The ^{11}B MAS NMR spectrum of **dehydrated zeolite [B]Beta** with the n_{Si}/n_B ratio of 15.4 in **Fig. 3**, recorded at ν_0 = 160.5 MHz, consists of three signals due to B^{IV} species ($\delta_{11B,iso}$ = -4 ppm) with neighbouring Na^+ cations, B^{III} species (C_Q = 2.56 MHz, η = 0.14, $\delta_{11B,iso}$ = 10.1 ppm), and B^{III*} species (C_Q = 2.5 MHz, η = 0.3, $\delta_{11B,iso}$ = 15 ppm) [10]. The determination of the ^{11}B solid-state NMR parameters of these three signals was

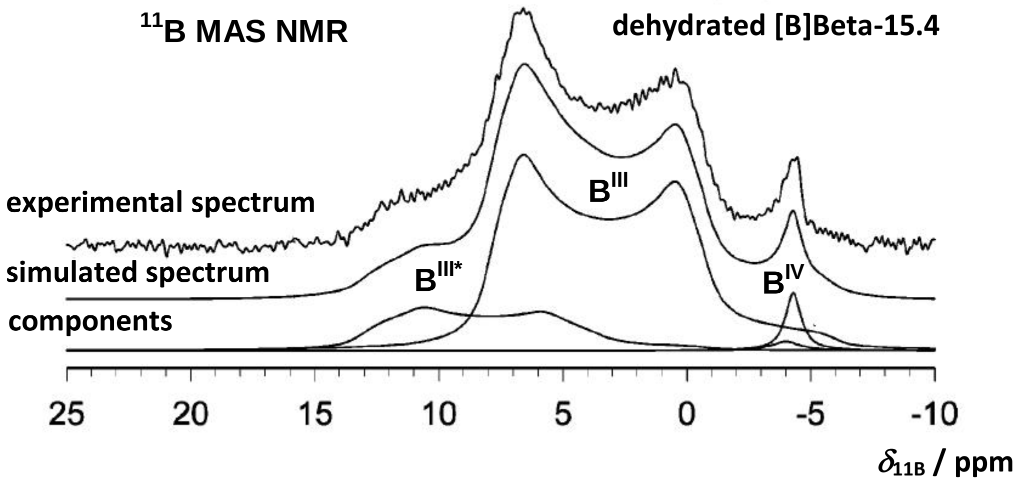


Fig. 3

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]. See Refs. [11] and [12] for basic principles of 2D MQMAS NMR spectroscopy.

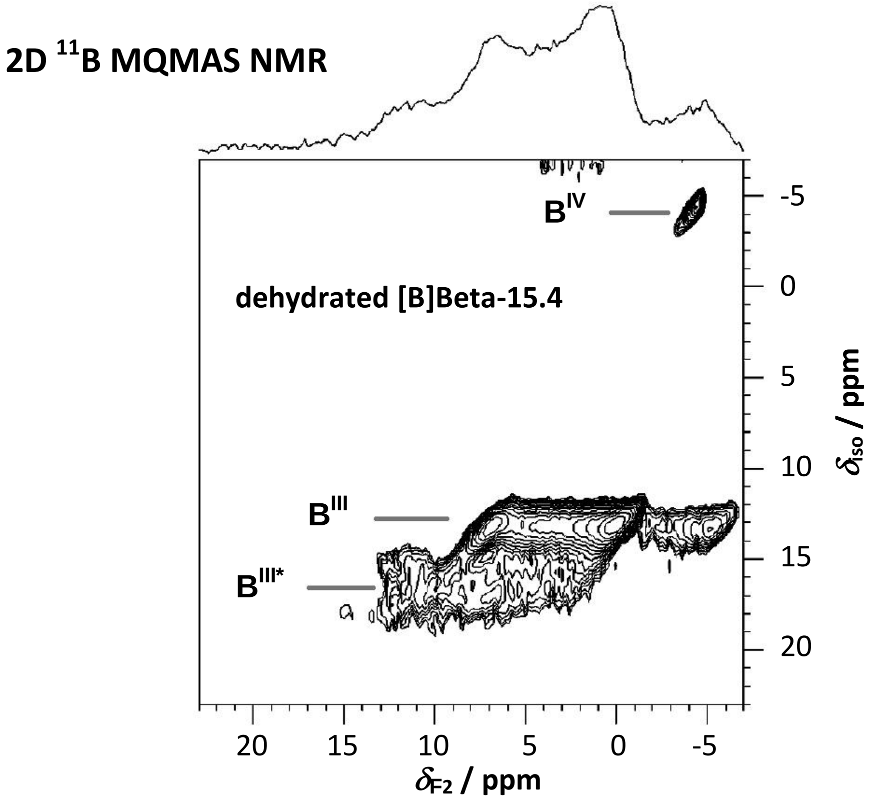
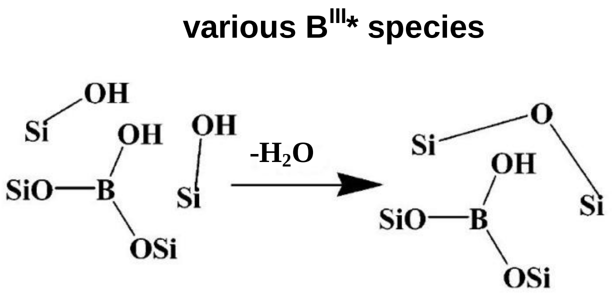


Fig. 4

2D ^{1}H/^{11}B HETCOR (Heteronuclear Correlation) spectroscopy of dehydrated zeolite [B]Beta-15.4 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 B^{III}* species. Therefore, the **B^{III}* signals** in the ^{11}B MAS NMR spectra of dehydrated zeolite [B]Beta-15.4 were explained by framework **B^{III} species, bearing hydroxyl groups,** in various structural environments (**Scheme 2**) [10].



Scheme 2

Boron atoms, which are partially extracted from the framework of zeolite [B]Beta by calcination up to T = 823 K, are trigonal coordinated (C_Q = 2.5 to 2.6 MHz) and have ^{11}B chemical shifts of $\delta_{11B,iso} \cong 15.5$ ppm for $B^{III}(OSi)(OH)_2$ and $\delta_{11B,iso} \cong 18.5$ ppm for $B^{III}(OH)_3$, while the signal of $B(OSi)_3$ species occurs at $\delta_{11B,iso} \cong 10.5$ ppm [13].

In a recent study, the dependence of the ^{11}B chemical shifts on the average B−O−T angles $<\Theta_{BOT}>$ (B, O, and T denote boron, oxygen, and tetrahedrally coordinated atoms, respectively) for **tetrahedrally coordinated framework B-sites** within zeolitic borosilicates was calculated by density-functional theory (DFT) methods and compared with experimental values [15]. For this purpose, the borosilicates **B-SSZ-53**, (SFH structure), **B-SSZ-55** (ATS structure), **B-SSZ-59** (SFN structure), and **B-SSZ-82** (SEW structure) were synthesized and investigated. Together with structural data and ^{11}B chemical shifts, $\delta_{11B,iso}$, already existing for minerals (see Ref. [16]), the following **relationship** was derived [15]:

$$\delta_{11B,iso} \,/\, \mathrm{ppm} = -0.241 <\Theta_{BOT}> + 30.93 \qquad (1)$$

A survey on the ^{11}B solid-state NMR parameters of above-mentioned and additional zeotype materials is given in **Table 1**. Refs. [17] and [18] are interesting papers on ^{11}B liquid and solid-state NMR spectroscopic studies of synthesis mixtures and zeotype materials as well as their detailed ^{11}B NMR data.

Materials / B Species	**C_Q / MHz**	**η_Q**	**$\delta_{11B,iso}$ / ppm**	**Refs.**
[B]ZSM-5				
B^{IV}, hydrated	≤ 0.85	0	-3.3 to -3.7	[4], [9]
B^{IV}, dehydrated + pyridine adsorption	≤ 0.85	0.1	-3.3 to -3.7	[9]
B^{III}, dehydrated	2.46 to 2.65	0.1	10±1	[2], [9]
[B]Beta				
B^{IV}			-4±0.5	[14]
B^{III}	2.5	0.15	10±0.5	[14]
B^{III*}	2.5	0.3	15±0.5	[14]
[B]Beta, calcined				
$B^{III}(OSi)_3$	2.6	0 to 0.1	10.5±0.5	[13]
$B^{III}(OSi)(OH)_2$	2.5	0 to 0.1	15.5±0.5	[13]
$B^{III}(OH)_3$	2.5	0 to 0.1	18.5±0.5	[13]

[B]Ferrierite B^{IV}, as-synthesized	0.6 to 0.8		-3.9 to -3.8	[14]
[B]SSZ-33				
B^{IV}			-3.2	[10]
B^{III}	2.54	0.13	10.1	[10]
B^{III}*	2.46	0.2	15.3	[10]
[B]SSZ-42				
B^{IV}			-3.4	[10]
B^{III}	2.6	0.18	10.7	[10]
B^{III}*	2.4	0.2	14.8	[10]

Table 1

Catalyst preparation: In the most cases, the observation of the quadrupole patterns of BO_3 units requires a dehydration of the powder samples at temperatures of at least 393 K or higher. For this purpose, a dehydration of the solid catalyst inside a “sample tube system 1“ at “vacuum line 1“ (see link “*In Situ* Solid-State NMR Techniques”) was performed. The dehydration starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature ramp from room temperature to T = 393 K within 2 hours. At this temperature, the sample was dehydrated for 2 hours. Subsequently, the temperature was increased up to T = 723 K within 3 hours and evacuated at this temperature for 12 hours. After this treatment, the sample tube system was 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 was 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”), purged with dry nitrogen gas.

^{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. The ^{11}B chemical shifts referenced to BF_3-$O(C_2H_5)_2$ (δ_{11B} = 0 ppm).

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