

***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** became possible. By this way, the coordination change of framework atoms and the adsorption sequence of molecules at surface sites and framework atoms could be studied. During *in situ* flow solid-state NMR investigations of the catalyst framework under flow conditions, e.g., **^1H MAS NMR** is utilized for determining the amounts of adsorbed molecules, while **alternately another resonance (^{11}B , ^{23}Na , ^{27}Al , ^{31}P etc.)** is used to study specific framework atoms of the catalyst.

Examples for solid-state NMR studies of catalysts utilizing the *in situ* flow technique are 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* ^1H and ^{27}Al flow MAS NMR spectra, alternately recorded during the adsorption of ammonia at a dehydrated silicoaluminophosphate H-SAP-34 [3]. The ^1H MAS NMR signal in **Fig. 1a, left**, at $\delta_{1\text{H}} = 3.6$ ppm is due to Brønsted 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 the tetrahedrally coordinated framework aluminium at $\delta_{27\text{Al}} = 34$ 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 ^1H MAS NMR signal occurred at $\delta_{1\text{H}} = 7.0$ ppm, indicating the formation of NH_4^+ ions at former Si(OH)Al groups. Simultaneously, the signal of the Si(OH)Al groups at $\delta_{1\text{H}} = 3.6$ ppm is significantly decreased. An adsorption of 2.0 mmol of NH_3 per gram caused a further decrease of the signal at $\delta_{1\text{H}} = 3.6$ ppm and the occurrence of a new signal at $\delta_{1\text{H}} = 5.4$ 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 $\text{Si}(\text{OH})\text{Al}$ groups [3].

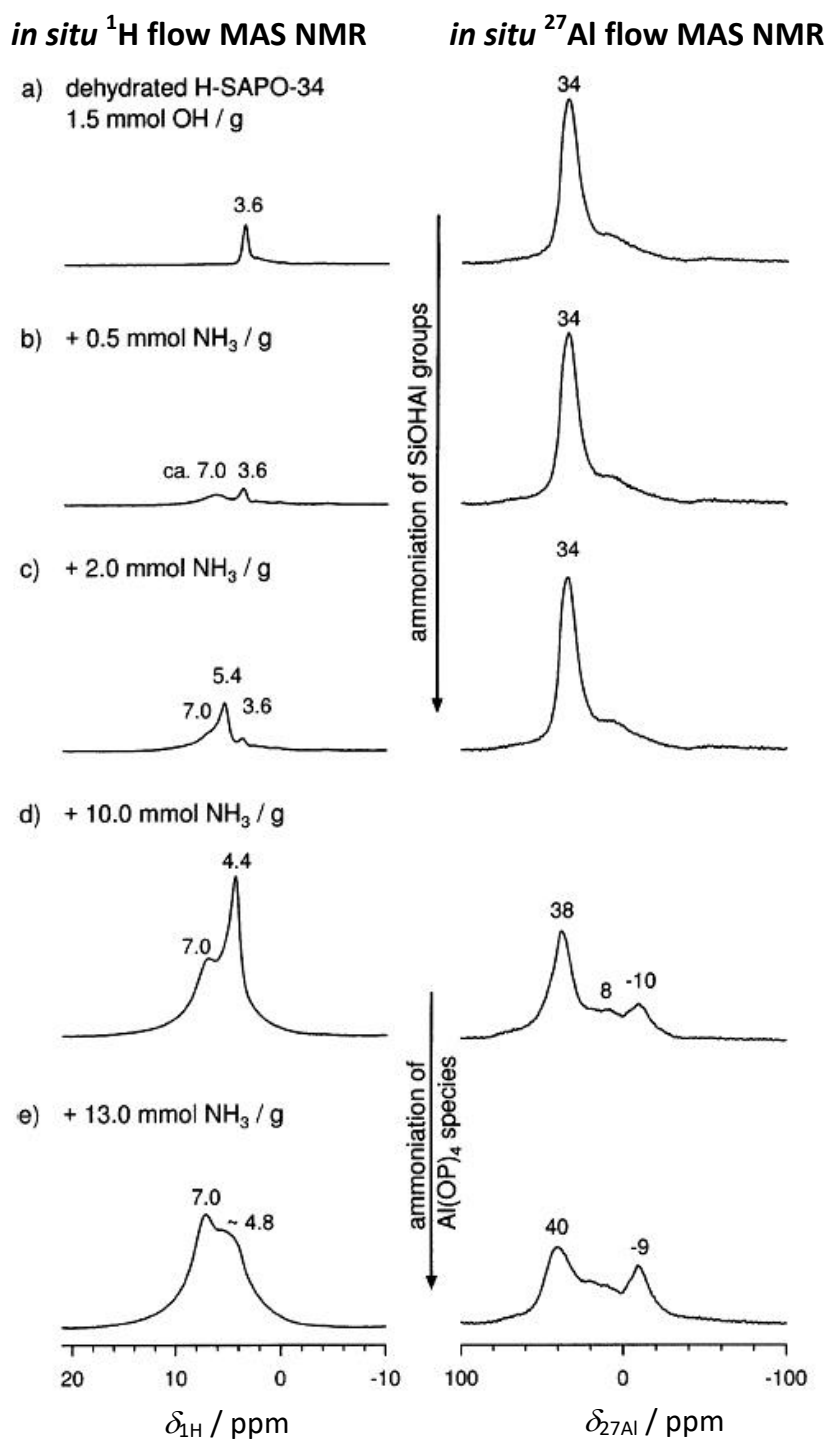
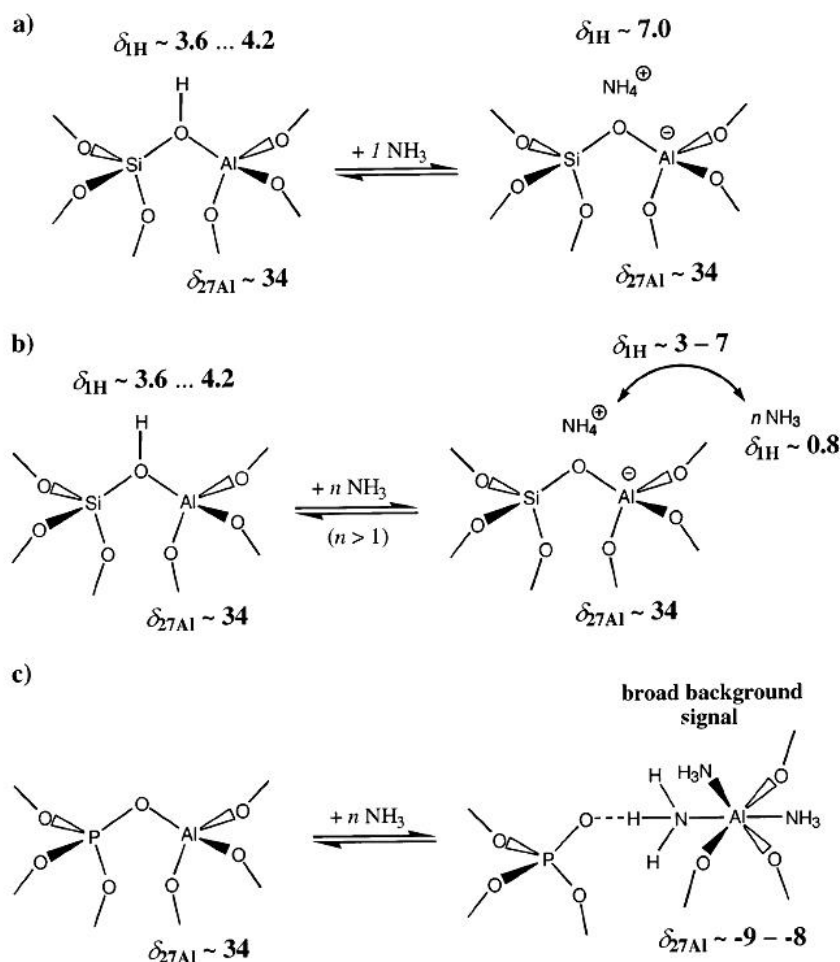


Fig. 1

After adsorption of 10.0 mmol and more ammonia molecules per gram H-SAPO-34, a ^{27}Al MAS NMR signal appeared at $\delta_{27\text{Al}} = -10$ ppm, which increased with the ammonia loading (**Figs. 1 d and 1e, right**). This signal hints to a transformation of

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tetrahedrally coordinated ($\delta_{27\text{Al}} = 38$ ppm) into octahedrally coordinated ($\delta_{27\text{Al}} = -10$ ppm) framework aluminium 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 ^1H MAS NMR spectrum of dehydrated H-[B]ZSM-5 is dominated by a signal of SiOH[B] groups at $\delta_{1\text{H}} = 2.5$ 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 $\delta_{1\text{H}} = 5.0$ ppm, which is shifted to $\delta_{1\text{H}} = 3.6$ ppm after a loading of 1.7 equiv. ammonia (**Figs. 2b to 2e, left**). The resonance position of the ^1H MAS NMR signal at $\delta_{1\text{H}} = 5$ ppm indicates a partial proton transfer from the zeolite framework to the ammonia molecules, but not the formation of NH_4^+ ions, which would give a signal at $\delta_{1\text{H}} = 7.0$ ppm (*vide supra*). With increasing

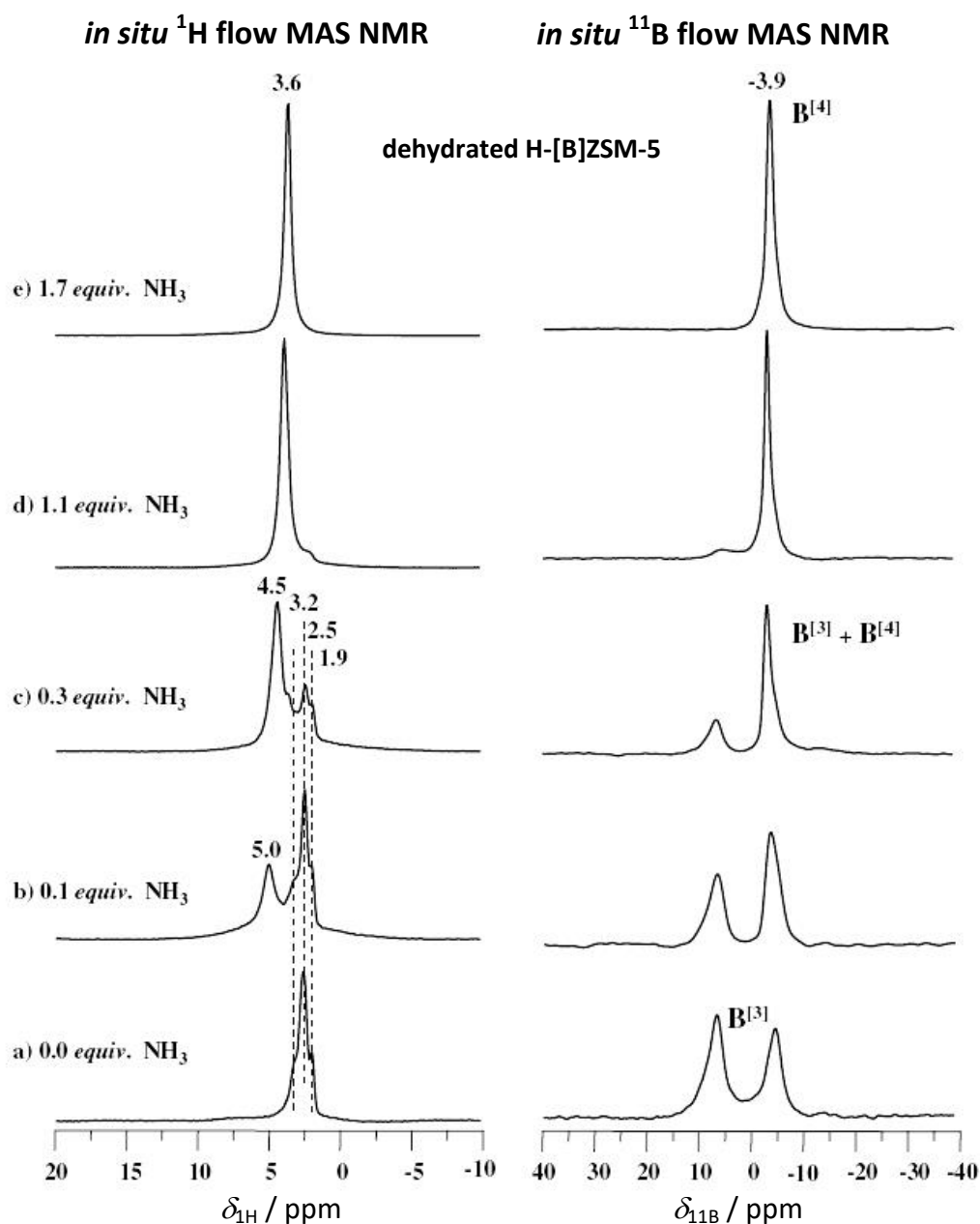


Fig. 2

ammonia loading, a rapid exchange between adsorbed ($\delta_{1\text{H}} = 5.0$ ppm) and gaseous ammonia ($\delta_{1\text{H}} = 0.3$ ppm [5]) occurs, shifting the above-mentioned ^1H MAS NMR signal to $\delta_{1\text{H}} = 3.6$ 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 $\delta_{11\text{B}} = -5$ 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 also Section “method 1”, accessible via link “NMR Methods for Heterogeneous Catalysis”). An increasing ammonia loading of zeolite H-[B]ZSM-5

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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 $\delta_{^{11}\text{B}} = 3.9$ ppm (**Figs. 2d and 2e**). Evaluation of the ^1H 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 (**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.

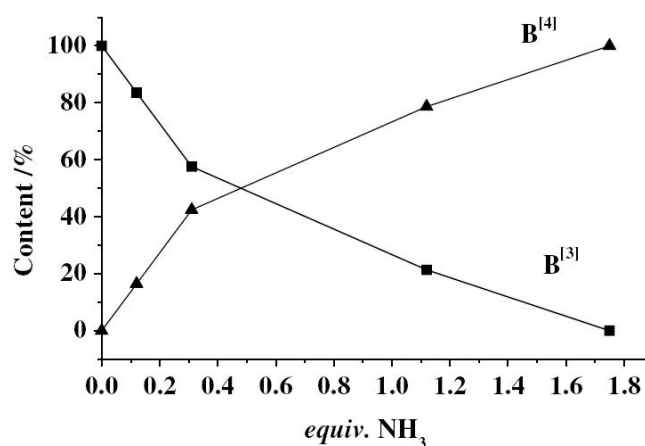


Fig. 3

Catalyst preparation: The zeolite H-[B]ZSM-5 was synthesized and ion exchanged according to 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 glass tube connected with a vacuum line (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 is dehydrated for 2 hours. Subsequently, the temperature is increased up to $T = 723$ K within 3 hours and evacuated at this temperature for 12 hours. Finally, the sample tube system is closed via the vacuum valve and disconnected from „vacuum line 1“ after this line is ventilated with air. The transfer of the dehydrated sample into the MAS NMR rotor is performed without air contact, e.g., in a glove box purged with dry nitrogen gas (see Section “mini glove box”, accessible via link “*In Situ* Solid-State NMR Techniques”).

In situ solid-state NMR studies: The ^1H , ^{27}Al , and ^{11}B MAS NMR studies in Figs. 1 and 2 were performed 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*”. Recording of the ^1H , ^{27}Al , and ^{11}B MAS NMR spectra was performed with sample spinning rates of $\nu_{\text{rot}} = 8.0$ to 9.0 kHz and at resonance frequencies of $\nu_0 = 400.1$ MHz, 104.3 MHz, and 128.3 MHz, respectively. Furthermore, single pulse excitation with pulse lengths of $2.2 \mu\text{s}$, $05 \mu\text{s}$, and $1.0 \mu\text{s}$, 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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