In situ solid-state NMR studies of the response of framework atoms in catalysts on adsorption of molecules under continuous flow conditions

Spectroscopic background: With the development and introduction of the flow MAS NMR technique (see Topic 3 of link "*In Situ* Solid-State NMR Techniques"), investigations of the **response of framework atoms in solid catalysts on the adsorption of molecules under continuous flow conditions** were possible. By this way, the coordination change of framework atoms and the adsorption sequence of molecules at surface sites and framework atoms can be studied. During *in situ* flow solid-state NMR investigations of the catalyst framework under flow conditions, **^{1}H MAS NMR** is utilized for determining the amounts of adsorbed molecules, while **alternately another resonances (^{11}B, ^{23}Na, ^{27}Al, ^{31}P etc.)** are used to study specific framework atoms of the catalyst.

Examples for solid-state NMR studies of catalysts utilizing the *in situ* flow technique were investigations of the **effect of water [1], acetone [2], ammonia [2, 3], and pyridine [2, 4] on the local structure of framework atoms in zeolites** H-SAPO-34 [1, 3] and H-SAPO-37 [1,3] as well as H,Na-Y [2] and H-[B]ZSM-5 [4].

For demonstration, **Fig. 1** shows *in situ* ^{1}H and ^{27}Al flow MAS NMR spectra, alternately recorded during the adsorption of ammonia at a dehydrated silicoaluminophosphate H-SAP-34 [3]. The ^{1}H MAS NMR signal at δ_{1H} = 3.6 ppm in **Fig. 1a, left,** is due to Broensted acidic bridging OH groups (Si(OH)Al) of the silicoaluminophosphate H-SAPO-34. These Si(OH)Al groups are formed in the local structure of framework silicon atoms incorporated at T-sites instead of phosphorous atoms. The ^{27}Al MAS NMR spectrum in **Fig. 1a, right**, is dominated by the signal of tetrahedrally coordinated framework aluminum at δ_{27Al} = 34 ppm, which is accompanied by a high-field shoulder of pentacoordinated aluminum species. After an adsorption of 0.5 mmol of NH_3 per gram (**Fig. 1b, left**), a broad ^{1}H MAS NMR signal occurred at δ_{1H} = 7.0 ppm, indicating the formation of NH_4^+ ions at former Si(OH)Al groups. Simultaneously, the signal of the Si(OH)Al groups at δ_{1H} = 3.6 ppm is significantly decreased. An adsorption of 2.0 mmol of NH_3 per gram caused a further decrease of the signal at δ_{1H} = 3.6 ppm and the occurrence of a new signal at δ_{1H} = 5.4 ppm, due to a rapid exchange of NH_4^+ ions and weakly physisorbed or gaseous NH_3 molecules. Until this ammonia coverage, no change occurs in the ^{27}Al

MAS NMR spectra of the dehydrated H-SAPO-34 (**Figs. 1b and 1c, right**). This observation indicates that at first the NH_3 molecules are adsorbed exclusively at the Si(OH)Al groups [3].

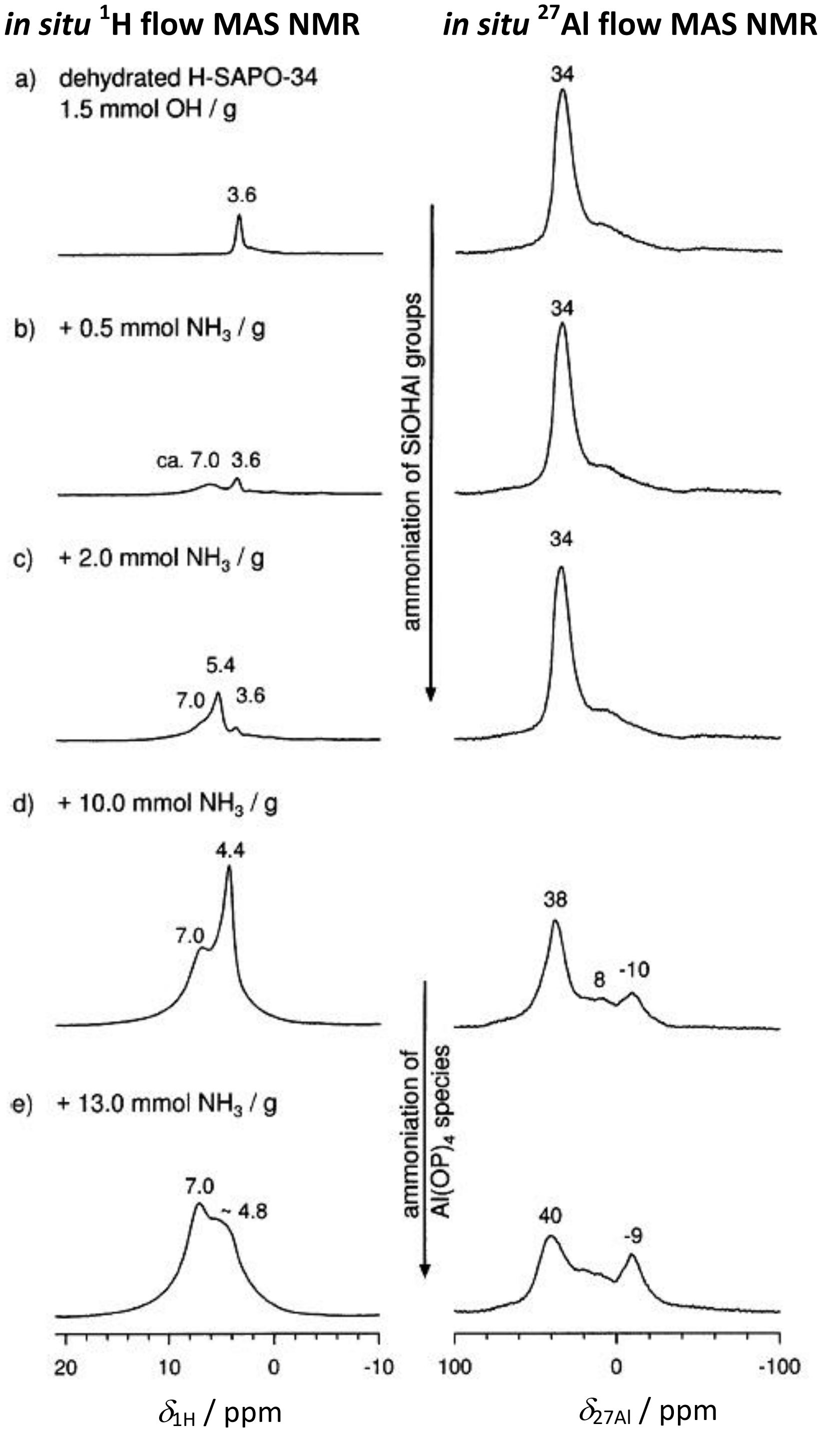
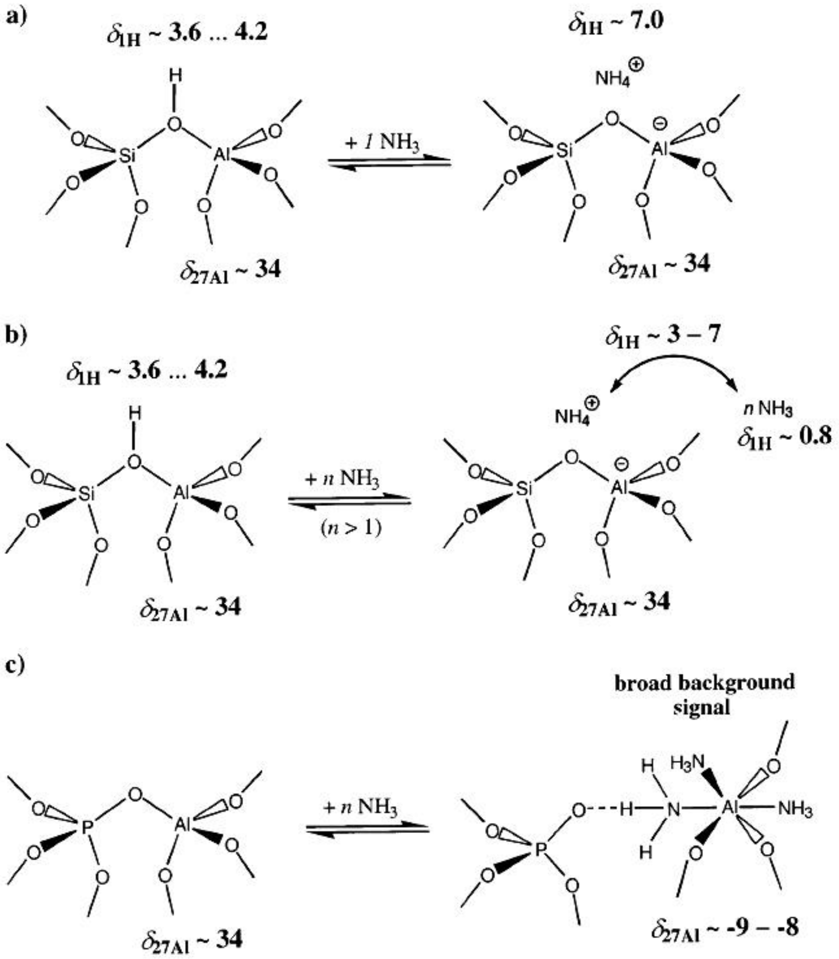


Fig. 1

After adsorption of 10.0 mmol and more ammonia molecules per gram of dehydrated H-SAPO-34, a ^{27}Al MAS NMR signal appeared at δ_{27Al} = -10 ppm, which increased with the ammonia loading (**Figs. 1 d and 1e, right**). This signal hints to a transformation of tetrahedrally coordinated (δ_{27Al} = 38 ppm) into octahedrally coordinated (δ_{27Al} = -9 to -8 ppm) framework aluminum atoms. Hence, ammonia adsorption on dehydrated H-SAPO-34 is at least a two-step process as described in **Scheme 1**.



Scheme 1

Another example for *in situ* flow MAS NMR studies of framework atoms in zeolites is the adsorption of ammonia on dehydrated boron-containing zeolite H-[B]ZSM-1 [4]. The ^{1}H MAS NMR spectrum of dehydrated H-[B]ZSM-5 is dominated by a signal of SiOH[B] groups at δ_{1H} = 2.5 ppm (**Fig. 2a, left**). Upon injection of 0.1 equiv. ammonia (1 equiv. corresponds to 1 molecule per boron atom) into the MAS rotor, filled with dehydrated H-[B]ZSM-5, a signal appeared at δ_{1H} = 5.0 ppm, which is shifted to δ_{1H} = 3.6 ppm after an adsorption of 1.7 equiv. ammonia (**Figs. 2b to 2e, left**). The resonance position of the ^{1}H MAS NMR signal at δ_{1H} = 5 ppm indicates a partial proton transfer from the zeolite framework to the ammonia molecules, but not the

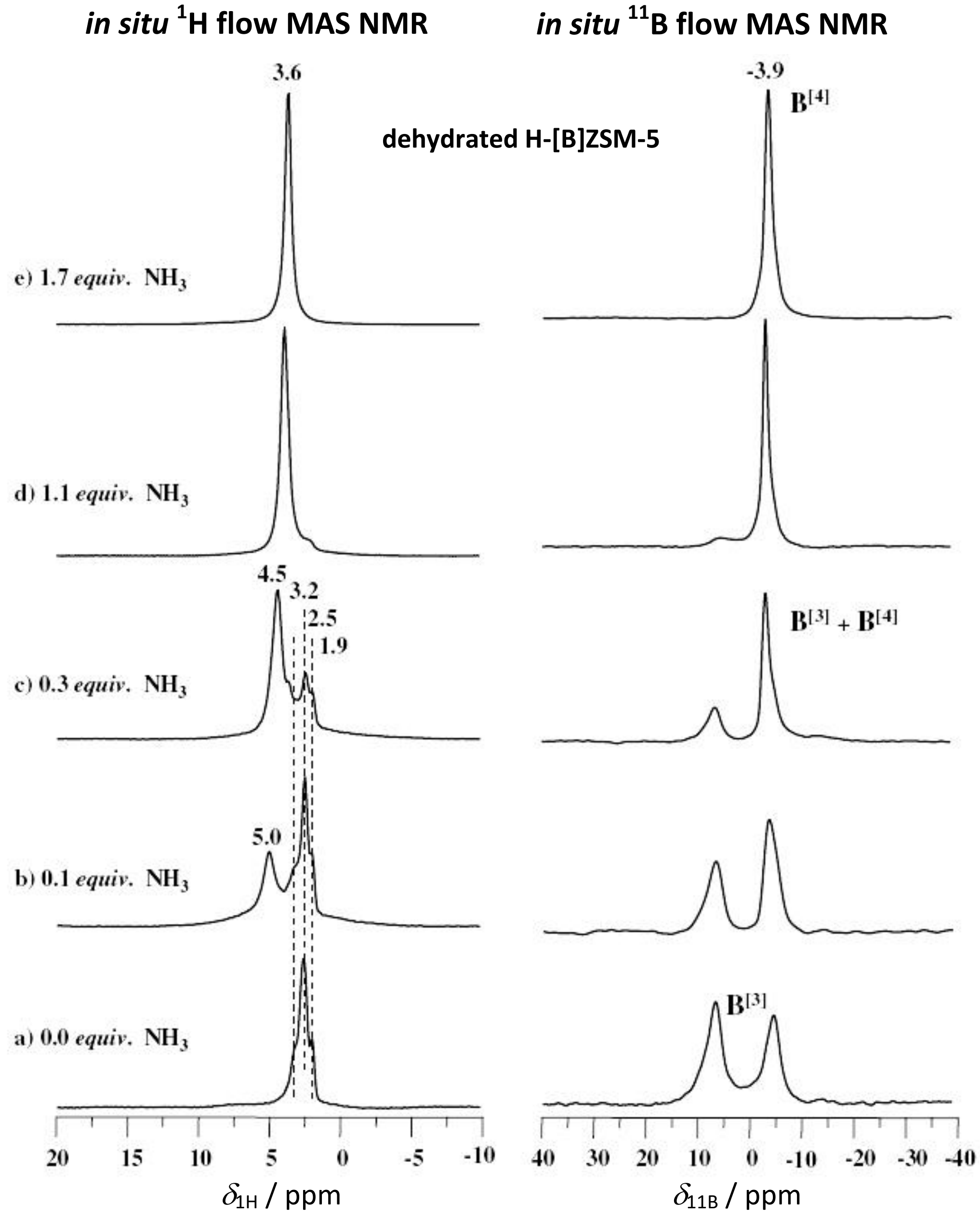


Fig. 2

formation of NH_4^+ ions, which would give a signal at δ_{1H} = 7.0 ppm (*vide supra*). With increasing ammonia loading, a rapid exchange between adsorbed (δ_{1H} = 5.0 ppm) and gaseous ammonia (δ_{1H} = 0.3 ppm [5]) occurs, shifting the above-mentioned ^{1}H MAS NMR signal to δ_{1H} = 3.6 ppm.

The alternately recorded ^{11}B MAS NMR spectra of dehydrated zeolite H-[B]ZSM-5, loaded with different amounts of ammonia, are shown in **Fig. 2, right** [4]. The quadrupole pattern with singularities at δ_{11B} = -5 ppm and 6 ppm, occurring in the ^{11}B

MAS NMR spectrum of the unloaded H-[B]ZSM-5, corresponds to trigonal BO_3 (B[3]) species [6] (see Section "method 4"). An increasing ammonia loading of zeolite H-[B]ZSM-5 leads to a transformation of trigonal BO_3 (B[3]) into tetrahedral BO_4 (B[4]) species, which results in a narrow ^{11}B MAS NMR signal at δ_{11B} = 3.9 ppm (**Figs. 2d and 2e**). Evaluation of the ^{1}H and ^{11}B MAS NMR signal intensities delivered the contents of B[3] and B[4] species as a function of the ammonia loading of zeolite H-[B]ZSM-5 (see **Fig. 3**). The curves in **Fig. 3** indicate that a complete transformation of B[3] into B[4] species requires the adsorption of about 1.7 equiv. ammonia [4].

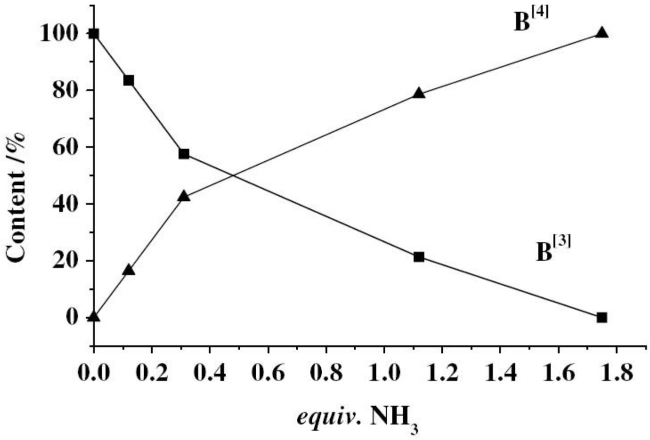


Fig. 3

Catalyst preparation: The zeolite H-[B]ZSM-5 was synthesized and ion exchanged as described in Refs. [4] and [6]. Before the use of this zeolite for *in situ* flow experiments, a dehydration was performed with the sample material in a "sample tube system 1" at "vacuum line 1" (see "sample tube system 1" and "vacuum line 1", accessible via link "*In Situ* Solid-State NMR Techniques"). This treatment 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. Finally, the sample tube system was closed via the vacuum valve and disconnected from „vacuum line 1" (after this line was ventilated with air). The transfer of the dehydrated sample into the MAS NMR rotor was performed without air contact in a mini glove box (see Section "mini glove box", accessible via link "*In Situ* Solid-State NMR Techniques"), purged with dry nitrogen gas.

In situ solid-state NMR studies: The ^{1}H, ^{27}Al, and ^{11}B MAS NMR studies in Figs. 1 and 2 were performed at a Bruker MSL 400WB spectrometer and using a 4 mm Bruker MAS NMR probe, modified as described in Section "flow probe 2", accessible via link "*In Situ* Solid-State NMR Techniques".

The ^{1}H, ^{27}Al, and ^{11}B MAS NMR spectra were recorded at resonance frequencies of ν_0 = 400.1 MHz, 104.3 MHz, and 128.3 MHz, respectively, and with sample spinning rates of ν_{rot} = 8.0 to 9.0 kHz. Single pulse excitations with pulse lengths of 2.2 µs, 05 µs, and 1.0 µs, repetition times of 10 s, 0.5 s, and 2 s, and accumulation numbers of 48 to 64, 1200, and 800, respectively, were used [3, 4].

References:

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