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

Spectroscopic background: ²⁷Al nuclei have a spin of I = 5/2 and a quadrupole moment of $Q = 14.66 \times 10^{-30} \text{ m}^2$. Therefore, ²⁷Al NMR signals of aluminum atoms in solids are affected by quadrupolar interactions. The ²⁷Al isotope has a natural abundance of 100 % and a sensitivity of 0.21 in comparison with ¹H nuclei (1.0), making this isotope a very suitable candidate for NMR studies of solids. While ²⁷Al 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 ²⁷Al 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 AI-O-AI bonds is forbidden (Loewenstein's rule) and only $AI(OSi)_4$ units exist. Therefore, the ²⁷AI MAS NMR spectra of pure hydrated zeolites consist of a single signal of tetrahedral framework aluminum atoms, AI^{IV} , in a chemical shift range of $\delta_{27AI} = 50$ ppm to 70 ppm, referenced to 0.1 M aqueous $AI(NO_3)_3$ solution (Fig. 1). In hydrated zeolites, only small deviations from the tetrahedral symmetry of the $AI(OSi)_4$ units exist, which results in a weak quadrupolar broadening of their ²⁷AI MAS NMR signals, corresponding to C_Q values of 1 to 2 MHz [1-4].



For the ²⁷AI MAS NMR signals of tetrahedrally coordinated framework aluminum atoms (AI^{IV}) in hydrated zeolites, no definite relationship between their chemical shift

 δ_{27AI} and the n_{Si}/n_{AI} ratio or the silicon and aluminum order scheme of the zeolite framework exists. However, a relationship between the ²⁷AI NMR chemical shift δ_{27AI} of AI(4Si) units and the mean AI-O-Si bond angle $\overline{\alpha}$ was found [5]:

$$\delta_{27AI} / \text{ppm} = 132 - 0.500 \ \alpha$$
 (1)

²⁷AI and ²⁹Si MAS NMR investigations of lithium and sodium halide aluminosilicate sodalites led to the following relationship between ²⁷AI and ²⁹Si NMR chemical shift values [6]:

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

Thermal treatments and subsequent rapid rehydration or acid leaching of H-form aluminosilicate-type zeolites may attack the zeolite framework and may cause a formation of extra-framework aluminum species. Often, these extra-framework species are octahedrally coordinated aluminum species, AI^{VI} , partially coordinated to water molecules in the hydrated state. In ²⁷AI MAS NMR spectra of aluminosilicates, these AI^{VI} species cause signals at $\delta_{27AI} \cong 0$ ppm. If extra-framework aluminum species exist as polymeric aluminum oxide in zeolite cages or pores, significant quadrupolar signal broadenings occur due to distortions of the octahedral symmetry of the extra-framework AIO_6 species [1-4].

In some cases, the strong thermal treatment of aluminosilicates is accompanied by the formation of framework aluminum species in a **disturbed tetrahedral coordination**, AI^{IV} , and of **pentacoordinated aluminum species**, AI^{V} . The ²⁷AI solid-state NMR signals of these two kinds of aluminum species occur at similar ²⁷AI chemical shifts of $\delta_{27AI} = 30$ to 40 ppm [1, 2]. The disturbed tetrahedral oxygen coordination of AI^{IV} species is accompanied by a high electric field gradient in the local structure. Therefore, these framework aluminum atoms are involved in strong quadrupolar interactions, which cause a resonance shift (second-order quadrupolar shift, δ_{QS}) of their ²⁷AI solid-state NMR signal to lower chemical shift values (high-field shift) into the chemical shift range of AI^{V} atoms (see **Fig. 1**) [3]. Furthermore, the strength of the magnetic B_0 field influences the experimentally observed second-order quadrupolar shift (compare Fig. 2 in Section "method 8" for ²³Na nuclei with spin *I* = 3/2).

For demonstrating typical results of ²⁷Al 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 ²⁷AI MAS NMR signals due to quadrupolar interactions of ²⁷AI 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 ²⁷AI 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 AI^{IV} and AI^{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 AI^{IV} is located beside the diagonal, but at the isotropic chemical shift ($\delta_{27AI,iso} = \delta_{F1}$) of AI(OSi)₄ units. The latter is typical for distorted AI(OSi)₄ units involved in strong quadrupolar interactions, i.e. for AI^{IV'} species. By quantitative evaluation of the signal positions in the 2D ²⁷AI MQMAS NMR spectra, https://michael-hunger.de

the isotropic chemical shifts $\delta_{27Al,iso}$ 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 ²⁷Al MAS NMR spectra (see **Fig. 2**) [4].



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

positions of their ²⁷AI MAS NMR signals are not influenced by second-order quadrupolar shifts. Therefore, the signal at $\delta_{27AI} = 30$ ppm in **Fig. 4** is to AI^V species.



Fig. 4

The frameworks of aluminophosphate (AIPOs) and silicoaluminophosphate (SAPOs) zeolites are built of AlO₄ and PO₄ tetrahedra in an alternating arrangement. In SAPO materials, some PO₄ tetrahedra are replaced by SiO₄ tetrahedra. The ²⁷Al MAS NMR signals of tetrahedrally coordinated Al(OP)₄ species, Al^{IV}, in these materials occur at $\delta_{27AI} \cong$ 30 to 45 ppm (Fig. 5) [15, 18, 19].



Signals at $\delta_{27AI} \cong -25$ to -10 ppm are caused by octahedrally coordinated framework aluminum atoms, AI^{VI} , additionally interacting with water molecules in the hydrated state. In the spectra of some materials, signals of **pentacoordinated aluminum** species, AI^{V} , at $\delta_{27AI} \cong 8$ to 13 ppm occurs (Fig. 5) [15, 18, 19].

The ²⁷AI DOR NMR spectrum of the dehydrated aluminophosphate VPI-5 in **Fig. 6**, **top**, consists of two signals at $\delta_{27AI} = 36$ ppm and 33 ppm (asterisks are DOR sidebands) due to tetrahedrally coordinated framework aluminum atoms (AI^{IV}) at crystallographically non-equivalent T-positions. Hydration of the VPI-5 shifts these signals to $\delta_{27AI} = 41$ ppm and 40 ppm (**Fig. 6**, **bottom**) [15]. Furthermore, a new signal appears at $\delta_{27AI} = -18$ ppm, i.e. in the chemical shift range of octahedrally coordinated aluminum species (AI^{VI}). In the case of hydrated VPI-5, the corresponding AI^{VI} species remain in the framework, but coordinate to additional water molecules [15].



Table 1 is a summary of the ²⁷Al solid-state NMR parameters of the abovementioned and some additional zeolites. For a broad survey on the ²⁷Al NMR parameters of crystalline and amorphous materials, see Table 8.1 of Ref. [3]. Refs. [16] and [17] are reviews on recent advances in the application of ²⁷Al liquid and

solid-state NMR spectroscopy for the study of synthesis mixtures, zeotype materials, and metal-organic frameworks (MOFs) as well as their ²⁷AI NMR parameters.

Materials	Al Species	$\delta_{ m 27Al}$ / ppm	Refs.
aluminosilicate H,Na-Y , hydrated	Al ^Ⅳ	60	[4]
	Al ^Ⅵ	0	[4]
dealuminated deH,Na-Y , hydrated	AI ^Ⅳ AI ^Ⅳ ' AI ^Ⅵ	60 61 (<i>C</i> _Q = 6.7 MHz) 0	[4] [11] [4]
aluminosilicate H-ZSM-5, hydrated	AI ^{IV}	54 to 55	[20]
aluminosilicate Na-ZSM-5 , hydrated	AIIV	55	[21]
amorphous silica-alumina ASA/70%AI	Al ^{IV}	55	[12-14]
	Al ^V	30	[12-14]
	Al ^{VI}	0	[12-14]
aluminophosphate VPI-5, dehydrated	AI ^{IV}	33, 36	[15]
aluminophosphate VPI-5 , hydrated	Al ^{IV}	40, 41	[15]
	Al ^{VI}	-18	[15]
H-SAPO-34, as-synthesized	Al ^{i∨}	39	[18]
	Al [∨]	13	[18], [19]
H-SAPO-34, calcined, hydrated	Al ^Ⅳ	42	[18]
	Al ^Ⅵ	-13	[18]
H-SAPO-37, as-synthesized	Al ^{IV}	36	[18]
	Al ^V	8	[18], [19]
	Al ^{VI}	-10	[18]
H-SAPO-37, calcined, hydrated	Al ^{IV}	42	[18]
	Al ^{VI}	-11	[18]

Table 1

Catalyst preparation: For decreasing quadrupolar interactions of the ²⁷Al nuclei studied by the spectroscopic methods described in the present section, the powder samples were hydrated at room temperature for ca. 12 h over water vapour in a desiccator.

²⁷Al solid-state NMR studies: Due to quadrupolar interactions of ²⁷Al nuclei, their single pulse excitation was 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 suitable. For reaching a high resolution of the ²⁷Al MAS NMR spectra, the sample spinning rate has to be as high as possible and at least 8 kHz. The 2D ²⁷Al MQMAS NMR experiments in Fig. 3 were performed at the Larmor frequency of v_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 v_{rot} = 12.5 kHz. Referencing of the chemical shift is performed with 0.1 M aqueous Al(NO₃)₃ solution (δ_{27Al} = 0 ppm).

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