Characterization of hydrated aluminum-containing catalysts by ^{27}Al solid-state NMR

Spectroscopic background: ^{27}Al nuclei have a spin of I = 5/2 and a quadrupole moment of Q = 14.66 x 10^{-30} m^2. Therefore, ^{27}Al NMR signals of aluminum atoms in solids are affected by quadrupolar interactions. The ^{27}Al isotope has a natural abundance of 100 % and a sensitivity of 0.21 in comparison with ^{1}H nuclei (1.0), making this isotope a very suitable candidate for NMR studies of solids. While ^{27}Al nuclei of non-hydrated (or dehydrated) aluminosilicates are involved in strong quadrupolar interactions corresponding to quadrupole coupling constants of up to C_Q = 16 MHz, hydration of these materials significantly decreases these interactions, leading to C_Q values of 1 to 2 MHz. Therefore, hydrated aluminosilicates-type materials are much easier to study by ^{27}Al solid-state NMR than these materials in the non-hydrated or dehydrated state. 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”.

For the framework of **crystalline aluminosilicates**, such as zeolites, the formation of Al-O-Al bonds is forbidden (Loewenstein's rule) and only Al(4Si) units exist. Therefore, the ^{27}Al MAS NMR spectra of pure hydrated zeolites consist of a single signal of tetrahedral framework aluminum atoms, **Al^{IV}**, in a chemical shift range of **δ_{27Al} = 50 ppm to 70 ppm** (referenced to 0.1 M aqueous $Al(NO_3)_3$ solution). In hydrated zeolites, only small deviations from the tetrahedral symmetry of the AlO_4 units exist, which results in a weak quadrupolar broadening of their ^{27}Al MAS NMR signals, corresponding to C_Q values of 1 to 2 MHz.

For the ^{27}Al MAS NMR signals of tetrahedrally coordinated framework aluminum atoms (Al^{IV}) in hydrated zeolites, no definite relationship between their chemical shift δ_{27Al} and the n_{Si}/n_{Al} ratio or the silicon and aluminum order scheme of the zeolite framework exists. However, a correlation between the ^{27}Al NMR chemical shift δ_{27Al} of Al(4Si) units and the mean Al-O-Si bond angle $\bar{\alpha}$ was found [5]:

$$\delta_{27Al} \text{ / ppm} = 132 - 0.500\,\bar{\alpha} \qquad (1)$$

^{27}Al and ^{29}Si MAS NMR investigations of lithium and sodium halide aluminosilicate sodalites led to the following correlation between ^{27}Al and ^{29}Si NMR chemical shift values [6]:

$$\delta_{27\text{Al}} \,/\, \text{ppm} = 1.03\ \delta_{29\text{Si}} \,/\, \text{ppm} + 151.94 \qquad (2)$$

Thermal treatments, subsequent rapid rehydration or acid leaching of H-form aluminosilicate-type zeolites can lead to a dealumination of their framework and to the formation of extra-framework aluminum species. Often, these species are octahedrally coordinated aluminum species, **Al$^{\text{VI}}$**, partially coordinated to water molecules, and causing ^{27}Al MAS NMR signals at **$\delta_{27\text{Al}}$ *ca.* 0 ppm**. If extra-framework aluminum species exist as polymeric aluminum oxide in zeolite cages or pores, a significant quadrupolar signal broadening may occur, due to distortions of the octahedral symmetry of the AlO_6 units.

The signals of **penta-coordinated** aluminum species, **Al$^{\text{V}}$,** and of framework aluminum species in a **disturbed tetrahedral coordination, Al$^{\text{IV}\,'}$,** have chemical shifts of **$\delta_{27\text{Al}}$ = 30 to 40 ppm** [1, 2].

The signal position of Al$^{\text{IV}\,'}$ species is influenced by the so-called second-order quadrupolar shift, δ_{QS}, which depends on the local electric field gradient and, therefore, on the quadrupolar coupling constant C_{Q} of the corresponding ^{27}Al nuclei [3]. Furthermore, the strength of the magnetic B_0 field significantly influences the experimentally observed δ_{QS} value (compare Fig. 2 in Section “method 3” for ^{23}Na nuclei (spin I = 3/2)).

An overview on the chemical shifts ranges of **Al$^{\text{IV}}$, A$^{\text{V}}$,** and **Al$^{\text{VI}}$ species** in hydrated aluminosilicates is given in **Fig. 1**. See Table 8.1 of Ref. [3] for detailed ^{27}Al chemical shifts $\delta_{27\text{Al}}$ of the above-mentioned aluminum species in various materials.

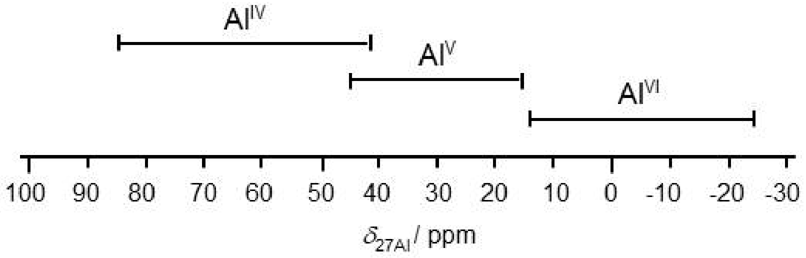

Fig. 1

For demonstrating typical results of ^{27}Al MAS NMR studies of hydrated aluminosilicate-type zeolites, **Fig. 2** shows spectra of weakly (left) and strongly (right) dealuminated zeolites H,Na-Y [4]. Upon dealumination by steaming, some of the former framework Al^{IV} species in zeolite H,Na-Y are disturbed in their tetrahedral oxygen coordination and cause the broad quadrupole pattern, assigned by $Al^{IV'}$ in **Fig. 2**, right-hand side.

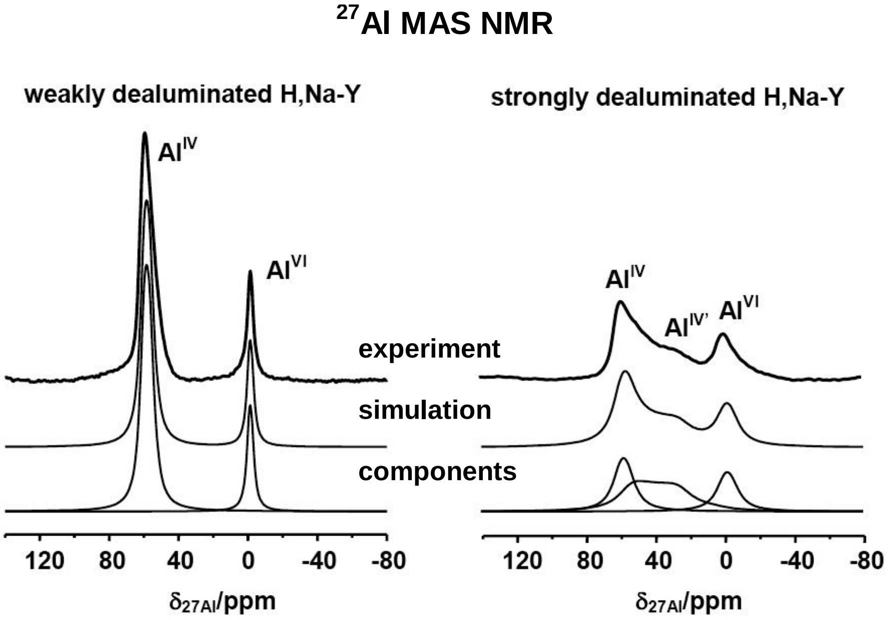

Fig. 2

The MAS technique reduces the broadening of ^{27}Al MAS NMR signals due to quadrupolar interactions of ^{27}Al nuclei by a factor of about 1/3.6. In contrast, application of the two-dimensional (2D) multiple-quantum MAS NMR (MQMAS) [7, 8] and the double-rotation (DOR) [9, 10] technique causes a complete averaging of this solid-state interaction.

The 2D ^{27}Al MQMAS NMR spectrum of a strongly dealuminated and hydrated zeolite H,Na-Y in **Fig. 3** consists of three signals [11]. Two of them, the signals Al^{IV} and Al^{VI}, are located near the diagonal (straight line) indicating low quadrupolar interactions, which is typical for ideal (high local symmetry) tetrahedrally and octahedrally coordinated framework and extra-framework aluminum species, respectively. In contrast, the broad signal $Al^{IV'}$ is located beside the diagonal, but at the isotropic chemical shift ($\delta_{27Al,so} = \delta_{F1}$) of Al(4Si) units. The latter is typical for distorted Al(4Si) units involved in strong quadrupolar interactions, i.e. for $Al^{IV'}$ species. By quantitative evaluation of the signal positions in the 2D ^{27}Al MQMAS NMR spectra, the isotropic chemical shifts $\delta_{27\mathrm{Al,iso}}$ and the second-order quadrupole effect parameters *SOQE* of the different aluminum species can be determined (see Refs. [3] and [7]). These values are helpful parameters for the simulation and quantitative evaluation of one-dimensional ^{27}Al MAS NMR spectra (see **Fig. 2**) [4].

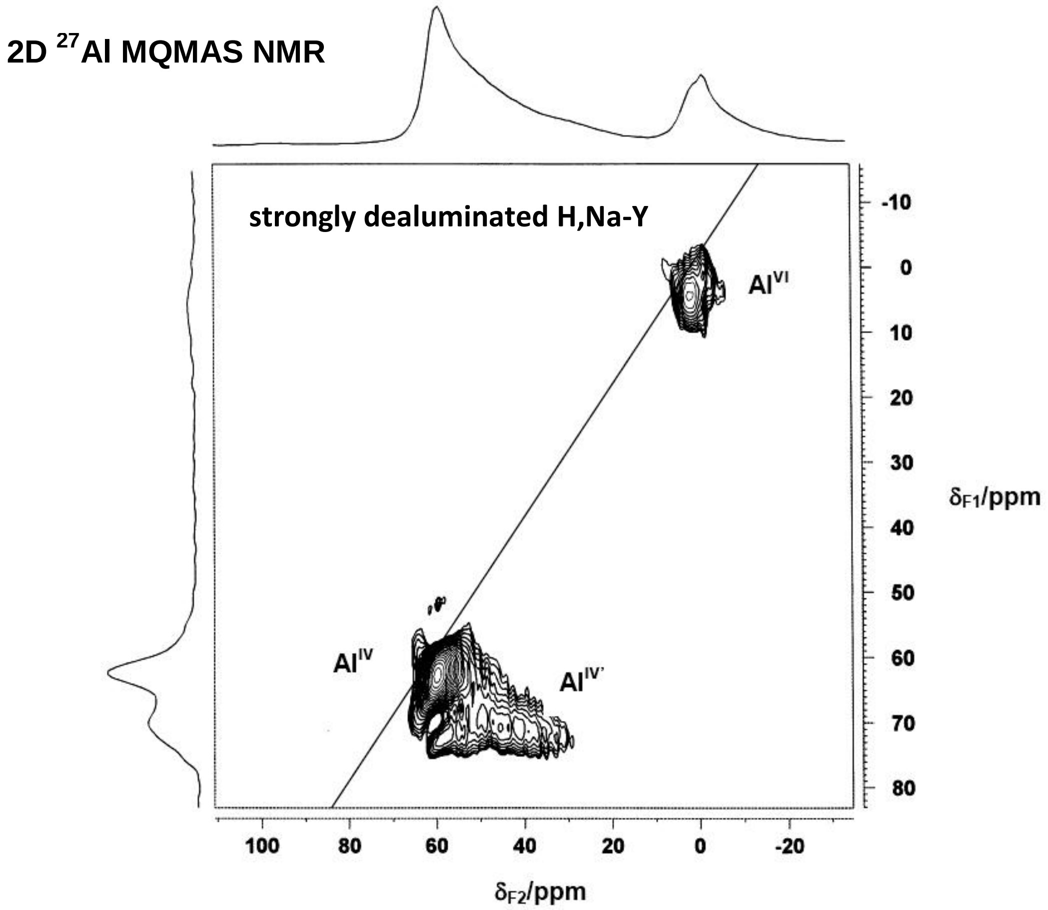

Fig. 3

In the ^{27}Al MAS NMR spectra of amorphous silica-aluminas (ASA) with high aluminum contents and synthesized by flame-spray pyrolysis, broad signals occur at $\delta_{27\mathrm{Al}}$ = 55, 30, and 0 ppm [12-14]. Also in this case the question arises, whether the ^{27}Al MAS NMR signal at $\delta_{27\mathrm{Al}}$ = 30 ppm, e.g. in the spectrum of a sample with 70 atom% aluminum (see **Fig. 4, top** [13]), is due to aluminum species in a disturbed tetrahedral coordination (Al$^{IV'}$) or caused by penta-coordinated aluminum (Al^{V}) species. The 2D ^{27}Al MQMAS NMR spectrum of this material in **Fig. 4, bottom**, shows three well-resolved signals near the diagonal [13]. Hence, all these signals are due to aluminum species, which are not involved in strong quadrupolar interactions. The positions of their ^{27}Al MAS NMR signals are not influenced by second-order quadrupolar shifts. Therefore, the signal at δ_{27Al} = 30 ppm is to Al^{V} species in this case.

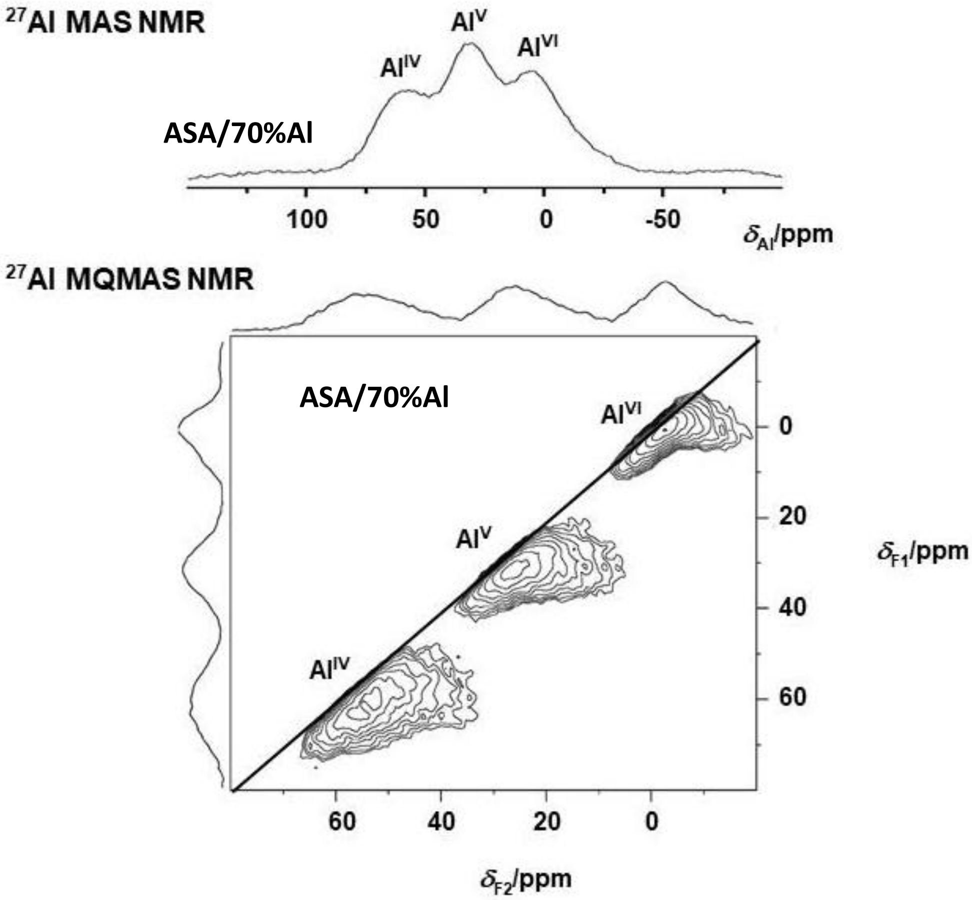

Fig. 4

The framework of **aluminophosphate-type zeolites**, such as VPI-5, is built of AlO_4 and PO_4 tetrahedra in an alternating arrangement. The ^{27}Al DOR NMR spectra of aluminophosphates consist of narrow signals at **δ_{27Al} *ca.* 30 to 40 ppm** due to tetrahedrally coordinated Al(4P) atoms, **Al^{IV},** in some cases at crystallographically non-equivalent T-sites. Signals at **δ_{27Al} *ca.* -20 ppm** are caused by octahedrally coordinated framework aluminum atoms, **Al^{VI}**, additionally interacting with adsorbed molecules, such as water. The ^{27}Al DOR NMR spectrum of dehydrated VPI-5 at the top of **Fig. 5, top**, consists of two Al(4P) signals at δ_{27Al} = 36 ppm and 33 ppm (asterisks are DOR sidebands). Hydration of VPI-5 shifts these signals to chemical shifts of δ_{27Al} = 41 ppm and 40 ppm and a new signal occurs at δ_{27Al} = -18 ppm in the range of octahedrally coordinated framework aluminum species, additionally bound to water molecules (**Fig. 5, bottom**) [15].

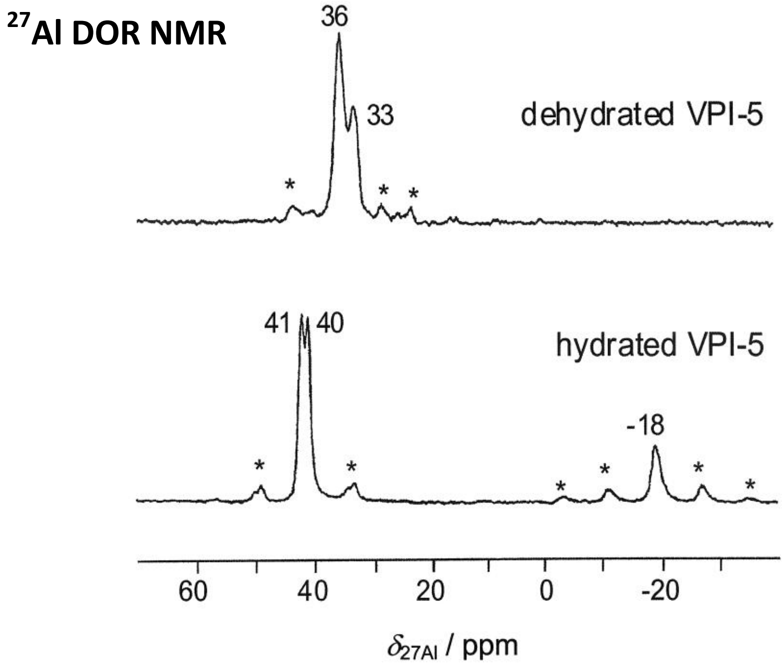

Fig. 5

Catalyst preparation: For decreasing quadrupolar interactions of the ^{27}Al nuclei studied by the spectroscopic methods described in the present section, the powder samples should be hydrated for ca. 12 h over water vapour in a desiccator.

^{27}Al solid-state NMR studies: Due to quadrupolar interactions of ^{27}Al nuclei, their single pulse excitation should be performed by less than $\pi/6$ and most suitable by $\pi/12$ pulses. Due to the low T_1 times of these quadrupole nuclei, repetition times of 500 ms to 2 s are often suitable. For reaching a high resolution of the ^{27}Al MAS NMR spectra, the sample spinning rate has to be as high as possible and at least 8 kHz. The 2D ^{27}Al MQMAS NMR experiments in Fig. 3 were performed at the Larmor frequency of ν_0 = 130.32 MHz and using the three-pulse z-filter pulse sequence [8] with pulse lengths of 3.9, 1.3, and 20.0 µs, a repetition time of t = 300 ms, and a 4 mm MAS NMR rotor with a sample spinning rate of ν_{rot} = 12.5 kHz. Referencing of the chemical shift is performed with 0.1 M aqueous $Al(NO_3)_3$ solution (δ_{27Al} = 0 ppm).

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