Zeolites

DOI: 10.1002/anie.200702628

Aluminum Siting in Silicon-Rich Zeolite Frameworks: A Combined High-Resolution ^{27}Al NMR Spectroscopy and Quantum Mechanics/Molecular Mechanics Study of ZSM-5**

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Dedicated to Süd-Chemie on the occasion of its 150th anniversary

Zeolites are crystalline microporous aluminosilicates widely used as molecular sieves and catalysts in industrial chemical processes. Silicon-rich zeolites (Si/Al > 12) such as ZSM-5 (MFI framework) have found particular attention. The catalytically active species, that is, protons, metal cations, and metal-oxo cations, compensate the negative charge of the microporous aluminosilicate frameworks $[Si_{n-m}Al_mO_{2n}]^{m-}$ made of corner-sharing TO$_4$ tetrahedra (T = Si, Al$^-$). A typical feature of many silicon-rich zeolites is a high number of crystallographically distinguishable T sites. Since the cationic species bind to the AlO$_4^-$ tetrahedra, the crystallographic position of aluminum in zeolite frameworks governs the location of the active sites, which in turn affects the catalytic activity and selectivity.

Thus, understanding the Al siting in zeolite structures is a priority, but it has remained a challenge. Diffraction methods are of limited use because of the similar scattering properties of Si and Al but also because of the low Al content in the most active zeolite catalysts. Solid-state ^{29}Si magic-angle spinning (MAS) NMR spectroscopy succeeded early in distinguishing between Si in different crystallographic positions of the MFI framework,[1] but for the quadrupolar ^{27}Al nucleus, the development of multiple quantum (MQ) NMR spectroscopy experiments[2] opened such possibilities only in the last decade.[3–6]

It is also not clear if there are preferred T sites for Al substitution or whether the T sites are occupied statistically. An X-ray diffraction study found three Cs$^+$ sites in extra-framework positions of ZSM-5, thus indicating nonrandom Al siting,[7] which is also supported by the effect of the Al concentration on the ^{27}Al MQ MAS NMR spectra of ZSM-5[4] and zeolite β.[5] As lattice energy minimizations with reliable force fields, for example, for MFI,[8,9] yielded only small energy differences for Al in different positions, the Al distribution might be kinetically controlled. This assumption implies that different synthesis procedures and different templates and cations could lead to different Al substitution patterns, thus increasing the total number of resolved ^{27}Al signals in the MQ MAS NMR spectra of a variety of samples. This strategy is followed herein.

For a set of 11 differently synthesized ZSM-5 samples, ten distinct resonances have been identified by ^{27}Al MQ MAS NMR spectroscopy, extending over a shift range of $\Delta\delta = 13.6$ ppm. Quantum-chemical calculations for simulated structures with Al in 24 different T sites yield a shift range of $\Delta\delta = 14.1$ ppm and show that the observed resonances belong to Al in different crystallographic sites. We conclude that the Al siting in ZSM-5 is not random and can be substantially varied by the conditions of zeolite syntheses.

A set of Na-ZSM-5 samples (**A**–**K**) with Si/Al framework ratios from 14 to 45 was prepared by using different silicon, aluminium, and sodium sources as well as different structure-directing agents; for details, see Table S1 of the Supporting Information. ^{27}Al 3Q MAS NMR spectroscopy[2,5] experiments were carried out on the calcined samples, which were dried only at ambient temperature to retain their full hydration inside the pores. Figure 1 shows a typical 2D plot of the ^{27}Al 3Q MAS NMR spectrum together with a simulation of the projections and selected spectra slices. Figure 2 shows the F1 and F2 projections of all spectra. Their shapes were simulated assuming three to four resonances per sample. The chemical shifts in the isotropic (δ_{F1}) and in the observed dimension (δ_{F2}) for all ten resonances together with the isotropic chemical shifts obtained according to $\delta_{iso} = (17\delta_{F1} + 10\delta_{F2})/27$ are listed in Table 1.

Resonances I, VII, VIII, and X arise from small shoulders, and it may be argued that they are less safely determined than the other six resonances. However, each of resonances I–VII

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[**] Supported by the Academy of Sciences of the Czech Republic (project no. 1ET400400413), the Grant Agencies of the Czech Republic (project no. 203/06/1449), and of the Academy of Sciences of the Czech Republic (project no. IAA4040308), by the German Research Foundation (DFG) and the Funds of the German Chemical Industry (FCI). We thank Prof. Peter F. Rogl of the University of Vienna, Austria for helpful discussions on crystallography questions.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

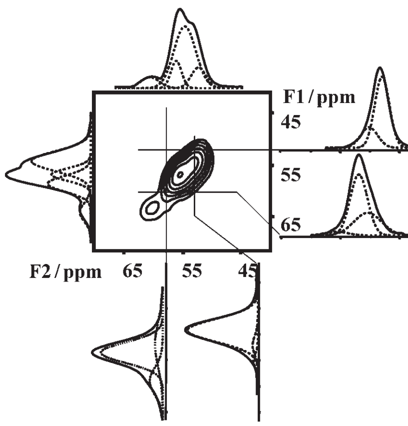

Figure 1. 2D plot of the ^{27}Al 3Q MAS NMR sheared spectrum of Na-ZSM-5/B, F1 and F2 projections and selected normalized slices with simulations (dotted lines).

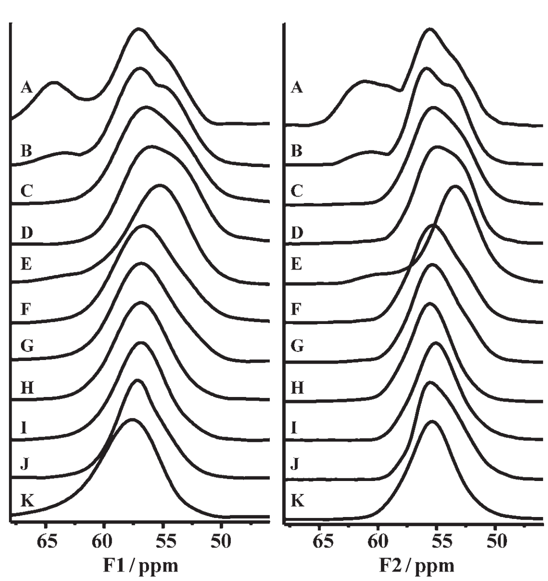

Figure 2. F1 (left) and F2 (right) projections of the 2D ^{27}Al 3Q MAS NMR spectra of Na-ZSM-5 zeolites.

and IX was found for at least two samples, and resonances III, V, and X for sample **E** were also observed for ZSM-5 exchanged with two different counterions, Li^+ and H^+ (see Table S2 of the Supporting Information). Note that samples with similar Si/Al ratios (**A**, **E**, **G**, **K**) can show different resonances, whereas samples with rather different Si/Al ratios (e.g. **A**, **B**) can show similar shifts, though with different intensities. We conclude that at least ten framework T sites are occupied by Al atoms in the 11 different Na-ZSM-5 samples, which is substantial progress compared to previous studies. Sarv et al.[3] examined just one ZSM-5 sample and, thus, could report only three ^{27}Al resonances. Furthermore, we find that only between three and four T sites are occupied by Al in a given sample, but 11 different ZSM-5 samples have been studied. Han et al.[4] reported only two resonances for a set of samples with different Si/Al ratios, but all of those samples were prepared by the same procedure; furthermore, the structure-directing agent was not removed. It can be excluded that several observed ^{27}Al resonances belong to the same framework T site, because we have shown that in samples **A**–**K**, there are no Al-O-Si-O-Al pairs (by ^{29}Si NMR spectroscopy), and the population of close Al atoms (Al-O-(Si-O)$_2$-Al sequences) is low (by Co^{II} exchange experiments). There is also no correlation between the presence of close Al atoms and the observed ^{27}Al resonances.

If the atomic positions are known, DFT can be used to calculate the chemical shifts using finite cluster models around the magnetic nucleus.[10–13] This approach succeeded in reproducing the correct sequence of the 12 lines in the ^{29}Si NMR spectrum of the orthorhombic ZSM-5 structure.[10] We determined the atomic positions for the ZSM-5 structures with Al in the 24 different crystallographic positions by hybrid quantum mechanics/molecular mechanics (QM/MM) calculations as implemented in the QMPOT code.[14,15] The latter treats the atoms around the magnetic nucleus by DFT using TURBOMOLE[16–18] (BLYP[19,20] functional with TZVP basis set[21]), whereas the surrounding atoms in an MFI double cell are described by a DFT-parametrized shell-model ion-pair potential[15] using GULP.[22] A cluster of five coordination shells around Al (Al-O-Si-O-Si-O-H$_{link}$) is adopted.[10]

High resolution of ^{27}Al MAS NMR spectra can be reached only for fully hydrated matrices because of strong quadrupolar interactions in dehydrated zeolites.[23] To avoid the massive computational problem connected with the large number of possible atomic configurations of the hydrated cations in the zeolite cavities, we use a bare framework with a single Al atom in a unit cell as a simple model. We expect the effect of the hydrated countercation on the local geometry of AlO_4 tetrahedra to be small, because in hydrated silicon-rich zeolites the counterion is located close to the center of the cavity or channel[24] and does not directly interact with the AlO_4 tetrahedra.[25] Furthermore, comparison of Na-exchanged ZSM-5 (sample **E**) with the corresponding Li^+- and H^+-exchanged samples shows that the effect of the hydrated countercation on the ^{27}Al isotropic chemical shift is negligible (0.1 ppm, see Table S2 of the Supporting Information),[26] which has also been found for calculated ^{29}Si NMR spectroscopic shifts of monosilicate species.[27] Hence, the shielding depends primarily on the local structure around the magnetic nucleus, and solvent and counterions do not affect the shielding by "through-space" effects.

Our QM/MM calculations (P1 symmetry) resulted in 24 distinguishable structures corresponding to Al substitution at the 24 T sites of monoclinic ZSM-5. Subsequently, the NMR spectroscopic shielding tensors of the atoms of the optimized five-shell clusters were calculated by the gauge-independent atomic orbital method (GIAO)[28] using Gaussian03.[29] The calculated ^{27}Al shielding values (see Table S3 in the Supporting Information) were converted to isotropic shifts using the experimental shift ($\delta = 60$ ppm)[30] and calculated shielding ($\delta = 490$ ppm) of a silicon-rich (Si/Al = 35) chabasite structure as a secondary internal standard.

Figure 3 compares the calculated and measured ^{27}Al isotropic chemical shifts for ZSM-5 (see also Table 1). The values for the different sites extend over ranges of $\Delta\delta = 14.1$ and 13.6 ppm, respectively. This finding strongly supports the

Table 1: NMR parameters of the individual ^{27}Al resonances of the ZSM-5 samples A–K determined from spectra and two T site assignments.

Sample	A	B	C	D	E	F	G	H	I	J	K	Resonance	Assignment 1		Assignment 2	
Si/Al$_f$[a]	15	45	35	25	15	25	15	25	35	26	14		DFT	T site	DFT	T site
δ_{F1}			49.2	49.3		49.5						I				
δ_{F2}			51.1	51.2		51.3						50.0 ± 0.1	50.7	20	50.7	20
δ_{iso}			**49.9**	**50.0**		**50.2**										
δ_{F1}			53.2	53.3		53.3						**II**				
δ_{F2}			52.4	52.4		52.3						**52.9 ± 0.1**	**53.3**	**8**	**53.3**	**8**
δ_{iso}			**52.9**	**53.0**		**52.9**										
δ_{F1}	54.6	54.4			54.9		54.1				54.4	**III**				
δ_{F2}	52.5	52.5			52.3		52.5				52.4	**53.7 ± 0.2**	**53.4**	**4**	**53.4**	**4**
δ_{iso}	**53.8**	**53.7**			**53.9**		**53.5**				**53.7**					
δ_{F1}								55.1	55.4	55.5		**IV**				
δ_{F2}								53.6	53.6	53.6		**54.7 ± 0.2**	**55.1**	**6**	**55.1**	**6**
δ_{iso}								**54.5**	**54.7**	**54.8**						
δ_{F1}	56.9	56.9	56.7	57.4	57.1	56.8	57.1	56.9	57.0	57.4	57.6	**V**				
δ_{F2}	55.5	55.4	55.3	55.7	55.6	55.3	55.4	55.5	54.9	55.4	55.3	**56.5 ± 0.3**				
δ_{iso}	**56.4**	**56.6**	**56.2**	**56.8**	**56.5**	**56.2**	**56.5**	**56.4**	**56.2**	**56.7**	**56.7**					
δ_{F1}		59.2	59.0			59.0	59.5		59.0	59.3		**VI**				
δ_{F2}		56.6	56.8			56.6	56.5		56.4	56.1		**58.1 ± 0.2**				
δ_{iso}		**58.2**	**58.2**			**58.1**	**58.4**		**58.0**	**58.1**						
δ_{F1}							60.0	59.9				VII				
δ_{F2}							57.3	57.4				59.0				
δ_{iso}							**59.0**	**59.0**								
δ_{F1}											60.9	VIII				
δ_{F2}											58.5	60.0	60.0	7	60.8	12
δ_{iso}											**60.0**					
δ_{F1}	64.1	63.9										**IX**				
δ_{F2}	61.0	60.7										**62.8 ± 0.1**	**62.5**	**17**	**63.7**	**1**
δ_{iso}	**62.9**	**62.7**														
δ_{F1}					64.5							X				
δ_{F2}					62.0							63.6	63.7	1	64.8	24
δ_{iso}					**63.6**											

[a] Si/Al framework ratio as determined by NMR spectroscopy.

conclusion that the ten identified resonances belong to Al in different crystallographic sites. A previous study,[4] in which only two resonances were resolved, came to a different conclusion. The authors employed the correlation between empirical chemical shift and average T-O-T angle.[31] The isotropic ^{27}Al shifts calculated from the (orthorhombic) XRD structure of a ZSM-5 sample for the 12 T sites varied over a range of only $\Delta\delta = 5.1$ ppm, and all the F1 and F2 parameters fell into the observed 3Q spectrum.[4] The present calculations show that this result is an artifact owing to the bond angles, which are essentially Si-O-Si angles with only small contributions of Si-O-Al angles because of the low Al content (Si/Al ratio 86).[32]

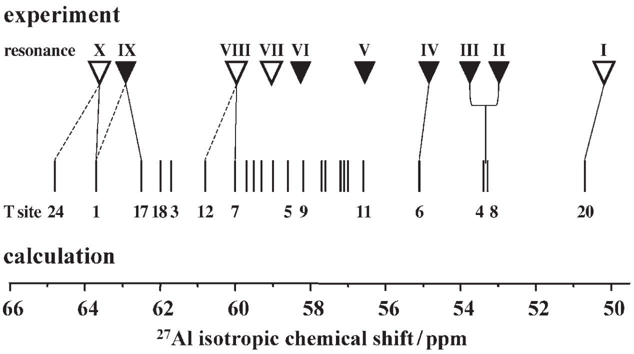

Figure 3. Comparison of the theoretical (lines) and observed (▼,▽; ▽ resonances arising from shoulders in Figure 2) indicates a tentative assignment) ^{27}Al isotropic chemical shifts of Na-ZSM-5 samples. Full and broken connecting lines indicate two different possible assignments (see text).

The patterns of the predicted and observed isotropic shifts in Figure 3 show significant similarities. Based on similar spacing and least deviations between calculated and observed shifts, a partial assignment to crystallographic sites in ZSM-5 is possible (Table 1): Resonance I (hereafter R-I) corresponds to T20 and R-IV to T6. The R-II, R-III pair can be assigned to the T4, T8 pair. At the low-shielding end, two assignments are plausible. The smallest deviations between the calculated and observed shifts are reached if it is assumed that T24 ($\delta =$ 64.8 ppm) is not occupied in the samples and that R-X belongs to T1, R-IX to T17, and R-VIII to T7. The shift deviations are all between $\Delta\delta = +0.7$ and -0.3 ppm, and the calculated range is $\Delta\delta = 13.0$ ppm, only 0.6 ppm smaller than the I–X range of observed resonances (13.6 ppm). It follows that sites T12 (60.8), T3 (61.7), and T18 (62.0) are most likely not occupied by Al in our ZSM-5 samples. To which of the remaining 13 T sites R-V to R-VII belong remains open (Figure 3). If we assume that the calculated shifts are systematically larger by $\delta = 0.7$–1.2 ppm than those observed (see Figure 3 and Table 1) owing to a shift of the secondary standard, we can assign R-X and R-IX with the largest shifts to the least shielded T24 and T1 sites, respectively, and R-VIII to T12. Then the sites T3 (61.7), T18 (62.0), and T17 (62.5) would be unoccupied by Al in our ZSM-5 samples. This second assignment leads to deviations between $\Delta\delta = +1.2$ and -0.3 ppm, and the calculated shift range ($\Delta\delta = 14.1$ ppm) would be 0.5 ppm larger than the observed one.

Even if four of the ten resonances remain tentative (▽ in Figure 3), the above results represent significant progress in interpreting ^{27}Al MAS NMR spectra of zeolites and demonstrate the power of high-resolution NMR spectroscopy combined with DFT (QM/MM) calculations. We conclude that the Al distribution over framework T sites is neither random nor controlled by a simple rule but depends on the conditions of zeolite synthesis. This approach can be employed to investigate the effect of the Al siting on the physicochemical properties and activity of zeolite catalysts.

Received: June 15, 2007
Revised: August 14, 2007

Keywords: aluminum · density functional calculations · NMR spectroscopy · zeolites

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[32] Moreover, the correlation between chemical shift and bond angle seems to be of limited validity for high-silica zeolites, as the data in Table S3 and Figure S1 of the Supporting Information indicate; see also reference [13].