

Effect of Dehydration on the Local Structure of Framework Aluminum Atoms in Mixed Linker MIL-53(Al) Materials Studied by Solid-State NMR Spectroscopy

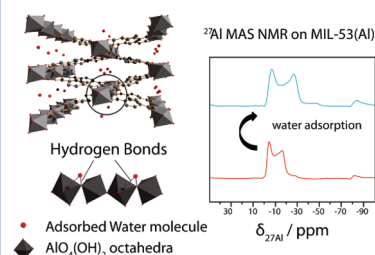
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ABSTRACT The present study features ¹H and ²⁷Al MAS NMR spectroscopic investigations on mixed ligand metal–organic frameworks (MOFs) of MIL-53(Al) type with benzene-1,4-dicarboxylate (BDC) and 2-aminobenzene-1,4-dicarboxylate (ABDC) linkers. The excellent resolution of the ¹H spectra allowed an elegant and facile quantitative analysis of the organic linkers using solid-state NMR. The actual molar fraction of ABDC in the dehydrated mixed linker MOFs was determined by evaluating the intensity of the –NH₂ signal at 5.6 ppm. The incorporation of amine groups led to higher field shifts of the corner-sharing AlOH signals and a more homogeneous charge distribution in the local structure of framework aluminum atoms corresponding to a decrease of the quadrupole coupling constant by ~1 MHz compared to that of aluminum coordinated to BDC. Upon rehydration, the local structures of the framework aluminum atoms exhibited a much lower symmetry, as indicated by an increase of the ²⁷Al quadrupole coupling constant by up to 3 MHz.

SECTION Nanoparticles and Nanostructures



Metal–organic frameworks (MOFs), which are constructed of metal ions and organic linkers, are attracting considerable interest because of their potential applications in areas such as separation technology, gas storage, sensors, and catalysis.^{1–8} A key strategy to make MOF materials interesting for catalysis is to integrate functionalities into these solid-state materials.⁹ Many important postsynthetic modifications involving functionalization of organic linkers or incorporation of metal ions into the MOF structure have been employed to achieve more sophisticated materials.^{10–13}

Aluminum-based MIL-53 (MIL: Materials of Institut Lavoisier) [Al(OH)BDC] (BDC = benzene-1,4-dicarboxylate) is one of the first MOFs that has been commercially available and intensively used due to its high thermal stabilities (up to 773 K), selective adsorption behaviors, and catalytic properties.^{14–16} Its framework is built of trans corner-sharing (via OH bridges) AlO₄(OH)₂ octahedra interconnected with BDC organic linkers. Recently, incorporation of catalytically active amine groups (–NH₂) of 2-aminobenzene-1,4-dicarboxylate (ABDC) instead of the organic BDC linker of pure MIL-53(Al) has been demonstrated.^{17–20} This approach allows the fine-tuning of the catalytic activity and the thermal stability of functionalized MIL-53(Al) by using mixtures of two types of organic linker molecules, which can lead to a promising modification of this material for catalytic applications.²¹

MIL-53(Al) exhibits an unusually large pore diameter of 0.85 × 0.85 nm and a specific surface area of up to 1600 m²/g.¹⁴

The presence of water in the confined nanoporous spaces significantly reduces the volume of the unit cell by stuffing the pores. It is expected that the interaction between guest water and host framework aluminum atoms can be responsible for the changes of the local structure in the mixed linker MOFs. In the present work, ¹H MAS NMR spectroscopy was used to investigate the effect of water molecules and –NH₂ groups on the mixed linker MIL-53(Al) with 0, 10, 50, 90, and 100% of BDC replaced by ABDC. The corresponding ¹H MAS NMR spectra of the different mixed linker MOFs and their simulations are shown in Figures 1 and S1 (Supporting Information).

For all of the dehydrated samples presented in Figures 1 and S1 (Supporting Information), the ¹H MAS NMR spectra showed a strong signal at 7.6 ppm from the aromatic CH groups.¹⁴ No signals due to COOH groups were observed. The efficient removal of free acid molecules has also been proven in previous studies by infrared spectroscopy.²¹ It is important to note that a weak high-field shoulder at ~5.6 ppm was exclusively observed in the spectra of MIL-53(Al) materials functionalized by –NH₂ groups (see Figures 1 and S1b (Supporting Information)). The assignment of this signal was further supported by the systematically increased intensity of the –NH₂ signal as a function of the increasing content

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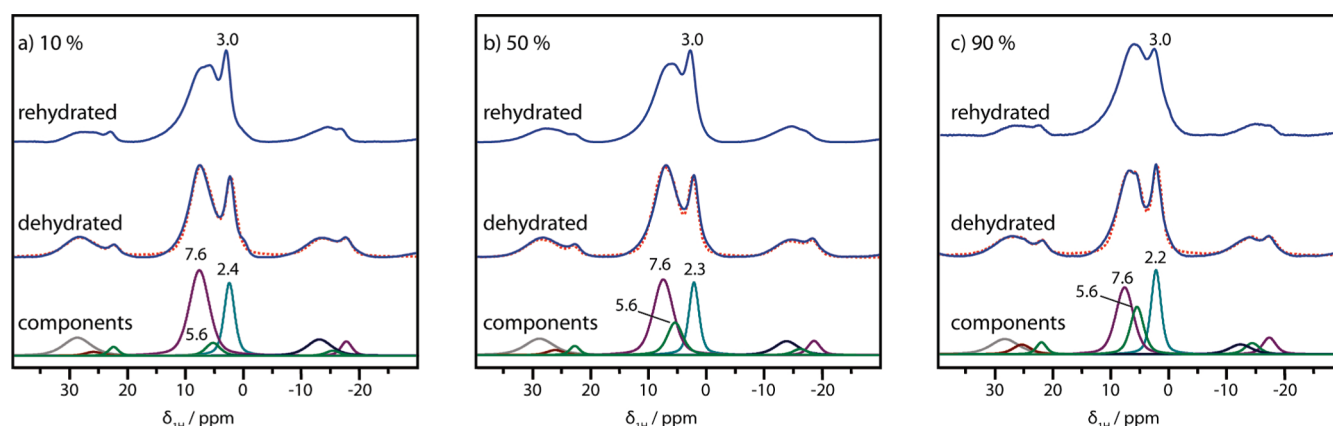


Figure 1. ^1H MAS NMR spectra of the mixed linker MIL-53(Al) with 10 (a), 50 (b), and 90% (c) of BDC replaced by ABDC after dehydration at 373 K (middle) and rehydration (top). The experimental spectra recorded under dehydration are compared with simulated spectra (bottom).

Table 1. Relative Intensities of the ^1H MAS NMR Signals of the Mixed Linker MIL-53(Al) Materials with 0, 10, 50, 90, and 100% of the Organic BDC Linkers Replaced by ABDC Determined after Dehydration at 373 K

sample	AIOH groups 2.1–2.6 ppm content %	$-\text{NH}_2$ groups 5.6 ppm content %	aromatic CH atoms 7.6 ppm content %	$-\text{NH}_2/\text{CH}$ % ratio ^a :ratio ^b
0%	19.8		80.2	
10%	26.3	3.5	70.2	5.0 5.1
50%	25.4	17.2	57.4	30.0 28.6
90%	30.0	25.0	45.0	55.6 58.1
100%	41.6	23.6	34.8	67.8 66.7

^a Ratio determined from the simulated ^1H MAS NMR spectra. ^b Ratio given by the stoichiometric amount used in synthesis.

of the organic ABDC linkers in the MOFs. The signal occurring at $\delta_{\text{HH}} = 2.1\text{--}2.6$ ppm was assigned to AIOH groups. Generally, the ^1H MAS NMR signals of undisturbed metal OH groups, such as AIOH groups at the outer surface of Al_2O_3 particles, occur at chemical shifts of ~ 0 ppm. In the case of internal AIOH groups interacting via hydrogen bondings with neighboring oxygen atoms, the ^1H MAS NMR signal shifts to lower magnetic fields up to 3.6 ppm.²² It is interesting to note that with increasing contents of $-\text{NH}_2$ groups in the MIL-53(Al) materials, the AIOH signal moved toward higher chemical shifts from 2.6 to 2.1 ppm.

Due to the absence of $-\text{NH}_2$ groups in pure MIL-53(Al) (0% of ABDC), the spectrum of the dehydrated sample consisted only of the signals of AIOH groups (2.6 ppm) and aromatic CH groups (7.6 ppm), which were used for peak deconvolution. This simulated spectrum is in good agreement with the experimental one. In the ^1H MAS NMR spectrum of MIL-53(Al)- NH_2 with 100% organic ABDC linkers (Figure S1b, Supporting Information), the low-field signal was dominated by a peak at 5.6 ppm due to the large content of $-\text{NH}_2$ groups. Table 1 gives a survey of the molar fractions of AIOH groups, $-\text{NH}_2$ groups, and aromatic CH groups in the dehydrated mixed linker MIL-53(Al) materials, as obtained by the decomposition of the ^1H MAS NMR spectra shown in Figures 1 and S1 (Supporting Information). The corresponding molar ratios of $-\text{NH}_2$ to aromatic CH groups

were 5.0, 30.0, and 55.6 for the mixed linker MOFs with 10, 50, and 90% of BDC replaced by ABDC, respectively. These values correlate very well with the given stoichiometric ratios during synthesis, as shown in the last column in Table 1. Hence, quantitative evaluation of ^1H MAS NMR spectra allowed the determination of the actual molar fraction of the amine group in mixed linker MOFs.

Upon rehydration of the dehydrated samples, the ^1H MAS NMR signal occurring in the dehydrated state at 2.1–2.6 ppm shifted to 3.0 ppm (Figures 1 and S1, top (Supporting Information)). Furthermore, the relative intensity of this high-field signal was enhanced in comparison with that of the corresponding dehydrated sample. These findings can be explained by the presence of water molecules forming weak hydrogen bonds to neighboring oxygen atoms of the organic linkers with a large O–O distance. According to empirical correlations, the experimentally observed ^1H NMR shift of 3.0 ppm indicates the formation of $\text{O}(\text{w})\text{--H}\cdots\text{O}$ arrangements with O–O distances of 0.33–0.34 nm.²³ In this case, the high-field signal at 3.0 ppm is a superposition of the signals of AIOH groups and hydrogen-bonded water molecules.

For a number of aluminum-containing solid materials, hydration improves the resolution of ^{27}Al solid-state NMR spectra.²⁴ However, the hydration of calcined MOF materials may result in changes of the coordination number and/or geometry of the framework aluminum atoms. Therefore, the ^{27}Al MAS NMR investigation of dehydrated MOFs is a powerful approach to get direct insight into the local structure of these materials. In the present work, a magnetic field of $B_0 = 16.4$ T (700 MHz) was utilized to separate the ^{27}Al MAS NMR signals of aluminum atoms with strong quadrupolar interactions in the mixed linker MIL-53(Al) materials. Figure 2 shows ^{27}Al MAS NMR spectra of the mixed linker MIL-53(Al) materials with 10, 50, and 90% of organic BDC linkers replaced by ABDC recorded after dehydration and rehydration. The corresponding ^{27}Al MAS NMR spectra of the pure MIL-53(Al) (0% ABDC) and MIL-53(Al)- NH_2 (100% ABDC) are presented in the Supporting Information (Figure S2).

Deconvolution of the ^{27}Al MAS NMR spectra in Figures 2 and S2, bottom (Supporting Information) allows the determination of the isotropic chemical shift, $\delta_{27\text{Al}}$, the quadrupole coupling

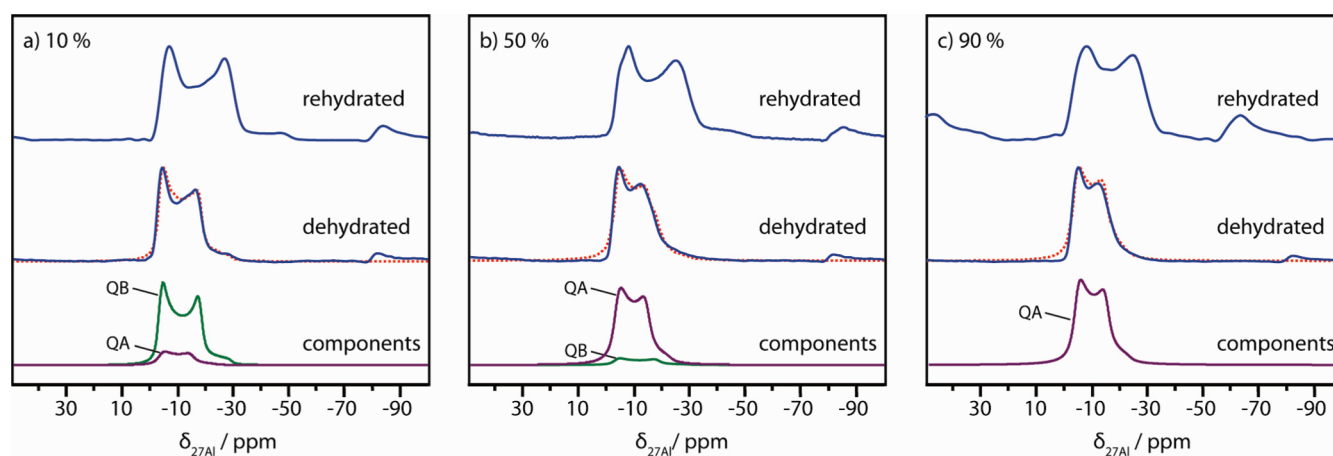


Figure 2. ^{27}Al MAS NMR spectra of the mixed linker MIL-53(Al) with 10 (a), 50 (b), and 90% (c) of BDC replaced by ABDC after dehydration at 373 K (middle) and rehydration (top). The experimental spectra recorded under dehydration are compared with simulated spectra (bottom).

Table 2. Isotropic Chemical Shifts, $\delta_{27\text{Al}}$, Quadrupole Coupling Constants, C_Q , Asymmetry Parameters, η_Q , and Symmetric Broadenings, EM, of the ^{27}Al MAS NMR Signals of the Mixed Linker MIL-53(Al) Materials with 0, 10, 50, 90, and 100% of BDC Replaced by ABDC after Dehydration at 373 K and Rehydration

sample		$\delta_{27\text{Al}}/\text{ppm}$	C_Q/MHz	η_Q	EM/Hz
0%	dehydrated	QB: 2.0	8.3	0.10	6
10%	dehydrated	QB: 1.8	8.1	0.10	12
		QA: -0.5	7.1	0.12	30
	hydrated	1.9	10.4	0.12	12
50%	dehydrated	QB: 1.8	8.1	0.10	12
		QA: -0.5	7.0	0.12	30
	hydrated	1.7	10.1	0.15	16
90%	dehydrated	QA: -0.5	7.0	0.12	30
	hydrated	1.4	10.1	0.20	20
100%	dehydrated	QA: -0.6	7.1	0.12	30

constant, C_Q , the asymmetry parameter, η_Q , and the symmetric broadening, EM, as summarized in Table 2. The spectrum of the dehydrated MIL-53(Al) with 0% ABDC (Figure S2a, Supporting Information) features a single quadrupolar pattern with an isotropic chemical shift of $\delta_{27\text{Al}} = 2$ ppm, which is assigned to octahedrally coordinated aluminum atoms ($\text{AlO}_4(\text{OH})_2$). When the organic BDC linkers are totally replaced by ABDC, the signal of octahedrally coordinated aluminum atoms in the dehydrated MIL-53(Al)- NH_2 material (Figure S2b, Supporting Information) occurs at the slightly higher isotropic chemical shift of $\delta_{27\text{Al}} = 0$ ppm. The ^{27}Al MAS NMR spectrum recorded after dehydration of the mixed linker MOFs containing 10% ABDC shows a superposition of two quadrupolar patterns, denoted QA and QB (Figure 2). Hence, the octahedrally coordinated framework aluminum atoms of the dehydrated mixed linker MOFs exist in two nonequivalent local structures.

As shown in Figure 2a, the simulation of the broad quadrupolar pattern (denoted QB) gives very similar spectroscopic parameters like those obtained by simulating the spectrum of pure MIL-53(Al), that is, $\delta_{27\text{Al}} = 1.8$ ppm, $C_Q = 8.1$ MHz, and

$\eta_Q = 0.10$. This quadrupolar pattern is caused by framework aluminum atoms coordinated by organic BDC linkers. The narrow quadrupolar pattern (denoted QA), characterized by $\delta_{27\text{Al}} = -0.5$ ppm, $C_Q = 7.1$ MHz, and $\eta_Q = 0.12$, corresponds to framework aluminum atoms connecting with at least one organic ABDC linker in the four equatorial coordination positions of Al atoms. This finding demonstrates that the functionalization of MIL-53(Al) by amine groups induced the decrease of the C_Q value by ~ 1 MHz. A smaller C_Q value indicates a more isotropic charge distribution in the local structure of the resonating quadrupolar ^{27}Al nuclei.²⁵ Moreover, the very small asymmetry parameter of ~ 0.1 (see Table 2) used to simulate both the quadrupolar patterns QB and QA is a hint to a high local symmetry for aluminum atoms in the above-mentioned nonequivalent local structures. The relative intensity of 15% corresponding to the molar fraction of framework aluminum atoms coordinated to organic ABDC linkers is very similar to the molar fraction of 10% ABDC utilized as organic linkers in the synthesis mixture. A much smaller molar fraction of the QB quadrupolar pattern for the dehydrated mixed linker MIL-53(Al) with 50% of BDC replaced by ABDC was observed in Figure 2b. However, in the case of the spectra shown in Figure 2c, the molar fractions of the QB quadrupolar pattern were too low to be detectable.

Upon rehydration of the mixed linker MOFs (Figure 2a–c, top), the ^{27}Al MAS NMR spectra consist of the same signals of octahedrally coordinated aluminum species characterized by isotropic chemical shifts of $\delta_{27\text{Al}} = 1.9$, 1.7, and 1.4 ppm for the materials with 10, 50, and 90% of BDC replaced by ABDC in the mixed linker MIL-53(Al), respectively. It seems that the introduction of amine groups influences only slightly the isotropic chemical shift of the framework aluminum atoms in the rehydrated samples. However, the quadrupole coupling constants were found to significantly increase from ~ 7 to 10 MHz. This finding reflects a strong strain of the $\text{AlO}_4(\text{OH})_2$ octahedra in the mixed linker MOFs upon rehydration.

In the dehydrated state, the corner-sharing AlO_6 octahedra, which coordinate four oxygen atoms of organic linkers and two OH groups, exhibit a high local symmetry in the x – y

plane, as indicated by the low asymmetry parameters η_Q . The experimentally obtained η_Q values do not depend on the content of amine groups in the organic linkers. On the other hand, with an increase of the molar fractions of $-\text{NH}_2$ groups, the ALOH signals shifted to higher chemical fields. Upon rehydration of the dehydrated mixed linker MOFs, the formation of $\text{O}(\text{w})-\text{H}\cdots\text{O}$ hydrogen bonds of water molecules to carboxylic oxygen atoms caused a decrease of the symmetry in the local structure of the framework aluminum atoms, as indicated by the increased quadrupole coupling constant.

In this work, ^1H and ^{27}Al MAS NMR spectroscopy was successfully applied for investigating the effect of dehydration on the local structure of framework aluminum atoms in the mixed linker MIL-53(Al) materials with increasing amounts of functional amine groups. The mixed linker MOFs were prepared by using mixtures of BDC and ABDC as organic linker molecules in the synthesis. ^1H MAS NMR spectroscopy of the dehydrated materials allowed the determination of the actual molar fractions of organic ABDC linkers in the obtained mixed linker MOFs via determination of the relative intensity of the signal of $-\text{NH}_2$ groups at 5.6 ppm. With increasing ABDC content in the dehydrated mixed linker MIL-53(Al) materials, the ^1H MAS NMR signal of ALOH groups shifts to higher magnetic field from 2.6 to 2.1 ppm. The ^{27}Al MAS NMR signals of framework aluminum atoms in the dehydrated materials indicate that the functionalization by amine groups leads to a more homogeneous charge distribution in their local structure, corresponding to a decrease of the quadrupole coupling constant by ~ 1 MHz.

Upon rehydration of the dehydrated MOFs, the physisorbed water molecules form hydrogen bonds to neighboring carboxylic oxygen atoms with O–O distances of 0.33–0.34 nm responsible for the experimentally observed ^1H MAS NMR signal at 3.0 ppm. In the presence of water, the framework aluminum atoms experience a lowering of their local symmetry in comparison with the dehydrated state, corresponding to an increase of the quadrupole coupling constant from ~ 7 to 10 MHz.

SUPPORTING INFORMATION AVAILABLE Experimental details of the preparation of MIL-53(Al) as well as a description of the dehydration and rehydration experiments, parameters of the NMR measurements, and the corresponding data evaluation. Additional ^1H and ^{27}Al MAS NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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