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Structure of Framework Aluminum Lewis Sites and Perturbed Aluminum Atoms in Zeolites as Determined by ^{27}Al{^{1}H} REDOR (3Q) MAS NMR Spectroscopy and DFT/Molecular Mechanics**

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Abstract: *Zeolites are highly important heterogeneous catalysts. Besides Brønsted SiOHAl acid sites, also framework* Al_{FR} *Lewis acid sites are often found in their H-forms. The formation of* Al_{FR} *Lewis sites in zeolites is a key issue regarding their selectivity in acid-catalyzed reactions. The local structures of* Al_{FR} *Lewis sites in dehydrated zeolites and their precursors—"perturbed"* Al_{FR} *atoms in hydrated zeolites—were studied by high-resolution MAS NMR and FTIR spectroscopy and DFT/MM calculations. Perturbed framework Al atoms correspond to* $(SiO)_3AlOH$ *groups and are characterized by a broad* ^{27}*Al NMR resonance* ($\delta_i = 59$–62 *ppm,* $C_Q = 5$ *MHz, and* $\eta = 0.3$–0.4) *with a shoulder at 40 ppm in the* ^{27}*Al MAS NMR spectrum. Dehydroxylation of* $(SiO)_3AlOH$ *occurs at mild temperatures and leads to the formation of* Al_{FR} *Lewis sites tricoordinated to the zeolite framework. Al atoms of these* $(SiO)_3Al$ *Lewis sites exhibit an extremely broad* ^{27}*Al NMR resonance* ($\delta_i \approx 67$ *ppm,* $C_Q \approx 20$ *MHz, and* $\eta \approx 0.1$).

Zeolites are crystalline microporous aluminosilicates made of corner-sharing TO_4 tetrahedra ($T = Si, Al^-$). Protons and metal cations balance the charge of framework AlO_4^- tetrahedra. H-forms of zeolites are widely used industrial heterogeneous acid catalysts applied in oil processing, petrochemistry, and the production of fine chemicals. Besides Brønsted acid SiOHAl groups formed by protons compensating tetrahedral AlO_4^-, also electron-pair-acceptor Lewis sites related to framework (Al_{FR}) and extraframework (Al_{EF}) atoms are often present in zeolite catalysts.[1] The detailed structure and origin of Al Lewis sites are not clear despite their importance, since these sites affect the selectivity of transformations of hydrocarbons and cause the formation of undesired polyaromatic deposits. Besides tetrahedral Al_{FR} (^{27}Al NMR resonances at 50–60 ppm), octahedral Al_{EF} (between -10 and 5 ppm), pentacoordinated Al_{EF} (around 30 ppm), and some "NMR-invisible" Al_{EF} atoms with highly distorted coordination, most zeolites (namely, those of industrial provenance) also contain "perturbed" Al_{FR} atoms reflected in a broad shoulder at around 40 ppm in the ^{27}Al MAS NMR spectra of hydrated samples (see Figures 1 and 2 as well as the Supporting Information).[2]

There is an ongoing discussion regarding the presence, structure, and origin of Al Lewis sites created in catalytic processes performed over dehydrated H-zeolites at high temperatures and under an atmosphere without any water vapor. IR spectroscopy with adsorbed bases provided only indirect evidence of the formation of both Al_{FR} and Al_{EF} Lewis sites in various zeolite structures.[2b,3] Only a K-edge XAS study indicated the presence of a low amount (10 % of Al at 700 °C) of tricoordinated Al_{FR} attributable to Al_{FR} Lewis sites in dehydrated β-zeolites.[4] The formation of Al_{EF} atoms can be prevented by zeolite synthesis under appropriate conditions and further processing. However, there is very little knowledge regarding the local structure of Al_{FR} Lewis sites and the mechanism of their creation. The development of high-resolution solid-state NMR spectroscopy and the ability to carry out reliable DFT/molecular-mechanics (MM) calculations that enable interpretation of the results of NMR spectroscopic experiments opened a route for the structural analysis of perturbed framework Al atoms and the corresponding Al Lewis sites.

^{27}Al{^{1}H} REDOR (rotational-echo double-resonance) 3Q MAS, ^{27}Al 3Q MAS, and ^{27}Al{^{1}H} CP 3Q MAS (cross-polarization triple-quantum magic-angle-spinning) NMR spectroscopic experiments on zeolites with the FER and CHA structures (which do not contain Al_{EF} atoms), coupled with DFT/MM calculations of the model Si-rich CHA structure and FTIR spectroscopic measurements of H-FER, show that "perturbed" Al_{FR} atoms in hydrated zeolites and zeolites dehydrated at 300 °C correspond to terminal tetrahedral $(SiO)_3AlOH$ entities tricoordinated to the zeolite frame-

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work. The presence of these atoms is reflected by a broad resonance with an isotropic chemical shift $\delta_i = 59$–62 ppm, $C_Q = 5$ MHz, and $\eta = 0.3$–0.4. The O−H stretching mode of $(SiO)_3AlOH$ in the IR spectrum lies at 3655 cm^{-1}, and the ^{1}H chemical shift of the corresponding hydrogen atom is 1.6 ppm. Both of these values are similar to those already suggested for extraframework AlOH species.

The dehydroxylation of AlOH, followed by the formation of Al_{FR} Lewis sites, occurs upon heating the samples at high temperature (above 350 °C), as evidenced by FTIR spectroscopy of [D$_3$]acetonitrile adsorbed on the zeolite. The structure of the Al_{FR} Lewis sites with the Al_{FR} atoms tricoordinated to the zeolite framework was suggested by the results of 1) the ^{27}Al{^{1}H} REDOR experiments on H-FER (extremely broad ^{27}Al NMR resonance with $\delta \approx 67$ ppm, $C_Q \approx 20$ MHz, and $\eta \approx 0.1$), 2) DFT/MM modeling, and 3) FTIR spectroscopy of adsorbed [D$_3$]acetonitrile at the Al_{FR} Lewis sites.

^{27}Al MAS NMR spectra of Na-FER/A-hy and Na-FER/B-hy exhibited only one resonance typically observed for tetrahedrally coordinated Al in the framework, and not the broad resonance indicative of perturbed Al atoms that was observed for Na-FER/C-hy (see the Supporting Information). The ^{27}Al{^{1}H} REDOR 3Q MAS NMR and ^{27}Al 3Q MAS NMR spectra for hydrated Na-FER/C-hy and Ca-CHA zeolites are compared in Figures 1 and 2. Both zeolites exhibited two ^{27}Al resonances. The first is the high-intensity central resonance of the tetrahedral Al_{FR} atoms in CHA ($\delta_i = 55.8$ ppm, C_Q (quadrupolar splitting) = 2.8 MHz) and FER ($\delta_i = 59.0$ ppm, $C_Q = 2.3$ MHz).[5] This signal is unaffected by {^{1}H} REDOR dipolar dephasing, as Al_{FR} atoms are balanced by solvated mobile extraframework cations surrounded by water molecules. The second is the broad resonance of the "perturbed" Al atoms reflected in the ^{27}Al MAS NMR spectrum as a shoulder around 40 ppm overlapping with the intense narrow resonance of Al_{FR} atoms (Figures 1 and 2; see also the Supporting Information and Ref. [2a]). The broad resonance is of low intensity, asymmetrical, and elongated along the anisotropy axis, with the second-order C_Q value ranging up to 5.5 MHz, thus indicating a considerably larger electric-field gradient as compared to that of the Al_{FR} atoms. Moreover, the complete suppression of the broad resonance by {^{1}H} REDOR dephasing clearly indicates strong dipolar interactions between the perturbed Al_{FR} atoms and the neighboring protons, which are significantly immobilized by chemical bonds. Their strong mutual interaction is confirmed by a marked relative increase in their signal in the ^{27}Al{^{1}H} CP 3Q MAS NMR spectrum owing to a strong dipolar coupling (Figures 1 and 2). The NMR spectroscopic parameters obtained for the "perturbed" Al_{FR} atoms by the simulation of ^{27}Al 3Q MAS NMR spectra are listed in Table 1.

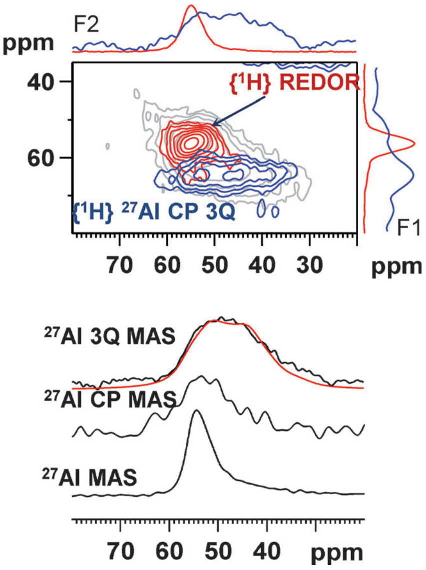

Figure 1. Top: ^{27}Al 3Q (black), ^{27}Al{^{1}H} REDOR 3Q (red), and ^{27}Al{^{1}H} CP 3Q MAS NMR spectra (blue) and the F1 and F2 projections of the hydrated Na-FER/C-hy zeolite; bottom: ^{27}Al MAS and ^{27}Al CP MAS NMR spectra of the hydrated Na-FER/C-hy zeolite, and a slice of the ^{27}Al 3Q MAS NMR spectrum at F1 = 68 ppm (black) and its simulation (red).

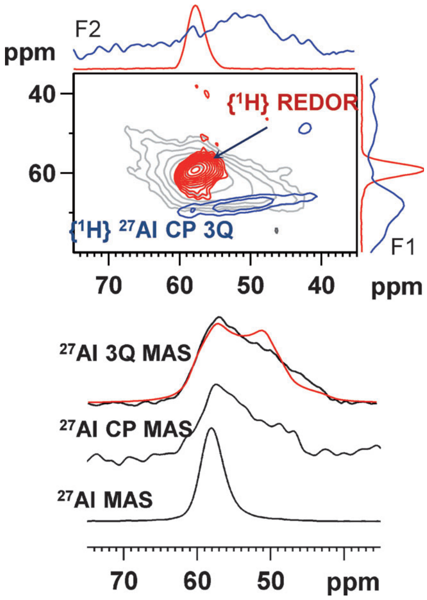

Figure 2. Top: ^{27}Al 3Q (black), ^{27}Al{^{1}H} REDOR 3Q (red), and ^{27}Al{^{1}H} CP 3Q MAS NMR spectra (blue) and the F1 and F2 projections of the hydrated Ca-CHA zeolite; bottom: ^{27}Al MAS and ^{27}Al CP MAS NMR spectra of the hydrated Ca-CHA zeolite, and a slice of the ^{27}Al 3Q MAS NMR spectrum at F1 = 69 ppm (black) and its simulation (red).

Values of δ_i of around 60 ppm are typical for AlO_4^- tetrahedra in a zeolite environment.[6] The significant broad-

Table 1: ^{27}Al NMR spectroscopic parameters of perturbed Al_{FR} atoms and Al atoms of Al_{FR} Lewis sites in Na- and H-FER/C and Ca-CHA zeolites, and calculated ^{27}Al NMR spectroscopic parameters of $(SiO)_3AlOH$ and $(SiO)_3Al$ atoms in CHA.

Sample	Perturbed Al_{FR}			Al_{FR} Lewis sites		
	δ_i [ppm]	C_Q [MHz]	η	δ_i [ppm]	C_Q [MHz]	η
Na-FER/C-hy	58.9	5.3	0.38			
H-FER/C-300	58.9	5.3	0.38			
H-FER/C-450				67	20	0.1
Ca-CHA	62.4	4.8	0.30			
calculation	66.9	4.1	0.32	75	35	0.1

ening of the NMR resonance reveals negligible mobility of the Al species immobilized in the zeolite framework. Conversely, the tetrahedral Al_{EF} species formed during zeolite desilication in alkaline media are mobile and therefore exhibit a narrow symmetrical signal,[7] and Al_{EF} species created upon steaming show an octahedral Al signal or are NMR-invisible.[8] Thus, a terminal $(SiO)_3AlOH$ group, an analogue of silanol groups well-known in zeolites,[9] could explain the nature of the "perturbed" Al_{FR} atoms. We calculated the NMR spectroscopic parameters of $(SiO)_3AlOH$ in the model of the Si-rich CHA by using the QMPOT approach in analogy with our calculations for SiOH in zeolites[5a] to verify this assumption. The sound agreement between the computed and experimental values of δ_i, C_Q, and η of Al in $(SiO)_3AlOH$ in CHA and FER (Table 1) confirms the attribution of the perturbed Al_{FR} atoms to terminal $(SiO)_3AlOH$ species (Figure 3). This assignment is supported by the presence of the IR vibration at 3655 cm^{-1} assigned to the O–H stretching mode of terminal $(SiO)_3AlOH$ in the spectrum of H-FER/C-300 dehydrated at 300 °C (see the Supporting Information).

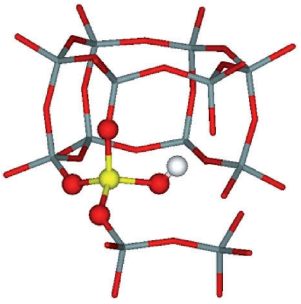

Figure 3. Structure of a terminal $(SiO)_3AlOH$ group in the CHA zeolite with the atoms corresponding to O_3AlOH displayed as balls. Silicon atoms are gray, the aluminum atom is yellow, oxygen atoms are red, and the hydrogen atom is white.

This IR band was suggested to belong to extraframework AlOH species, the presence of which is also often reflected in ^{27}Al MAS NMR spectra.[10] ^{27}Al (3Q) MAS (Figure 4) and ^{1}H MAS NMR spectroscopic experiments (see the Supporting Information) were carried out on the H-FER/C-300 sample, which was dehydrated under the same conditions as those used for the sample examined in the FTIR experiment, to confirm the assignment of the IR band at 3655 cm^{-1} to framework AlOH species. The ^{27}Al MAS NMR spectra of dehydrated H-FER/C-300 exhibited four ^{27}Al resonances (three of which were also observed in the ^{27}Al 3Q MAS NMR spectrum): a narrow peak due to tetrahedral framework Al atoms (Al^{IV}_1 with $\delta_i = 56$ ppm, $C_Q = 3.5$ MHz, and $\eta = 0.5$, 67 % of Al); a broad resonance due to framework tetrahedral $(SiO)_3AlOH$ groups (Al^{IV}_2 with $\delta_i = 58.9$ ppm, $C_Q = 5.3$ MHz, and $\eta = 0.38$, 1.6 % of Al); a signal attributable to extraframework pentacoordinated Al species (Al^{V} with $\delta_i = 26$ ppm, $C_Q = 1.7$ MHz, and $\eta = 1.0$, 0.4 % of Al); and an extremely broad resonance, which has not been described previously and which was attributed to trigonal framework Al atoms ($\delta_i = 65$ ppm, $C_Q = 20$ MHz, and $\eta = 0.1$, 31 % of Al; see details below). The ^{1}H MAS NMR spectrum of the dehydrated H-FER/C-300 sample (see the Supporting Information) showed, besides resonances of silanols (at 0.8 ppm) and bridging AlOHSi groups (at 3.3 and 5.9 ppm), also a signal at 1.6 ppm, which was previously assigned to extraframework AlOH species.[11] However, our ^{27}Al (3Q) MAS NMR spectroscopic experiments revealed only negligible dealumination of the dehydrated H-FER/C-300 sample (up to 0.4 % of Al). Therefore, the ^{1}H NMR resonance at 1.6 ppm and the IR band at 3655 cm^{-1} correspond to both framework tetrahedral $(SiO)_3AlOH$ groups and OH groups of extraframework Al species, and they cannot be distinguished from each other.

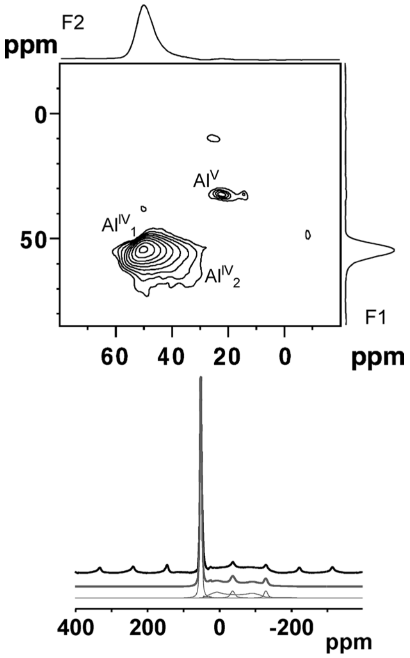

Figure 4. Top: ^{27}Al 3Q MAS NMR spectrum with the F1 and F2 projections of the H-FER/C-300 zeolite dehydrated at 300 °C; bottom: ^{27}Al MAS NMR single-pulse spectrum of the H-FER/C-300 zeolite dehydrated at 300 °C with its simulation and individual components.

Our DFT/MM calculations also show that the proton in $(SiO)_3AlOH$ species is strongly bound to the oxygen atom, since $Al_{FR}O_4$ possesses a negative charge of -1. Unlike the proton of SiOHAl groups, it is not replaced by cations during metal–ion exchange. Note that the analysis of $(SiO)_3AlOH$ by ^{29}Si MAS NMR spectroscopy is significantly limited by the only 25 % difference in the intensity between the Si(3 Si,1 Al) and Si(3 Si,1 AlOH) NMR signals.[12] Also, the application of ^{27}Al single-pulse MAS NMR spectroscopy considerably underestimates the concentration of $(SiO)_3AlOH$ groups owing to the overlap of their resonance with that of the framework Al atoms.

We propose that $(SiO)_3AlOH$ entities of hydrated zeolites are precursors for the formation of Al_{FR} Lewis sites in H-zeolites upon high-temperature treatment. The concentrations of Brønsted acid SiOHAl sites and Al_{FR} Lewis sites in dehydrated H-FER/C-450 (the sample containing perturbed Al_{FR} atoms that was dehydrated at 450 °C) were compared with those in H-FER/A-450 and H-FER/B-450, which

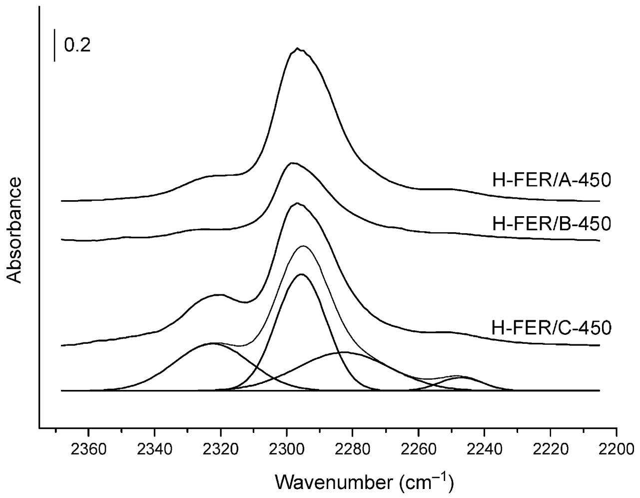

Figure 5. FTIR spectra of [D$_3$]acetonitrile adsorbed on the H-FER/A-450, H-FER/B-450, and H-FER/C-450 samples dehydrated at 450 °C, with simulated H-FER/C spectra.

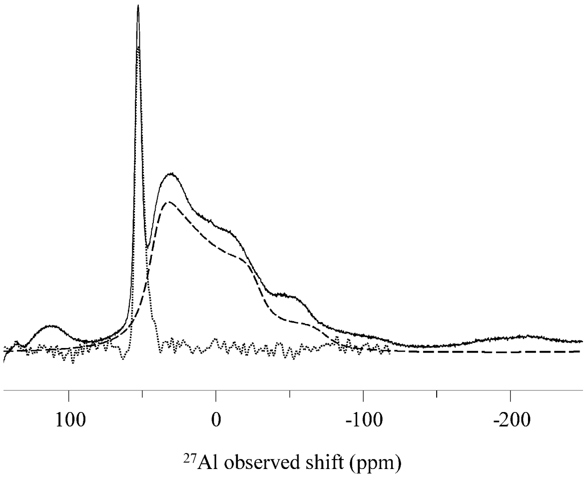

Figure 6. ^{27}Al MAS NMR spectra of dehydrated H-FER/B-450 (dotted line) and H-FER/C-450 (solid line), and simulation of the H-FER/C spectrum (dashed line).

exhibited exclusively tetrahedrally coordinated Al_{FR} atoms; note that H-CHA is not a stable structure. FTIR spectra of adsorbed CD_3CN on the FER/A–C-450 samples dehydrated at 450 °C and simulated spectra are shown in Figure 5. The bands at 2323, 2296, 2282, and 2252 cm^{-1} correspond to C≡N interaction with the Al_{FR} Lewis sites, SiOHAl, residual Na^+ ions, and physisorbed CD_3CN, respectively.[13] The formation of a low concentration of Al Lewis sites in H-FER/A-450 and H-FER/B-450, which do not contain $(SiO)_3AlOH$ in the hydrated state, is explained by the partial dehydroxylation of two Brønsted SiOHAl groups[13,14] (see Table 2).

Table 2: Concentration of Al Lewis sites (L) and Brønsted SiOHAl sites (B) in dehydrated H-FER at 450 °C from FTIR spectra of adsorbed CD_3CN at room temperature.

Sample	L[a]	B[a]	L/(L+B)	Al[a]	2L+B[a]
H-FER/A-450	0.18	1.21	0.13	1.75	1.57
H-FER/B-450	0.04	0.34	0.11	0.60	0.42
H-FER/C-450	0.35	0.97	0.27	1.75	1.67

[a] The values are given in mmol g^{-1}.

Substantially greater formation of Al_{FR} Lewis sites in the dehydrated H-FER/C-450 is coupled with the presence of $(SiO)_3AlOH$ groups and their dehydroxylation to $(SiO)_3Al$. Both mechanisms of formation of Al_{FR} Lewis sites are supported by the mass balance close to $B+2L=Al_{FR}$. The tricoordinated framework $(SiO)_3Al$ atoms serve as the Al_{FR} Lewis electron-pair-acceptor sites in the zeolite. To confirm this suggestion, we calculated the ^{27}Al NMR parameters of $(SiO)_3Al$ in the Si-rich CHA model and compared them with the experimental values for the dehydrated H-FER/C-450 sample (Table 1). The marked broadening of the ^{27}Al NMR signal of $(SiO)_3Al$ can be overcome by an increase in the intensity of the excitation field (700 MHz) and an increase in acquisition time (1 day). The ^{27}Al MAS NMR spectrum of the dehydrated H-FER/B-450 sample exhibited one ^{27}Al resonance corresponding to Al_{FR} ($\delta_i = 56$ ppm, $C_Q = 3.5$ MHz, and $\eta = 0.5$; Figure 6).

In contrast, besides the Al_{FR} resonance, the spectrum of the dehydrated H-FER/C-450 sample also contained a very broad signal with $\delta_i = 67$ ppm, $C_Q = 20$ MHz, and $\eta = 0.1$ (Figure 6 and Table 1). Taking into the account the difference between the model for the calculation of Al_{FR} Lewis sites (CHA structure, Si/Al 35) and the investigated sample (H-FER, Si/Al 10) as well as the inaccuracy of the estimation of the NMR parameters of an extremely broad signal, the experimental data fit well with the theoretical prediction. Thus, the broad resonance in the ^{27}Al MAS NMR spectrum of dehydrated H-FER/C-450 can be attributed to the Al_{FR} Lewis sites. The Al atom of the $(SiO)_3Al$ structure of the Al_{FR} Lewis sites is tricoordinated to the framework, exhibits threefold symmetry, and is located on the top of a nearly flat trigonal pyramid with a base of framework oxygen atoms (Figure 7).

The structure of $(SiO)_3Al$ Al_{FR} Lewis sites, formed predominantly by the dehydroxylation of $(SiO)_3AlOH$ precursors at mild temperatures, also serves as a reasonable model for the dehydroxylation of more stable Brønsted SiOHAl groups in H-zeolites at high temperature. To prevent the formation of Al_{FR} Lewis sites in H-zeolites dehydrated at

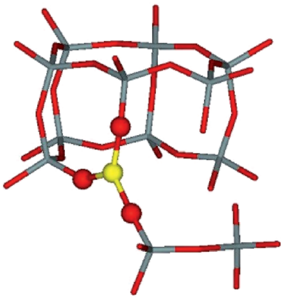

Figure 7. Structure of $(SiO)_3Al$ at the Al_{FR} Lewis sites in the CHA zeolite with the atoms corresponding to O_3Al displayed as balls. Silicon atoms are gray, the aluminum atom is yellow, and oxygen atoms are red.

mild temperatures, the formation of defective terminal $(SiO)_3AlOH$ groups should be, if not excluded, at least minimized during the synthesis of the zeolite.

Experimental Section

A FER/A zeolite (Si/Al 8.5:1; Tosoh Corporation), a FER/B zeolite (Si/Al 27:1; Zeolyst International, Inc.), a FER/C zeolite (Si/Al 8.5:1; UNIPETROL, a.s., Czech Republic), and a CHA zeolite (Si/Al 2.4:1; natural zeolite, Sebuzin, Czech Republic) were investigated by a combination of ^{27}Al MAS NMR and FTIR spectroscopy. Calculations of the local Al atom structure and the NMR spectroscopic parameters on the basis of a model of Si-rich CHA (Si/Al 35:1) were performed with the QMPOT and Gaussian programs, respectively. ^{27}Al MAS NMR spectra of the hydrated zeolites and the dehydrated H-FER/C-300 sample (dehydrated at 300°C) were recorded on an 11.7 T Bruker Avance 500 WB/US spectrometer. Triple-quantum (2D) ^{27}Al 3Q MAS NMR spectra were recorded with a z-filtered three-pulse sequence with a DR 4 mm probe head; ^{27}Al{^{1}H} REDOR 3Q MAS NMR spectra were recorded with a double-resonance 3.2 mm probe head. ^{27}Al MAS NMR spectra of dehydrated H-FER/B-450 and H-FER/C-450 (dehydrated at 450°C) were recorded on a 16.4 T Bruker Avance III 700 SB NMR spectrometer with a DR 4 mm probe head. FTIR spectra of the OH groups of H-FER/B-300 and H-FER/C-300 dehydrated at 300°C and of adsorbed $[D_3]$acetonitrile on H-FER/A-450, H-FER/B-450, and FER/C-450 dehydrated at 450°C were recorded on a Nexus 670 spectrometer with a resolution of 2 cm^{-1}. For details of samples and experiments, see the Supporting Information.

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