# Effect of Al–Si–Al and Al–Si–Si–Al Pairs in the ZSM-5 Zeolite Framework on the <sup>27</sup>Al NMR Spectra. A Combined High-Resolution <sup>27</sup>Al NMR and DFT/MM Study

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The effect of the presence of Al–O–Si–O–Al and Al–O–Si–O–Si–O–Al sequences in the ZSM-5 zeolite framework on the local geometry of AlO<sub>4</sub><sup>-</sup> tetrahedra and the <sup>27</sup>Al NMR parameters was investigated employing <sup>27</sup>Al 3Q MAS NMR spectroscopy and DFT/MM calculations. The presence of an Al atom as a next-nearest (Al–O–Si–O–Al) and next-next-nearest (Al–O–Si–O–Al) neighbor can significantly affect both the local geometry of AlO<sub>4</sub><sup>-</sup> tetrahedra as well as <sup>27</sup>Al NMR isotropic chemical shift (up to 4 ppm). There is no systematic contribution of Al in Al–O–Si–O–Al or Al–O–(Si–O)<sub>2</sub>–Al chains to the <sup>27</sup>Al isotropic chemical shift, and not even the direction can be predicted without explicit DFT calculations. Our combined experimental and computational approach employing <sup>27</sup>Al (3Q) MAS NMR spectroscopy supported by DFT/ MM calculations (Sklenak, S.; Dědeček, J.; Li, C.; Wichterlová, B.; Gábová, V.; Sierka, M.; Sauer, J. *Angew. Chem., Int. Ed.* 2007, *46*, 7286.) can be employed only for ZSM-5 samples having a low or negligible concentration of Al–O–(Si–O)<sub>n</sub>–Al (n = 1 and 2) sequences in the zeolite matrix, otherwise <sup>27</sup>Al (3Q) MAS NMR spectroscopy cannot be used to even identify the number of framework T sites occupied by Al.

#### 1. Introduction

Zeolites are crystalline microporous aluminosilicates widely used as ion exchangers, adsorbents, and catalysts in industrial chemical processes. In the past 30 years, attention has been drawn to silicon-rich zeolites (Si/Al > 8) of ZSM-5 (MFI), ferrierite (FER), mordenite (MOR), and  $\beta$  (BEA) structures. The protonic forms of these zeolites are used as acid catalysts for (hydro)cracking, skeletal isomerization, and alkylation of hydrocarbons in the petrochemical industry.<sup>1,2</sup> Transition metal exchanged forms of these zeolites have been discovered as exceptional redox catalysts.<sup>3</sup> Since the protons, single metal ions, and metal-oxo complexes representing the active sites in catalytic and adsorption processes are bound to the AlO<sub>4</sub><sup>-</sup> tetrahedra, the crystallographic positions of Al and the local aluminum distribution govern the location of the active sites and their properties. Particular attention is paid to the presence of Al-O-Si-O-Al (next-nearest) and Al-O-Si-O-Si-O-Al (next-next-nearest) Si-Al sequences, so-called "Al pairs", and "single" Al atoms that are far distant from each others  $(Al-O-(Si-O)_n-Al, n > 2)$ . Al-O-Al sequences do not occur in zeolite frameworks.4-6

<sup>29</sup>Si MAS NMR experiments show that Al–O–Si–O–Al chains dominate in Al-rich zeolite materials with Si/Al  $1-3^{7-10}$  (e.g., FAU and LTA structures). Al–O–Si–O–Al pairs are reported for the ferrierite and mordenite structural types with Si/Al  $\approx 5.^{11,12}$  The concentration of Al–O–Si–O–Al chains considerably decreases as the Si/Al increases, and for Si/Al >

8 their concentration becomes negligible.<sup>11,12</sup> However, the occurrence of sequences containing Al atoms close enough to be balanced by a divalent cation in silicon-rich zeolites such as ZSM-5,  $\beta$ , mordenite, and ferrierite (having Si/Al > 8) is suggested by a high ion-exchange capacity for divalent cations of hydrated zeolites.<sup>3</sup> Most of these close Al atoms occur in cationic sites accommodating bare (coordinated exclusively to framework oxygen atoms) divalent cations in the dehydrated zeolite.<sup>13,14</sup> Several types of cationic sites (designated as the  $\alpha$ -.  $\beta$ -, and  $\gamma$ -types in refs 15–17) were suggested on the basis of X-ray diffraction studies (for mordenite and ferrierite) and on visible spectra of d-d transitions of the exchanged Co(II) ions (for ZSM-5 and  $\beta$  frameworks).<sup>3,16-18</sup> Figure 1 shows the structure of the cationic sites for divalent cations in ZSM-5 frameworks. For ZSM-5, the  $\alpha$  and  $\beta$  types of cationic sites highly prevail<sup>13-15</sup> (>85%), and they contain Al-O-(Si-O)<sub>2</sub>-Al sequences located in the six-membered rings. It has been shown that the presence of  $AI-O-(Si-O)_2$ -Al pairs in ZSM-5 frameworks strongly depends on both the concentration of aluminum in the framework and the conditions of zeolite synthesis.13,14,19

Recent studies indicate that the presence of Al–O– (Si–O)<sub>2</sub>–Al sequences and single Al atoms in the zeolite framework can considerably affect the activity of zeolite-based catalysts.<sup>20–22</sup> To shed further light on the effects of Al distribution in the framework on the properties and activity of zeolite catalysts, the knowledge of the Al siting as well as the location of various Al–O–(Si–O)<sub>n</sub>–Al sequences in the zeolite framework is necessary. Recently, a combination of <sup>27</sup>Al (3Q) MAS NMR spectroscopy with calculations of the <sup>27</sup>Al isotropic chemical shifts using a quantum mechanics-molecular mechanics hybrid approach (QM-Pot) was examined for ZSM-5.<sup>23</sup> This methodology allowed a partial identification of the Al sites and

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**Figure 1.** Structures of the  $\alpha$  (a1) and  $\beta$  (a2) sites of ZSM-5 and the corresponding five coordination shell clusters (b1-b5). Clusters of the  $\alpha$  sites are formed by (b1) Al(T2)-O-(Si-O)\_2-Al(T23) and (b2) Al(T8)-O-(Si-O)\_2-Al(T17). Clusters of the  $\beta$  sites are formed by (b3) Al(T17)-O-(Si-O)\_2-Al(T23), (b4) Al(T7)-O-(Si-O)\_2-Al(T1), and (b5) Al(T16)-O-(Si-O)\_2-Al(T22). The atoms corresponding to the  $\alpha$  and  $\beta$  sites are in yellow; the Al atoms are displayed as balls. Silicon atoms are in gray, oxygen atoms in red, and link hydrogen atoms in white.

their variability in ZSM-5 samples synthesized by various procedures.<sup>23</sup> However, the described approach was intentionally applied only to ZSM-5 samples having a low content of the framework Al and a negligible or low concentration of  $Al-O-(Si-O)_n-Al$  (n = 1, 2) sequences.

In this article, we make use of our combined approach<sup>23</sup> to investigate the effect of an Al atom as a next-nearest and nextnext-nearest neighbor on the local structure and the <sup>27</sup>Al isotropic chemical shift of  $AlO_4^-$  sites. One of the aims of our study is to find out whether there is a systematic <sup>27</sup>Al isotropic chemical shift contribution (similar to that for <sup>29</sup>Si NMR<sup>7-10</sup>) due to the presence of neighboring Al atoms (Al–O–(Si–O)<sub>n</sub>–Al, n =1 and 2 sequences) and if this can be used to assist assignments of Al isotropic chemical shifts to individual sites even for samples containing such sequences of neighboring Al atoms.

# 2. Experimental Section

**2.1. Sample Preparation.** Two commercial Na-ZSM-5/1 and NH<sub>4</sub>-ZSM-5/2 samples with Si/Al ratio 14.1 and 12.5, respectively, were kindly provided by the Institute of Hydrocarbon Gases, Slovnaft Inc. and purchased from TOSOH Co., respectively. Such ZSM-5 zeolites represent commonly used materials for catalytic applications. A ZSM-5 sample (ZSM-5/3) with an

unusually high concentration of aluminum (Si/Al 8.1) in the framework was employed to study the effect of Al-O-Si-O-Al sequences on the local AlO<sub>4</sub><sup>-</sup> geometry. ZSM-5/3 was compared with ZSM-5/4 (Si/Al 15.0, sample E in our previous NMR study<sup>23</sup>) since both samples were synthesized using the same procedure, but with a different Al concentration in the synthesis gel. The ZSM-5/3 and ZSM-5/4 samples were prepared at hydrothermal conditions and autogenous pressure with agitation at temperature of 170 °C. AlCl<sub>3</sub> served as aluminum, tetraethylorthosilicate as silicon, and NaOH as sodium sources. Tetrapropylammonium hydroxide was used as the structure directing agent. The calcined NH<sub>4</sub>-ZSM-5/2, ZSM-5/3, and ZSM-5/4 samples were ion exchanged with 0.5 M NaCl to obtain fully exchanged Na-ZSM-5. The samples were thoroughly washed and then equilibrated on open air at room temperature for several days to guarantee their full hydration for <sup>27</sup>Al NMR measurements. A part of the Na-ZSM-5/3 sample was ion exchanged with 1.0 M NH<sub>4</sub>NO<sub>3</sub> and subsequently deamonized in an oxygen stream at 450 °C to get H-ZSM-5/3. This sample was subsequently washed on a filter and equilibrated on open air at ambient temperature. An ion exchange of the Na-ZSM-5 samples with 0.05 M Co(NO<sub>3</sub>)<sub>2</sub> at ambient temperature led to samples loaded with the maximum  $[Co^{2+}(H_2O)_6]^{2+}$  ions without

TABLE 1: Chemical Composition of ZSM-5 Samples (Si/Al), Framework Si/Al<sub>FR</sub> from <sup>29</sup>Si MAS NMR, and Exchange Capacity for  $[Co^{2+}(H_2O)_6]^{2+}$  Ions  $(Co_{MAX}/Al)$ 

sample	Si/Al	Si/Al <sub>FR</sub>	Na/Al	Co <sub>MAX</sub> /Al <sup>a</sup>	Al-O-Si-O-Al <sup>b</sup>	Al-O-(Si-O) <sub>2</sub> -Al <sup>c</sup>
Na-ZSM-5/1	14.1	14	1.01	0.42	0	84
Na-ZSM-5/2	12.5	12	0.98	0.38	0	76
Na-ZSM-5/3	8.1	8-8.5	0.82	0.08	>80	16
NH <sub>4</sub> -ZSM-5/3	8.1	8-8.5	< 0.01		>80	16
Na-ZSM-5/4 <sup>d</sup>	15.0	15	1.01	0.12	0	24

<sup>*a*</sup> Values for CoNa-ZSM-5. <sup>*b*</sup> Al in Al–O–Si–O–Al pairs (rel %) determined from <sup>29</sup>Si NMR. <sup>*c*</sup> Al in Al–O–(Si–O)<sub>2</sub>–Al pairs (rel %) determined from (Co<sub>MAX</sub>/Al). <sup>*d*</sup> Sample E in our previous study.<sup>23</sup>



Figure 2. 2D plot of the <sup>27</sup>Al 3Q MAS NMR sheared spectrum of Na-ZSM-5/1 (a), Na-ZSM-5/2 (b), Na-ZSM-5/3 (c), and Na-ZSM-5/4 (d), F1 projections of the spectra and selected normalized slices and projection and slice simulations.

the presence of Co $-OH^+$  species, both evidenced by vis spectroscopy. The chemical composition of the Na-, NH<sub>4</sub>-, and Co-ZSM-5 zeolites and the  $[Co^{2+}(H_2O)_6]^{2+}$  ion-exchange capacity are given in Table 1.

XRD, KBr-FTIR, and SEM indicated good crystallinity of the calcined Na<sup>+</sup> ion-exchanged samples. Moreover, <sup>27</sup>Al and <sup>29</sup>Si NMR showed a negligible amount of extra-framework Al atoms (<3%). The slightly lower Na/Al value for Na-ZSM-5/3 might indicate special restrictions of some Al atoms to be balanced by hydrated Na<sup>+</sup> ions.

**2.2. MAS NMR Spectroscopy.** <sup>29</sup>Si and <sup>27</sup>Al MAS NMR and <sup>27</sup>Al 3Q MAS NMR experiments were carried out on a Bruker Avance 500 MHz (11.7 T) Wide Bore spectrometer using 4-mm o.d. ZrO<sub>2</sub> rotors with a rotation speed of 5 kHz for <sup>29</sup>Si MAS NMR and 12 kHz for <sup>27</sup>Al MAS NMR. A <sup>29</sup>Si MAS NMR high-power decoupling experiment with the  $\pi/6$  (1.7  $\mu$ s) excitation pulse and the relaxation delay of 30 s was applied to collect a single pulse spectrum. The chemical shifts were referenced to Q8M8. The content of the framework aluminum (Si/Al<sub>FR</sub>) was estimated from the <sup>29</sup>Si NMR data (Table 1).

To allow a quantitative evolution of the <sup>27</sup>Al MAS NMR spectra, high-power decoupling pulse sequences with  $\pi/12$  (0.7

 $\mu$ s) excitation pulse were applied. The isotropic chemical shifts were referenced to the aqueous solution of Al(NO<sub>3</sub>)<sub>3</sub>. Twodimensional multiquantum experiments (2D 3Q) were used to determine the <sup>27</sup>Al isotropic chemical shift,  $\delta_{iso}$  <sup>27</sup>Al. The 3Q experiments were performed using the z-filtered procedure. A  $\pi$  pulse was used for the excitation and a  $\pi/3$  pulse for the conversion. The pulses were individually optimized for each sample. The 2D contour plots presented in Figure 2 are the results of a 2D Fourier transformation followed by a shearing transformation. The isotropic chemical shift was estimated using

$$\delta_{\rm iso} = (17\delta_{\rm F1} + 10\delta_{\rm F2})/27$$

where  $\delta_{F1}$  is the chemical shift in the isotropic and  $\delta_{F2}$  is the observed dimension obtained from the spectra simulations. The <sup>27</sup>Al 3Q MAS NMR spectroscopy of silicon-rich zeolites is discussed by van Bokhoven et al.<sup>24</sup> and Sarv et al.,<sup>25</sup> and the 3Q MAS NMR technique is explained in detail by Alemany.<sup>26</sup>

# 3. Experimental Results

**3.1.** <sup>29</sup>Si MAS NMR Spectra of Zeolites. The <sup>29</sup>Si MAS NMR spectra of the investigated samples are shown in Figure



Figure 3.  $^{29}$ Si MAS NMR spectra of Na-ZSM-5/1 (a), Na-ZSM-5/2 (b), Na-ZSM-5/3 (c), and Na-ZSM-5/4 (d).



**Figure 4.** <sup>29</sup>Si MAS NMR spectrum of Na-ZSM-5/3 (-), spectrum simulation (- -), and individual Gaussian bands of the spectrum simulation (...).

3. The spectra of Na-ZSM-5/1 (a), Na-ZSM-5/2 (b), and Na-ZSM-5/4 (d) are similar to those reported previously for ZSM-5 zeolites.<sup>23,27,28</sup> Thus, the obtained resonances above -110 ppm were assigned to Si(4Si) sites. The bands between -103 and -108 ppm correspond to Si(3Si,1Al) sites (i.e., Si atoms with one neighboring Al atom). Resonances with chemical shifts below -100 ppm representing Si(2Si,2Al) sites with two Al neighbors were not observed for ZSM-5/1, 2, and 4. On the other hand, the spectrum of Na-ZSM-5/3 (c) significantly differs. Figure 4 shows it in detail. Two new signals below -100 ppm centered at -99 and -94 ppm, which can be assigned to Si(2Si,2Al) and Si(1Si,3Al) sites, were found. The resonances above -110 as well as between -103 and -108 ppm correspond well to those observed in the spectra of Na-ZSM-5/1, Na-ZSM-5/2, and Na-ZSM-5/4 therefore can be assigned to Si(4Si) and Si(3Si,1Al) sites, respectively.

The silicon-to-framework aluminum ratio (Si/Al<sub>FR</sub>; Table 1) of the samples was estimated  $using^{29}$ 

$$\mathrm{Si}/\mathrm{Al}_{\mathrm{FR}} = I/\sum 0.25 n I_n$$

where *I* denotes the total intensity of the <sup>29</sup>Si NMR signal in the single pulse experiment and  $I_n$  denotes the intensity of the NMR signal corresponding to the Si(4-*n*Si,*n*Al) atoms. In ZSM-5/1, 2, and 4, only Si(3Si,1Al) atoms were observed. On the other hand, in the case of ZSM-5/3 the assignment of both resonances at -99 and -94 ppm to Si(2Si,2Al) sites gives reasonable agreement between the Si/Al 8.1 (chemical analysis) and Si/Al<sub>FR</sub> 8.5. Nevertheless, the attribution of the resonance at -94 ppm to Si(1Si,3Al) sites yields also good agreement (Si/Al<sub>FR</sub> 8.0) with the value from chemical analysis. Thus, Si(2Si,2Al) and Si(3Si,1Al) atoms are present and Si(1Si,3Al) might exist in this sample.

The values of Si/Al<sub>FR</sub> for all four ZSM-5 samples correspond well to the Si/Al values obtained from chemical analysis. This fact clearly shows that extra-framework Al atoms are not present in any of the samples including ZSM-5/3 with an extremely high concentration of Al. Note that such unusually "Al-rich" ZSM-5 sample has already been reported by Fyfe et al.,<sup>28</sup> and it exhibits a stable structure even after its calcination. Mutinaite,<sup>30,31</sup> which is the natural analogue of ZSM-5, has a very high Si/Al value of 7.6 as well.<sup>30,31</sup>

In addition, the correspondence of Si/Al<sub>FR</sub> and Si/Al values shows that the concentration of silanol OH groups Si(3Si,1OH) in the ZSM-5/1–4 samples is low. This is further supported by the results of <sup>29</sup>Si MAS NMR cross-polarization experiments that show very low efficiency of the transfer of magnetization from proton to <sup>29</sup>Si even for ZSM-5/3, and for all <sup>29</sup>Si NMR signals from -94 to -106 ppm this efficiency is similar (not shown in the figures).

The concentration of Al atoms in the Al–O–Si–O–Al sequences of ZSM-5/3 cannot be determined because of the uncertainty of the locations of the Al–O–Si–O–Al sequences in the ZSM-5 framework. Nevertheless, Al in Al–O–Si–O–Al sequences represents a significant fraction of Al atoms in ZSM-5/3. Note that while resonances at -94.0 and -99.0 ppm correspond exclusively to Al atoms in Al–O–Si–O–Al sequences, resonances at -102.8 and -106.2 ppm reflect both isolated Al atoms and Al atoms in Al–O–Si–O–Al sequences.<sup>32</sup>

3.2. Co<sup>2+</sup> Ion-Exchange Capacity of Zeolites. Table 1 shows the maximum ion-exchange capacity of the zeolite samples for divalent  $[Co^{2+}(H_2O)_6]^{2+}$  complexes. The estimation of the distribution of framework Al atoms by Co<sup>2+</sup> ions as a probe is discussed in detail elsewhere.<sup>13,14</sup> The high ion-exchange capacity of the ZSM-5/1 and ZSM-5/2 samples for  $[Co^{2+}(H_2O)_6]^{2+}$  complexes indicates that the close Al atoms balancing the Co(II) ions prevail in their zeolite frameworks (84 and 76% of Al atoms, respectively). The low ion-exchange capacity of the ZSM-5/4 sample shows that the concentration of close Al atoms is much lower. Since the <sup>29</sup>Si NMR spectra evidenced the absence of Si(2Si,2Al) atoms for the ZSM-5/1, ZSM-5/2, and ZSM-5/4 samples, the exchanged Co(II) ions should be balanced in these samples only by Al-O-(Si-O)<sub>2</sub>-Al sequences. Because the ion-exchange capacity of ZSM-5/4 for divalent  $[Co^{2+}(H_2O)_6]^{2+}$  complexes is low (Table 1), this sample contains dominantly single Al atoms in the framework. On the contrary, according to our <sup>29</sup>Si MAS NMR results, the Al-O-Si-O-Al sequences highly prevail in ZSM-5/3 while the concentration of close Al atoms in this sample as indicated by Co<sup>2+</sup> ion-exchange capacity is low (16%). This disagreement can be explained by assuming that the close Al atoms of the majority of the Al-O-Si-O-Al pairs do not face the same channel and therefore they are not able to accommodate a divalent  $[Co^{2+}(H_2O)_6]^{2+}$  complex. Note that one [Co<sup>2+</sup>(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> complex replaces two solvated Na<sup>+</sup> ions.

**3.3.** Al–O–(Si–O)<sub>n>1</sub>–Al Sequences. Visible spectroscopy of dehydrated Co-ZSM-5 zeolites allows distinguishing between Al–O–(Si–O)<sub>2</sub>–Al sequences located in one ring and facing the same channel and those chains of Al atoms located in different rings. Two Al atoms in one ring accommodate bare Co<sup>2+</sup> ion, and this is reflected in the Co<sup>2+</sup> d–d transitions.</sub>

<b>FABLE 2: NMR Parameters of the Individual</b>	<sup>27</sup> Al Resonances of ZSM-5/1-4 Determined from Spec	ctra
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sample	resonance	ZSM-5/1	ZSM-5/2	resonance	Na-ZSM-5/3	H-ZSM-5/3	ZSM-5/4 <sup>a</sup>
Si/Al <sub>FR</sub>		14	12		8-8.5	8-8.5	15
$\delta_{ m F1}$	Α	54.5	54.3	Α	54.9	54.8	54.9
$\delta_{\mathrm{F2}}$		52.6	52.8		52.4	52.4	52.3
$\delta_{ m iso}$		53.8	53.7		54.0	53.9	53.9
$\delta_{ m F1}$	В	56.3	56.3	B'	57.2	57.2	57.1
$\delta_{ m F2}$		55.2	55.0		55.1	55.4	55.6
$\boldsymbol{\delta}_{\mathrm{iso}}$		55.9	55.8		56.4	56.5	56.5
$\delta_{ m F1}$	С		57.7				
$\delta_{ m F2}$			56.2				
$\delta_{ m iso}$			57.1				
$\delta_{ m F1}$	D	59.3					
$\delta_{ m F2}$		57.7					
$\delta_{ m iso}$		58.7					
$\delta_{ m F1}$				E	62.7	63.0	
$\delta_{ m F2}$					60.1	60.1	
$\delta_{ m iso}$					61.7	61.9	
$\delta_{ m F1}$				F	64.2	64.4	64.5
$\delta_{ m F2}$					61.6	61.7	62.0
$\delta_{ m iso}$					63.2	63.4	63.6

<sup>*a*</sup> Sample E in our previous study.<sup>23</sup>

Moreover, this method allows identification of rings with two Al atoms and determination of their concentration in the zeolite framework. The method is described in detail in refs 13-18.

The distributions of Al atoms in both the ZSM-5/1 and ZSM-5/2 samples were previously investigated using Co(II) ions as probes monitored by UV–vis spectroscopy.<sup>13,14</sup> It was found that Al–O–(Si–O)<sub>n</sub>–Al sequences were located mainly in sixmembered rings of the  $\alpha$  and  $\beta$  sites of the ZSM-5 samples.<sup>15</sup> The <sup>29</sup>Si MAS NMR experiments reported in this article indicated a negligible concentration of Al–O–Si–O–Al sequences in these materials. Therefore, 84 and 76% of Al atoms in ZSM-5/1 and ZSM-5/2, respectively, belong to the Al–O–(Si–O)<sub>2</sub>–Al sequences located in six-membered rings.<sup>15</sup>

**3.4.** <sup>27</sup>AI (**3Q**) MAS NMR Spectra of Zeolites. All investigated samples exhibit exclusively a signal centered around 55 ppm in the single-pulse <sup>27</sup>Al MAS NMR spectrum (not shown in the figures). This signal corresponds to Al atoms with a tetrahedral coordination.<sup>33</sup> A resonance around 0 ppm corresponding to octahedrally coordinated Al atoms was not observed in the spectrum, confirming the conclusion based on the <sup>29</sup>Si MAS NMR experiment (see above) of the exclusive presence of Al atoms in the zeolite framework.

The <sup>27</sup>Al 3Q MAS NMR method was employed to resolve the individual resonances corresponding to tetrahedrally coordinated Al atoms occupying different T sites. The 2D plots of the spectra of Na-ZSM-5 together with the F1 projections (note that Gaussian bands correspond to the individual resonances in the F1 projection) as well as with the selected F1 slices are shown in Figure 2. The resonances corresponding to the Al atoms in individual framework T sites exhibit close NMR parameters because of small differences of the local geometry of AlO<sub>4</sub><sup>-</sup>. Thus, simulations of the F1 and F2 projections and F1 and F2 slices were performed to obtain the NMR parameters of the individual resonances of the spectra. The resulting NMR parameters (the  $\delta_{F1}$  and  $\delta_{F2}$  values and the <sup>27</sup>Al isotropic chemical shifts ( $\delta_{iso}$ ) of Na- and H-ZSM-5 samples) are listed in Table 2. The data further reveal essentially no differences between the spectra of the hydrated Na- and H-ZSM-5/3 samples, indicating that there is no observable effect of the type of countercation balancing the framework negative charge on the <sup>27</sup>Al NMR parameters of the hydrated ZSM-5 zeolite sample.

Seven resonances were identified in the spectra of the ZSM-5 samples. Resonance A was observed for all the samples,

resonance B for ZSM-5/1 and ZSM-5/2, resonance B' for ZSM-5/3 and ZSM-5/4, resonance C only for ZSM-5/2, resonance D only for ZSM-5/1, resonance E only for ZSM-5/3, and resonance F for ZSM-5/3 and ZSM-5/4. Resonances A, B', and F correspond to R-III, R-V, and R-X, respectively, in our prior study.<sup>23</sup> On the other hand, resonances C, D, and E were not previously reported for the ZSM-5 samples containing only single Al atoms.<sup>23</sup> Table 2 shows that the presence of Al–O–Si–O–Al sequences in the framework of ZSM-5/3 does not significantly affect the <sup>27</sup>Al NMR spectrum (cf. results for ZSM-5/3 and ZSM-5/4). Resonances A and B' are unchanged, resonance F is most likely resonance F of ZSM-5/4, which is shifted to a lower value, and only one new weak resonance E appears.

# 4. Computational Models and Methods

**4.1. Computational Model.** A bare zeolite framework model that includes neither cations nor water molecules and has proven useful in our previous study<sup>23</sup> is adopted to calculate the local structure around the  $AlO_4^-$  tetrahedra and to predict the <sup>27</sup>Al NMR shielding. The model features one Al-O-Si-O-Al or  $Al-O-(Si-O)_2-Al$  sequence in a unit cell of ZSM-5 and possesses *P*1 symmetry. Each Al atom bears a formal charge of -1. The starting structure was generated from the X-ray structure of mutinaite,<sup>30,31</sup> which is the natural analogue of ZSM-5. Our previous study<sup>23</sup> of ZSM-5 structures containing one Al atom per unit cell resulted in 24 distinguishable structures corresponding to Al substitution into the 24 T sites of monoclinic ZSM-5. The 24 calculated <sup>27</sup>Al isotropic chemical shifts were in very good agreement with the corresponding experimental values.<sup>23</sup>

**4.2. QM-Pot Method.** The QM-Pot method employed<sup>34,35</sup> partitions the whole system (S) into two parts. The inner part (I) is treated by quantum mechanics (QM), and the outer part (O) as well as all the interactions between the inner and outer layers are treated by parametrized interatomic potential functions (Pot). The dangling bonds of the inner part are saturated by link hydrogen atoms. The atoms of the inner part together with the link atoms form the cluster (C). The QM-Pot approach and its application to single Al sites as well as Al–O–Si–O–Al pairs is discussed in detail elsewhere.<sup>36,37</sup>

The calculations were performed by the QM-Pot program,<sup>35</sup> which utilizes the Turbomole program<sup>38–42</sup> for the QM part and



**Figure 5.** Positions of the T1, T7, and T15 atoms in the ZSM-5 framework (a). The clusters centered around Al(T1) (b), Al(T15) (c), and Al(T7) (d). The merged clusters for Al(T15)-O-Si-O-Al(T1) (e) and Al(T1) $-O-(Si-O)_2-Al(T7)$  (f). Silicon atoms are in gray, aluminum atoms in yellow, oxygen atoms in red, and link hydrogen atoms in white.

the Gulp program<sup>43,44</sup> for the periodic potential function calculations. The pure DFT method employing the BLYP<sup>45–47</sup> functional and the TZVP basis set of Ahlrichs et al.<sup>48</sup> were used for the QM calculations. As interatomic potential functions (Pot), shell-model ion-pair potentials<sup>49</sup> parametrized on DFT results for zeolites<sup>50</sup> were employed. The electrostatic energy was evaluated by standard Ewald summation techniques for all cores and shells. A cutoff radius of 10 Å was chosen for the summation of short-range interactions.

**4.3. Optimization of Structures.** Both the lattice constants and the atomic positions of the all-silica MFI (ZSM-5) structure were optimized by the Gulp program at constant pressure. Then two silicon atoms were replaced by two aluminum atoms to form one Al-O-Si-O-Al or Al $-O-(Si-O)_2-Al$  chain, and subsequently the structure and the lattice constants were further optimized by Gulp at constant pressure. The optimized structure was then used for defining a cluster around the two Al atoms for our QM-Pot calculations. The clusters were embedded into a super cell composed of two (for Al-O-Si-O-Al) or four (for Al $-O-(Si-O)_2-Al$ ) unit cells of the zeolite framework,

and the structure of the entire system was optimized by QM-Pot at constant volume.

**4.4. Cluster Models.** For all Al(1)–O–Si–O–Al(2) and Al(1)–O–(Si–O)<sub>2</sub>–Al(2) chains, clusters were prepared by merging two five coordination shell clusters (Al(1)–O–Si–O–Si–O–H<sub>link</sub> and Al(2)–O–Si–O–Si–O–H<sub>link</sub>), which were centered around the Al(1) and Al(2) atoms (Figure 5).<sup>23,51</sup> The clusters used were cut out from the corresponding optimized super cells. Because of the presence of silicate rings in the framework of ZSM-5, the created clusters contained pairs of very close H<sub>link</sub> atoms. Since the close H<sub>link</sub> atoms represented the same Si atom, they were replaced by the corresponding Si(OH<sub>link</sub>)<sub>2</sub> moiety. This was repeated until the cluster contained no such pairs.

To investigate the effect of an Al(1)–O–(Si–O)<sub>n</sub>–Al(2) (n = 1 and 2) sequence on the local AlO<sub>4</sub><sup>-</sup> geometry as well as the <sup>27</sup>Al isotropic chemical shift, calculations were performed for three variants of the cluster for each sequence (Figure 6). The first variant contains both Al atoms (Al(1)–O–(Si–O)<sub>n</sub>–Al(2)), and the other two variants include only one

Effect of Al-Si-Al and Al-Si-Si-Al on <sup>27</sup>Al NMR Spectra



**Figure 6.** Three variants of the cluster for Al(T15)-O-Si-O-Al(T1) (a1-a3) and  $Al(T1)-O-(Si-O)_2-Al(T7)$  (b1-b3) sequences. The first variant contains both Al atoms; (a1) and (b1). The other two variants include only one Al atom (a2), (a3), (b2), and (b3). Silicon atoms are in gray, aluminum atoms in yellow, oxygen atoms in red, and link hydrogen atoms in white. The atoms corresponding to the Al(T15)-O-Si-O-Al(T1) and  $Al(T1)-O-(Si-O)_2-Al(T7)$  sequences are displayed as balls.

Al atom in Al(1) $-O-(Si-O)_n-Si(2)$  and Si(1) $-O-(Si-O)_n-$ Al(2) chains. This allows comparing the calculated geometry and isotropic chemical shift using the clusters of the same size and shape.

**4.5.** Calculated Sequences. Al-O-Si-O-Al Chains. As described in section 3.2, the Al-O-Si-O-Al sequences of ZSM-5/3 (Si/Al 8–8.5) do not accommodate divalent Co<sup>2+</sup> hexaaqua complex and therefore the Al atoms face different channels. There are many possible locations of such sequences in a unit cell of ZSM-5. However, the observed resonance of 63.6 ppm, which is well resolved in the <sup>27</sup>Al 3Q MAS NMR spectrum, was assigned to the Al atom occupying either T1 or T24 for the ZSM-5/4 sample.<sup>23</sup> Therefore, we selected all five possible Al-O-Si-O-Al sequences (Table 3 and Figure 7) containing one Al atom occupying either T1 or T24 and the other one facing a different channel. This Al-O-Si-O-Al set was enriched by additional three plausible Al-O-Si-O-Al chains having Al in neither T1 nor T24 (Table 3).

*Al*-*O*-(*Si*-*O*)<sub>2</sub>-*Al Chains.* The Co(II) ion-exchange capacity, the presence of Al-O-(Si-O)<sub>n</sub>-Al (n = 1 and 2) sequences, and the cationic sites for bare divalent ions were already studied in detail for the ZSM-5/1 and ZSM-5/2 samples.<sup>13-15</sup> Since our <sup>29</sup>Si MAS NMR measurements indicated no Al-O-Si-O-Al sequences in ZSM-5/1 and ZSM-5/2 (section 3.1), we can conclude that the cobalt exchange experiments<sup>13,14</sup> revealed that some 80% of the framework Al atoms are in Al-O-(Si-O)<sub>2</sub>-Al chains. These Al sequences form the three types of cationic sites of Co(II) ions designated as the α, β, and γ sites (Figure 1).<sup>15</sup> Since only a small fraction of Al-O-(Si-O)<sub>2</sub>-Al chains is present in the γ site,<sup>13-15</sup> only the selected sequences forming six-membered rings of the α and β sites were calculated (Table 4).

**4.6. Calculation of <sup>27</sup>Al NMR Shielding.** After the QM-Pot structure determination, the Gaussian program<sup>52</sup> was employed to calculate NMR shielding tensors of the atoms of the optimized clusters at the BLYP/TZVP level using the gauge-independent atomic orbital (GIAO) method.<sup>53</sup> Since clusters of different shapes and sizes depending on the studied

Al–O–(Si–O)<sub>n</sub>–Al (n = 1 and 2) sequence were employed, the calculated <sup>27</sup>Al NMR shielding values were not directly converted into isotropic chemical shifts.<sup>23</sup> Instead, the isotropic chemical shift  $\delta$ (Al(1)) of the Al(1) atom forming an Al(1)–O–(Si–O)<sub>1,2</sub>–Al(2) sequence was evaluated using

$$\delta(Al(1)) = \delta(Al(1)_{single}) + \Delta(\sigma)$$

where  $\delta(Al(1)_{single})$  denotes the <sup>27</sup>Al isotropic chemical shift calculated for a single Al atom in the corresponding T site using the procedure employed in our previous study<sup>23</sup> and  $\Delta(\sigma)$  is the differences between the <sup>27</sup>Al NMR shielding values calculated for Al(1) in Al(1)–O–(Si–O)<sub>1,2</sub>–Al(2) and Al(1)–O– (Si–O)<sub>1,2</sub>–Si(2).

# 5. Computational Results

Tables 3 and 4 show the calculated average T-O-T angles and GIAO <sup>27</sup>Al NMR shieldings for Al-O-Si-O-Al and Al-O-(Si-O)<sub>2</sub>-Al sequences, respectively. The four individual T-O-T angles of the AlO<sub>4</sub><sup>-</sup> sites are given in Tables S1 and S2 of the Supporting Information.

**5.1.** Al–O–Si–O–Al Sequences. Table 3 reveals that the presence of an Al atom as a next-nearest neighbor can result in a significant deformation of the  $AlO_4^-$  tetrahedron. The calculated changes of the average T–O–T angle range from –6 to +8°, but the individual T–O–T angles can change significantly more (Table S1 of Supporting Information). The effect of Al as a next-nearest neighbor on the calculated <sup>27</sup>Al isotropic chemical shift is in the -4 to +2 ppm range (Table 3).

**5.2.** Al–O–(Si–O)<sub>2</sub>–Al Sequences. The presence of a more distant Al as a next-next-nearest neighbor can also significantly affect both the geometric structure of the AlO<sub>4</sub><sup>-</sup> tetrahedron and its <sup>27</sup>Al isotropic chemical shift (Table 4). The average T–O–T angles change by –6 to +7° for the  $\alpha$  site and by –2 to +1° for the  $\beta$  site. As for Al–O–Si–O–Al, individual T–O–T angles can change significantly more (Table S2 of Supporting Information). Al as a next-next-nearest neighbor changes the calculated <sup>27</sup>Al isotropic chemical shift by –3 to +4 and by –2 to +1 ppm for the  $\alpha$  and  $\beta$  sites, respectively (Table 4).

TABLE 3: Number of Atoms in the Clusters, BLYP GIAO <sup>27</sup>Al NMR Shieldings (ppm), and Average Al–O–Si Angles (deg) for Al–O–Si–O–Al Sequences

sequences	number of atoms	GIAO NM	IR shieldings	Δ	T-O-T average angles		Δ
Al(T1)-Si(T16)-Al(T17) Al(T1)-Si(T16)-Si(T17) Si(T1)-Si(T16)-Al(T17)	138 138 138	Al(T1) 493.1 489.3	Al(T17) 489.7 487.6	- <b>3.8</b> -2.1	Al(T1) 148.9 143.3	Al(T17) 141.3 140.8	- <b>5.6</b> -0.5
AI(T1)-Si(T16)-AI(T15) AI(T1)-Si(T16)-Si(T15)	153 153	Al(T1) 495.3 493.7	Al(T15) 493.1	-1.6	Al(T1) 152.1 151.7	Al(T15) 146.7	-0.4
$S_1(T_1) = S_1(T_16) = A_1(T_15)$	153	Al(T14)	493.8 Al(T24)	0.7	Al(T14)	Al(T24)	8.2
Ai(114) - Si(120) - Ai(124) $Ai(T14) - Si(T20) - Si(T24)$ $Si(T14) - Si(T20) - Ai(T24)$	159 159 159	491.6	483.7	1.5 - <b>0.8</b>	143.2	139.4	1.5 - <b>1.4</b>
Al(T21)-Si(T20)-Al(T24) Al(T21)-Si(T20)-Si(T24)	138 138	Al(T21) 497.1 494.9	Al(T24) 489.0	-2.2	Al(T21) 156.4 152.2	Al(T24) 142.3	-4.2
Si(121) - Si(120) - Al(124) Al(T22) - Si(T23) - Al(T24)	138	Al(T22) 489.6	485.6 Al(T24) 489.8	-3.4	Al(T22) 140.3	Al(T24) 144.5	-2.1
Al(T22)-Si(T23)-Si(T24) Si(T22)-Si(T23)-Al(T24)	144 144	490.3	486.2	0.7 - <b>3.6</b>	141.3	140.6	1.0 - <b>3.9</b>
Al(T8)-Si(T12)-Al(T11) Al(T8)-Si(T12)-Si(T11) Si(T8)-Si(T12)-Al(T11)	141 141 141	Al(T8) 496.1 496.7	AI(T11) 493.4 493.1	0.6 -0.3	Al(18) 148.7 149.8	Al(111) 145.7 145.8	1.1 0.1
Al(T9) - Si(T10) - Al(T11)	144	Al(T9) 492.4	Al(T11) 494.7	1.4	Al(T9) 148.9	Al(T11) 148.5	5.0
AI(19) - SI(110) - SI(111) Si(T9) - Si(T10) - AI(T11)	144 144	491.0 A1(T8)	492.7	-1.4 -2.0	143.0 A1(T8)	145.3	-5.9 -3.2
Al(T8)-Si(T9)-Al(T10) Al(T8)-Si(T9)-Si(T10) Si(T8)-Si(T9)-Al(T10)	138 138 138	496.1 497.2	492.7 492.4	1.1 -0.3	149.2 150.3	146.8 146.4	$1.1 \\ -0.4$

**5.3.** Correlation between the <sup>27</sup>Al NMR Isotropic Chemical Shift and the Average T–O–T Angle. On the basis of a comparison between the crystallographic and <sup>27</sup>Al NMR data of aluminum-rich zeolites, Lippmaa et al.<sup>33</sup> suggested a linear correlation between the <sup>27</sup>Al NMR isotropic chemical shift  $\delta$ (Al) and the average T–O–T angle ( $\theta$ ) of the zeolite framework.

# $\delta(AI) = -0.50 * \theta + 132 \text{ ppm}$

The calculated GIAO <sup>27</sup>Al NMR shielding values are plotted against the average Al–O–Si angles for Al–O–Si–O–Al and Al–O– $(Si-O)_2$ –Al sequences in Figures 8 and 9, respectively. The plots in Figures 8 and 9 show that the linear correlation does not hold for Al–O– $(Si-O)_{1,2}$ –Al sequences. This conclusion regarding the failure of the linear correlation is in agreement with that reached by Kucera and Nachtigall<sup>54</sup> for single Al atoms in the MCM-58 zeolite as well as that of Sklenak et al. for single Al atoms in ZSM-5.<sup>23</sup> Our results clearly reveal that the relationship between the <sup>27</sup>Al isotropic chemical shift and the local geometry of AlO<sub>4</sub><sup>–</sup> tetrahedron is more complex than a simple linear correlation between the shift and the average T–O–T angle.

#### 6. Discussion

**6.1. Effect of the Presence of Al–O–Si–O–Al Sequences on the** <sup>27</sup>**Al Isotropic Chemical Shift.** To investigate the effect of the presence of an Al atom as a next-nearest neighbor on the Al isotropic chemical shift, we compare the results for the ZSM-5/3 and ZSM-5/4 samples, which are similarly prepared but differ significantly in the concentration of aluminum (Table 2). The <sup>29</sup>Si MAS NMR measurements revealed (see also section 3.1) that a dominant fraction of the framework Al atoms forms Al-O-Si-O-Al sequences in the aluminum-rich ZSM-5/3 sample, whereas there are no Al-O-Si-O-Al sequences observed in ZSM-5/4. The results in Figure 2 and Table 2 show that there are no significant differences between the <sup>27</sup>Al MAS NMR and <sup>27</sup>Al 3Q MAS NMR spectra of Na-ZSM-5/3 and Na-ZSM-5/4. The three resonances at 54.0, 56.4, and 63.2 ppm of ZSM-5/3 correspond to R-A, R-B', and R-F of ZSM-5/4 (R-III, R-V, and R-X in our previous study<sup>23</sup>). Only R-F is slightly changed by 0.4 ppm, while R-A and R-B' are virtually unchanged by the presence of Al-O-Si-O-Al in ZSM-5/3. We also cannot rule out a different assignment of R-B' in ZSM-5/3 than in ZSM-5/4 since this resonance can correspond to Al in several T sites of ZSM-5<sup>23</sup> (Figure 10). In addition to these bands, a weak band corresponding to a new resonance R-E with an isotropic chemical shift of 61.7 ppm was observed in the <sup>27</sup>Al (3Q) MAS NMR spectrum of Na-ZSM-5/3. This resonance can be explained either by the effect of an Al atom as a nextnearest neighbor on one of the resonances R-A, R-B', and R-F or more likely by the occupation of a new T site in the ZSM-5/3 sample that has a significantly higher framework Al content (Si/Al 8-8.5) than ZSM-5/4 (Si/Al 15).



Figure 7. Positions of the possible Al–O–Si–O–Al sequences containing one Al atom occupying either T1 or T24 in the ZSM-5 framework. Silicon atoms are in gray, aluminum atoms in yellow, oxygen atoms in red, and link hydrogen atoms in white.

We will discuss the effect of an Al atom as a next-nearest neighbor on the <sup>27</sup>Al isotropic chemical shift for the specific case of an Al-O-Si-O-Al sequence containing Al in either a T1 or a T24 site (Figures 7 and 10). We showed that R-F corresponded to either T1 or T24 in ZSM-5/4.23 This resonance has the largest value of the isotropic chemical shift, and furthermore the gap between the isotropic chemical shifts of this resonance and the neighboring resonance (62.8 ppm<sup>23</sup>) is large (0.8 ppm observed and 1.1-1.2 ppm calculated) and therefore R-F cannot be confused with the neighboring resonances. It is therefore safe to conclude that the 0.4 ppm isotropic chemical shift decrease observed for R-F in ZSM-5/3 with respect to ZSM-5/4 is not due to the occupation of a new T site in ZSM-5/3 but is caused by the effect of Al as a next-nearest neighbor on the isotropic chemical shift of the Al atom occupying either T1 or T24. Therefore, we calculated five possible Al-O-Si-O-Al sequences (Table 3 and Figure 7) containing one Al atom occupying either T1 or T24 and the other one facing a different channel.

Figure 10 compares the measured <sup>27</sup>Al isotropic chemical shifts for the ZSM-5/3 and ZSM-5/4 samples with the <sup>27</sup>Al

isotropic chemical shifts calculated for isolated Al atoms in ZSM- $5^{23}$  as well as for the Al atoms forming Al–O–Si–O–Al sequences and occupying T1 and T24 sites. The isotropic chemical shifts of the latter atoms were calculated using the equation described in section 4.6.

The calculated influence of Al as a next-nearest neighbor of T1 or T24 ranges from -3.8 to -0.8 ppm (Table 3 and Figure 10). For the Al(T14)-O-Si(T20)-O-Al(T24) sequence, the calculated effect (-0.8 ppm) comes closest to the observed one (-0.4 ppm) (Figure 10). This result reveals that the assignment of <sup>27</sup>Al NMR resonances R-VIII, R-IX, and R-X of our prior study<sup>23</sup> to T12, T1, and T24 is more likely than the other assignment (T7, T17, and T1).<sup>23</sup>

The stability of the local geometry of the  $AIO_4^-$  tetrahedron for a T site depends on the AI-O-Si-O-AI chain (Table 3). For example, the change of the average T-O-T angle for Al occupying the T24 site is calculated to be  $-0.8^{\circ}$  for AI(T14)-O-Si(T20)-O-AI(T24),  $-3.4^{\circ}$  for AI(T21)-O-Si(T20)-O-AI-(T24), and  $-3.6^{\circ}$  for AI(T22)-O-Si(T23)-O-AI(T24). We identified no structural parameters (e.g., size of the ring (fivemembered ring)) responsible for the structural stability of the

TABLE 4: Number of Atoms in the Clusters, BLYP GIAO <sup>27</sup>Al NMR Shieldings (ppm), and Average Al–O–Si Angles (deg) for Al–O–(Si–O)<sub>2</sub>–Al Sequences

sequences	number of atoms	GIAO NMR shieldings		$\Delta$	T-O-T average angles		$\Delta$
α Al(T2)-Si(T1)-Si(T17)-Al(T23) Al(T2)-Si(T1)-Si(T17)-Si(T23) Si(T2)-Si(T1)-Si(T17)-Al(T23)	198 198 198	Al(T2) 494.6 491.9	Al(T23) 493.0 492.0	-2.7 -1.0	Al(T2) 149.6 143.3	Al(T23) 146.4 145.2	-6.3 -1.2
$\alpha$ Al(T8)-Si(T2)-Si(T1)-Al(T17) Al(T8)-Si(T2)-Si(T1)-Si(T17) Si(T8)-Si(T2-Si(T1)-Al(T17)	192 192 192	Al(T8) 494.4 498.7	Al(T17) 486.5 486.4	4.3 -0.1	Al(T8) 146.5 153.2	Al(T17) 138.8 138.2	6.7 -0.6
$\beta$ Al(T17)-Si(T16)-Si(T7)-Al(T23) Al(T17)-Si(T16)-Si(T7)-Si(T23) Si(T17)-Si(T16)-Si(T7)-Al(T23)	174 174 174	Al(T17) 489.2 487.9	Al(T23) 492.4 491.8	-1.3 -0.6	Al(T17) 141.4 139.9	Al(T23) 145.2 145.9	$-1.5 \\ 0.7$
$\beta$ Al(T7)-Si(T23)-Si(T22)-Al(T1) Al(T7)-Si(T23)-Si(T22)-Si(T1) Si(T7)-Si(T23)-Si(T22)-Al(T1)	201 201 201	Al(T7) 489.1 489.9	Al(T1) 488.2 488.2	0.8 0.0	Al(T7) 142.3 143.3	Al(T1) 141.5 141.8	1.0 0.3
$ \begin{array}{l} \beta \\ Al(T16)-Si(T7)-Si(T23)-Al(T22) \\ Al(T16)-Si(T7)-Si(T23)-Si(T22) \\ Si(T16)-Si(T7)-Si(T23)-Al(T22) \end{array} $	174 174 174	Al(T16) 493.1 492.4	Al(T22) 492.2 490.4	-0.7 -1.8	Al(T16) 143.4 143.4	Al(T22) 143.2 141.7	0.0 - 1.5

 $AIO_4^-$  tetrahedra, and therefore it can be predicted only from theoretical calculations.

We further investigated if the calculated effects of an Al atom as a next-nearest neighbor on the <sup>27</sup>Al isotropic chemical shift are caused only by the changes of the local AlO<sub>4</sub><sup>-</sup> geometry or whether there is also an electronic effect of the next-nearest neighbor Al atom. Therefore, the Al(T1) and Al(T15) atoms in the optimized Al(T1)–Si(T16)–Al(T15) cluster were replaced by Si without changing the geometry to form Si(T1)–Si(T16)– Al(T15) and Al(T1)–Si(T16)–Si(T15) clusters, respectively, and then the GIAO <sup>27</sup>Al shielding values were evaluated. The calculated shieldings were essentially unchanged (the differences were less than 0.2 ppm), indicating that the changes of the local geometry are responsible for the effects. This result is not surprising since Al in AlO<sub>4</sub><sup>-</sup> and Si in SiO<sub>4</sub> are isoelectronic.

**6.2. Effect of the Presence of Al–O–(Si–O)**<sub>2</sub>–Al Sequences on the <sup>27</sup>Al Isotropic Chemical Shift. The ZSM-5/1 and ZSM-5/2 samples with high concentrations (about 80% of the Al framework atoms) of Al–O–(Si–O)<sub>2</sub>–Al sequences located in the six-membered rings were investigated to study the effect of the presence of an Al atom as a next-next-nearest

neighbor on the Al isotropic chemical shift. Contrary to Al-O-Si-O-Al chains present in ZSM-5/3, the location of  $Al-O-(Si-O)_2$ -Al sequences can be studied experimentally by Co(II) ions monitored by UV-visible spectroscopy.<sup>13,14</sup> This method reveals the concentration of close Al atoms located in one ring and forming a cationic site for a bare Co(II) ion in a dehydrated zeolite. Since our <sup>29</sup>Si MAS NMR experiments for ZSM-5/1 and ZSM-5/2 show no bands below -100 ppm, which correspond to the Al-O-Si-O-Al chains, we can conclude that the close Al atoms accommodating bare Co(II) ions relate to Al-O-(Si-O)<sub>2</sub>-Al sequences located in the six-membered rings. Recent studies of ZSM-5/1 and ZSM-5/2 showed<sup>13-15</sup> that some 40% (50% of the close Al atoms) are located in the  $\beta$ cationic site of a deformed six-membered ring at the channel intersection and about 30% of the Al framework atoms (40% of the close Al atoms) lie in the  $\alpha$  cationic site located in the sinusoidal channel and corresponding to the six-membered ring formed by two five-membered rings (Figure 1).

Four <sup>27</sup>Al resonances – A (53.8 and 53.7 ppm for ZSM-5/1 and ZSM-5/2, respectively), B (55.9 and 55.8 ppm for ZSM-5/1 and ZSM-5/2, respectively), C (57.1 ppm for ZSM-5/2),



average T-O-T angle (degree)

**Figure 8.** GIAO <sup>27</sup>Al NMR shielding values plotted against the average T–O–T angles for the calculated Al–O–Si–O–Al sequences. Values for Al–O–Si–O–Al.  $\bigcirc$  Values for Al–O–Si–O–Si/Si–O–Si–O–Al. (Solid line) Linear fit for Al–O–Si–O–Al. (Dotted line) Linear fit for Al–O–Si–O–Al.



**Figure 9.** GIAO <sup>27</sup>Al NMR shielding values plotted against the average T–O–T angles for the calculated Al–O– $(Si-O)_2$ –Al sequences. Values for Al–O– $(Si-O)_2$ –Al. O Values for Al–O– $(Si-O)_2$ –Si/Si–O– $(Si-O)_2$ –Al. (Solid line) Linear fit for Al–O– $(Si-O)_2$ –Al. (Dotted line) Linear fit for Al–O– $(Si-O)_2$ –Al.



**Figure 10.** Effect of the presence of an Al atom as a next-nearest neighbor on the calculated <sup>27</sup>Al isotropic chemical shift of the Al atoms occupying T1 and T24 sites (Al(T1) and Al(T24), respectively). Experimental values of <sup>27</sup>Al isotropic chemical shift of ZSM-5/4 (no Al-O-Si-O-Al sequences) (a), calculated isotropic chemical shifts of isolated Al atoms in ZSM-5<sup>23</sup> (b), calculated isotropic chemical shifts of Al(T1) (blue) and Al(T24) (red) present in Al-O-Si-O-Al sequences employing  $\delta$ (Al(1)) =  $\delta$ (Al(1)<sub>single</sub>) +  $\Delta(\sigma)$  (section 4.6) (c), and experimental values of <sup>27</sup>Al isotropic chemical shift of ZSM-5/3 with Al atoms located predominantly in Al-O-Si-O-Al sequences (d).



**Figure 11.** Effect of the presence of an Al atom as a next-next-nearest neighbor on the calculated <sup>27</sup>Al isotropic chemical shift of the Al atoms of the  $\alpha$  and  $\beta$  sites. Calculated isotropic chemical shifts of isolated Al atoms in ZSM-5<sup>23</sup> (a), calculated isotropic chemical shifts of Al present in the  $\alpha$  (blue) and  $\beta$  (red) sites employing  $\delta$ (Al(1)) =  $\delta$ (Al(1)<sub>single</sub>) +  $\Delta(\sigma)$  (section 4.6) (b), and experimental values of <sup>27</sup>Al isotropic chemical shift of ZSM-5/1 and /2 with Al atoms located predominantly in Al–O–(Si–O)<sub>2</sub>–Al sequences (c). ( $\mathbf{V}$ ) Al possibly in pairs; ( $\nabla$ ) possible single Al.

and D (58.7 ppm for ZSM-5/1) — were identified (Table 2 and Figure 11). Since R-A and R-B are observed for both ZSM-5/1 and ZSM-5/2, they likely correspond to the Al atoms forming the Al–O–(Si–O)<sub>2</sub>–Al sequences. This suggestion is supported by the results of UV–visible study of the dehydrated Co-ZSM-5/1 and Co-ZSM-5/2 samples. The visible spectra of Co ions in the  $\alpha$  and  $\beta$  sites in both samples are identical.<sup>13–15</sup> On the other hand, R-C and R-D are measured only for a single sample and therefore they likely relate to two different single Al atoms. R-C is a new resonance that was not observed in our previous study, and it can be assigned to several T sites.<sup>23</sup> R-D might also be a new resonance or it is R-VII of our prior investigation.<sup>23</sup>

The QM-Pot calculations for the selected Al $-O-(Si-O)_2$ -Al sequences located in the  $\alpha$  and  $\beta$  sites (Table 4 and Figures 1 and 11) reveal the effect of an Al atom as a next-next-nearest neighbor on the Al isotropic chemical shift.

Figure 11 compares the observed <sup>27</sup>Al isotropic chemical shifts for the ZSM-5/1 and /2 samples with the <sup>27</sup>Al isotropic chemical shifts calculated for isolated Al atoms in ZSM-5<sup>23</sup> as well as for the Al atoms forming Al–O–(Si–O)<sub>2</sub>–Al sequences located in the  $\alpha$  and  $\beta$  sites. The isotropic chemical shifts of

the latter atoms were calculated using the equation described in section 4.6.

The calculated influence is larger for the  $\alpha$  site (-3 to +4 ppm) than that for the  $\beta$  site (-2 to +1 ppm). Therefore, it remains unclear whether R-B corresponds to R-B' or is a different resonance having its isotropic chemical shift altered by an Al atom as a next-next-nearest neighbor. Unfortunately, there is no systematic contribution of Al in Al-O-Si-O-Al or Al-O-(Si-O)<sub>2</sub>-Al chains to the <sup>27</sup>Al isotropic chemical shift, and not even the direction can be predicted without calculating the chain.

## 7. Conclusions

Our calculations revealed that the <sup>27</sup>Al NMR isotropic chemical shift of Al framework atoms in ZSM-5 can be significantly affected (up to 4 ppm) by the presence of an Al atom as a next-nearest and next-nearest neighbor because of changes of the local geometry of  $AlO_4^-$  tetrahedra. Thus, the presence of  $Al-O-(Si-O)_n-Al$  (n = 1 and 2) sequences in zeolites can result in a change of properties of the  $AlO_4^-$  tetrahedra.

In contrast to <sup>29</sup>Si chemical shifts, the presence of neighboring Al in Al–O–Si–O–Al or Al–O–(Si–O)<sub>2</sub>–Al sequences does not make a uniform contribution to <sup>27</sup>Al isotropic chemical shifts, and even the direction of the shift can differ.

This limits the use of <sup>27</sup>Al (3Q) MAS NMR spectroscopy combined with DFT calculations for identifying different Al sites in the framework of ZSM-5 and their partial assignment only to samples with a low or negligible concentration of Al–O–(Si–O)<sub>n</sub>–Al (n = 1 and 2) sequences. Otherwise, two <sup>27</sup>Al resonances with different isotropic chemical shifts can be observed for a single T site, because only a fraction of Al atoms in that site forms an Al–O–(Si–O)<sub>n</sub>–Al (n = 1 and 2) sequence.

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**Supporting Information Available:** Al–O–Si angles for Al–O–Si–O–Al pairs (Table S1) and Al–O–Si angles for Al–O–(Si–O)<sub>2</sub>–Al pairs (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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