Distribution of Aluminum in Different Periodical Building Units of MOR and BEA Zeolites

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Various commercial, homemade, and dealuminated mordenites (MOR) and beta (BEA) zeolites as well as cobalt modified BEAs have been characterized by ^{29}Si- and ^{27}Al solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy. The quantitative contributions of Si(nAl) and Si(OH)$_x$ sites to the NMR signal intensities were calculated from the various Si/Al ratios and relative ^{29}Si and ^{27}Al NMR signal intensities assuming a special distribution of aluminum in different periodical building units of the zeolite framework. A different dealumination and silanol formation mechanism for MOR and BEA was suggested. We conclude that we are able to distinguish the Si(OH)$_x$ groups that are original defect sites or produced in a dealumination or calcination process.

Introduction

Characterization of zeolites by solid-state magic angle spinning nuclear magnetic resonance (MAS-NMR) spectroscopy can be regarded as a routine method.[1] The framework structure of these micro- (zeolite) and mesoporous materials consists of TO$_4$ (T = tetrahedrally coordinated atom, generally Si^{4+} or Al^{3+}) tetrahedra assembled together through sharing oxygen atoms forming different subunits. These building blocks are repeating to infinite lattices. The presence of trivalent T atoms (Al^{3+}) generates negative charges, which are generally compensated by ion-exchangeable cations in the voids of the framework. In addition to cations, the cages or channels of the lattice usually contain water or organic molecules (templates), which can be removed by heating for instance. Finally, a regular porous structure forms with molecular dimensions.[2,3]

Zeolites can be submitted to various dealumination treatments in order to increase their thermal stability and the strength of their acid sites. The dealumination procedures can be classified to hydrothermal treatments and chemical treatments. The detailed mechanism of these treatments is not well-known, but during this process aluminum is extracted from the framework of the zeolite; therefore, the Si/Al ratio of the framework is increasing.[1]

The silicon-aluminum ordering in zeolites and the state of aluminum incorporated either in the framework or out-of-lattice (extraframework) positions can be obtained by ^{29}Si and ^{27}Al NMR spectroscopy. The Si/Al ratio of zeolites and the number of crystallographically distinct sites for the five different Si-(nAl) ($n = 0-4$) configurations can be determined by ^{29}Si NMR. The ratio of tetrahedral silicon and aluminum in the zeolite framework can be calculated directly from the line intensities in a ^{29}Si MAS-NMR spectrum by the following equation assuming that the Al−O−Al avoidance rule of Loewenstein is

obeyed and Si(OH)$_x$ signals are not included in the bands:[1]

$$(\text{Si/Al})_{\text{NMR}} = \sum I_{\text{Si}(n\text{Al})} / \sum n/4 \, I_{\text{Si}(n\text{Al})}$$
$$\text{summation is from } n = 0 \text{ to } n = 4 \quad (1)$$

The resulting Si/Al ratio may strongly underestimate the actual Si/Al ratio because defect sites (Si(OH)$_x$ groups) are generally present in the zeolite framework.

^{1}H-^{29}Si cross-polarization (CP) makes possible the detection of silicon atoms to which one or more hydroxyl groups are attached. In the CP spectra, the line intensities of silicon atoms bearing OH groups are selectively and strongly enhanced. ^{27}Al NMR characterizes aluminum species of different (tetra- or octahedral) coordination. The line (at ca. 55 ppm) of tetrahedral aluminum in the zeolitic lattice is well separated from the line (at 0 ppm) of out-of-lattice octahedral aluminum. Their quantities can be determined quantitatively following appropriate calibration.[1]

The dealumination mechanism of relatively high Al-containing Y zeolites has been studied intensively in the literature. The pioneering work of Engelhardt et al.[4] first estimated the degree of dealumination of Y zeolites quantitatively. Recently, Triantafillidis et al.[5] observed tetrahedral extralattice aluminum species, Wouters et al.[6] considered framework-related Al−OH as intermediate species, and Weitkamp et al.[7,8] studied 3-fold-coordinated framework aluminum atoms by NMR during hydrothermal dealumination of Y zeolites. Lutz et al.[9] claimed overestimation of the Si/Al ratios of ^{29}Si NMR compared to those obtained by infrared spectroscopy.

Both mordenite (MOR) and beta (BEA) zeolites possess 12-membered ring pores with similar dimensions. Mordenite exhibits a two-dimensional network of channels consisting of straight 12-membered ring pores connected by twisted 8-membered pores of side pockets. Beta zeolite has a three-dimensional channel system with 12-membered ring apertures.[10]

The silicon−aluminum ordering in mordenites and in their dealuminated forms was first determined by Debras et al.[11] The two diagonal sites, which constitute the four-membered rings in mordenites, are preferentially occupied by aluminum at-

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TABLE 1: Global or Bulk, Lattice or Framework, and NMR Si/Al Ratios, Relative Tetrahedral Al$_T$, and Si(nAl) (n = 2, 1, 0) Coordinations (%) of MOR and BEA Zeolites Calculated from ^{27}Al and ^{29}Si NMR Spectra

zeolite	Si/Al bulk[a]	^{27}Al Al$_T$	Si/Al fram[b]	^{29}Si NMR					2Si(OH)$_2$ + SiOH[d]
				Si/Al$_{NMR}$[c]	Si(2Al)	Si(1Al)	Si(0Al)$_A$	Si(0Al)$_B$	
MOR$_8$	8.37	100	8.37	7.00	8.0	41.3	16.3	34.4	9.4
MOR$_9$	8.70	100	8.70	8.55	7.6	31.5	6.9	54.0	0.8
MOR$_{10}$	10.25	100	10.25	9.71	5.9	29.4	18.0	46.7	2.2
MOR$_{12}$	11.90	100	11.90	9.62	5.6	30.3	14.4	49.7	7.9
MOR$_{16}$	15.92	100	15.92	8.50	7.6	31.9	27.7	32.8	21.9
MOR$_{18}$	18.00	82.4	21.83	20.62	2.8	13.8	60.3	23.1	1.1
HBEA$_{12}$	12.30	100	12.30	9.40	6.5	29.5	50.8	13.2	10.0
HBEA$_{18}$	18.21	73.8	24.69	16.55	0	24.2	65.2	10.6	8.0
CoBEA$_S$	19.50	87.1	22.40	13.80	1.1	26.9	62.0	10.0	11.1
CoBEA$_I$	19.50	98.7	19.75	18.90	0.6	20.0	65.7	13.7	0.9

[a] Mean of TG and PIGE. [b] Si/Al$_{fram}$ = (Si/Al$_{bulk}$)/Al$_T$ (fraction). [c] Calculated by eq 1. [d] Calculated by eq 3.

oms.[12,13] Nevertheless, the connectivity-configuration matrices method, developed for the determination of distribution of Al atoms in zeolites, excludes the existence of two Al-atoms containing four-membered rings in mordenites.[14,15]

Jia et al.[16] claimed that the appearance of octahedral Al in the NMR spectra of beta zeolites does not necessarily involve framework aluminum extraction. Kiricsi et al.[17] assigned octahedral Al NMR resonance to transient-state aluminum species that are leaving the framework. Bokhoven et al.[18] identified three-coordinate aluminum in MOR and BEA zeolites with in situ X-ray absorption near-edge spectroscopy (XANES). Abraham et al.[19] observed octahedrally coordinated framework-associated aluminum atoms in BEA zeolites by triple quantum ^{27}Al MAS-NMR. A nonrandom distribution of Al atoms in other zeolites was revealed by ultrahigh-field ^{27}Al MAS-NMR.[20,21]

Bodart el al.[22] computed the number of SiOH groups following dealumination of mordenites by combination of their bulk Si/Al ratios with ^{29}Si and ^{27}Al NMR results. They demonstrated that aluminum atoms preferentially occupy tetrahedral positions in the four-membered rings of the mordenite structure with each ring containing either two or no Al atoms. They suggested that the mechanism of dealumination is removing the aluminum atoms two by two from the four-membered rings. Four SiOH groups per extracted Al atom are generated in the beginning of the dealumination, and this number gradually decreases to two, suggesting that a structural reorganization must occur during the process.

The aim of this work is to develop the method of Bodart et al.[22] further in order to understand the distribution of Al sites over the crystallographic tetrahedral sites and the dealumination process of MOR and BEA zeolites in a deeper level. On the basis of our preliminary[23] and recent results, a new method will be presented for the calculation of the distribution of aluminum atoms in the different periodical building units of these zeolites. Assuming different formation mechanisms, we try to reveal the origin of defect Si(OH)$_x$ groups.

Experimental Section

Various commercial (Norton MOR$_8$ and Degussa MOR$_{16}$) and homemade (MOR$_{9-12}$) mordenites as well as homemade (HBEA$_{12}$, HBEA$_{18}$) beta zeolites with different global or bulk Si/Al ratios (designated in subscript) were studied by ^{29}Si and ^{27}Al MAS-NMR spectroscopy. Part of the MOR$_{16}$ sample was dealuminated by steaming for 20 min at 873 K (MOR$_{18}$). The homemade HBEA$_{18}$ zeolite was modified by cobalt chloride (2.6 wt % metal loading) either by solid-state ion exchange (CoBEA$_S$) or by incipient wetness impregnation (CoBEA$_I$).[24,25] The bulk Si/Al ratios (Table 1) were calculated from the results of thermogravimetric and PIGE[26] analysis. The NMR spectra were recorded on either a Bruker MSL 400 or Avance 500 spectrometer. For ^{29}Si (79.4 MHz), a 6 μs ($\Theta = \pi/6$) pulse was used with a repetition time of 6.0 s. For ^{27}Al (130.3 MHz), a 1 μs ($\Theta = \pi/12$) pulse was used with a repetition time of 0.1 s. The decomposition of the ^{29}Si NMR spectra into contributions of nonequivalent sites (Si(2Al), Si(1Al), and Si(0Al)) was carried out with a precision of about 5%. The effect of this fitting error on the proposed PBU and Si site contributions was also about 5%.

Results

The ^{29}Si NMR spectrum of mordenites with a typical Si/Al ratio of 5 displays three broad signals for Si(2Al), Si(1Al), and Si(0Al) at about −100, −106, and −113 ppm, respectively, the relative intensities of which are 1:2:2. Highly siliceous zeolites exhibit narrower lines with distinctly different intensity distributions of the three Si(nAl) lines. Splitting of the Si(0Al) signal reflects Si atoms in crystallographically nonequivalent T-sites.[1]

The ^{29}Si NMR spectra of MOR$_{8-12}$ samples (Figure 1) show broad signals for Si(2Al), Si(1Al), and Si(0Al) at about the above-mentioned chemical shifts but at different relative intensities (Table 1). The lines assigned to Si(2Al) and Si(1Al) configurations (at −99 and −105 ppm in Figure 1) include relatively few defect sites (Si(OH)$_x$ groups) in the spectra because the shape of normal (Figure 1) and CP (not shown) spectra are similar. However, the Si/Al$_{NMR}$ ratios calculated by eq 1 are lower than those of the global or bulk Si/Al ratios (Table 1), indicating the presence of some defect silanol groups in these mordenites.

The normal and CP ^{29}Si NMR spectra of MOR$_{16}$ and MOR$_{18}$ samples clearly show the effect of dealumination (Figure 2). The broad lines of MOR$_{16}$ (Figure 2a) are resolved to Si(2Al), Si(1Al), and Si(0Al) configurations (Table 1), and the signals assigned to the former two configurations contain defect hydroxyl groups at a high extent according to the CP spectrum (Figure 2b). Following dealumination (MOR$_{18}$), the relative intensity of signals assigned to the Si(2Al) and Si(1Al) configurations at −104 and −106 ppm (Figure 2a) decreases (Table 1) and the Si(0Al) band disrupts to two narrow signals at −113 and −115 ppm (Figure 2c) due to two groups containing distinct crystallographic sites. The signals assigned to Si(2Al) and Si(1Al) configurations also contain some defect silanol groups in the MOR$_{18}$ sample because their relative intensities compared to the Si(0Al) line are somewhat higher in the CP (Figure 2d) than in the normal (Figure 2c) spectrum. The big difference in the NMR (8.5) and bulk (15.9) Si/Al ratio of the MOR$_{16}$ sample (Table 1) clearly indicates that eq 1 is not applicable for this mordenite because of the presence of defect Si(OH)$_x$ silanol sites.
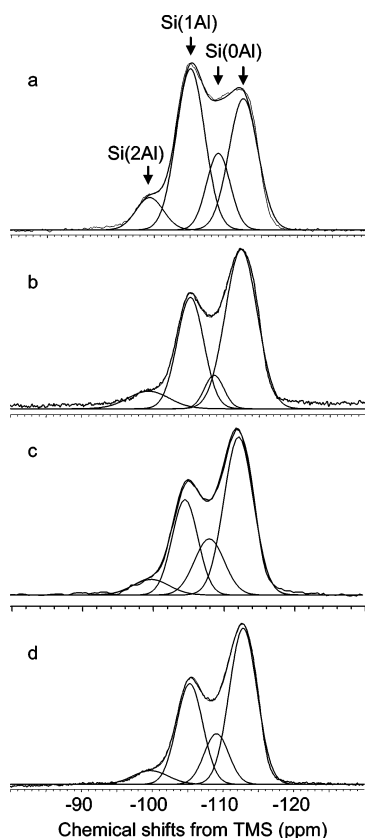
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Figure 1. ^{29}Si NMR spectra of MOR$_8$ (a), MOR$_9$ (b), MOR$_{10}$ (c), and MOR$_{12}$ (d) zeolites.
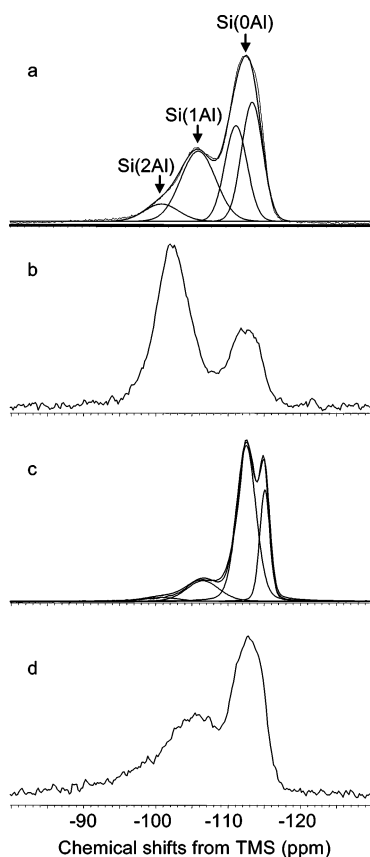

Figure 2. Normal (a, c) and CP (b, d) ^{29}Si NMR spectra of MOR$_{16}$ (a, b) and MOR$_{18}$ (c, d) zeolites.

Beta (BEA) zeolites contain nine crystallographically non-equivalent T-sites;[10] therefore, a rather complex ^{29}Si NMR
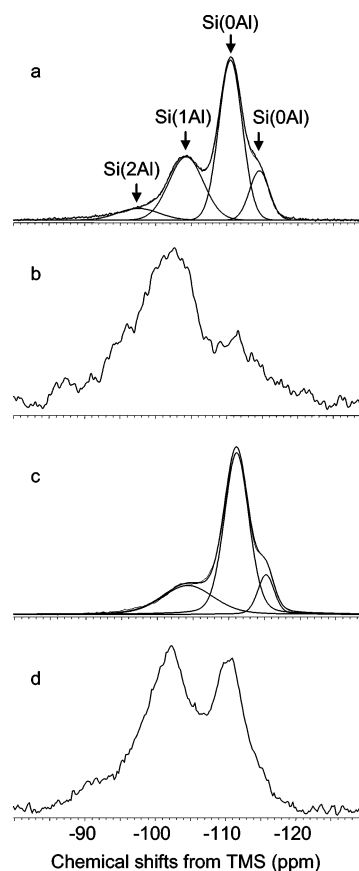

Figure 3. Normal (a, c) and CP (b, d) ^{29}Si NMR spectra of HBEA$_{12}$ (a, b) and HBEA$_{18}$ (c, d) zeolites.

spectrum is expected. The high resolution spectrum of highly dealuminated BEA exhibits three groups of nine lines,[27] but because of the high concentration of stacking faults in the zeolite structure, three signals are generally observed.[28]

The ^{29}Si NMR spectra of HBEA$_{12}$ and HBEA$_{18}$ zeolites (Figure 3) show four and three resonances at -98, -104, -111, and -115 ppm, which can be ascribed to Si(2Al), Si(1Al), Si-(0Al)$_A$, and Si(0Al)$_B$ sites, respectively (Table 1). Splitting of the signal assigned to Si(0Al) configuration is due to two groups of different crystallographic sites.[29] The CP spectra of both zeolites (Figure 3b and d) confirm the presence of SiOH groups in the bands assigned to Si(1Al) configuration (-104 ppm in the normal (Figure 3a and c) and -103 (Figure 3b) or -102 ppm (Figure 3d) in the CP spectra) because their intensities compared to the Si(0Al) bands are higher in the CP than in the normal spectra. In addition, the CP spectrum of HBEA$_{12}$ with its broad intense first line (Figure 3b) suggests the presence of Si(OH)$_2$ groups in the signal assigned to Si(2Al) site at -98 ppm (Figure 3a). The lower Si/Al$_{NMR}$ than bulk and framework Si/Al ratios of HBEA zeolites also exhibits the presence of defect silanol sites (Table 1).

The ^{29}Si NMR spectra of CoBEA zeolites (Figure 4) show four resonances, which can be ascribed to Si(2Al), Si(1Al), Si-(0Al)$_A$, and Si(0Al)$_B$ sites, respectively (Table 1). The Si(2Al) and Si(1Al) lines of CoBEA zeolites include some Si(OH)$_x$ defect sites confirmed by the enhancement of the corresponding lines in the CP spectra (Figure 4) and the lower Si/Al$_{NMR}$ than bulk and framework Si/Al ratios (Table 1).

^{27}Al NMR spectra give information on the Al distribution in structurally distinct sites of the lattice. The ^{27}Al NMR spectra of zeolites containing extraframework aluminum are shown in Figure 5. The sharp signals at 55 ppm are attributed to aluminum
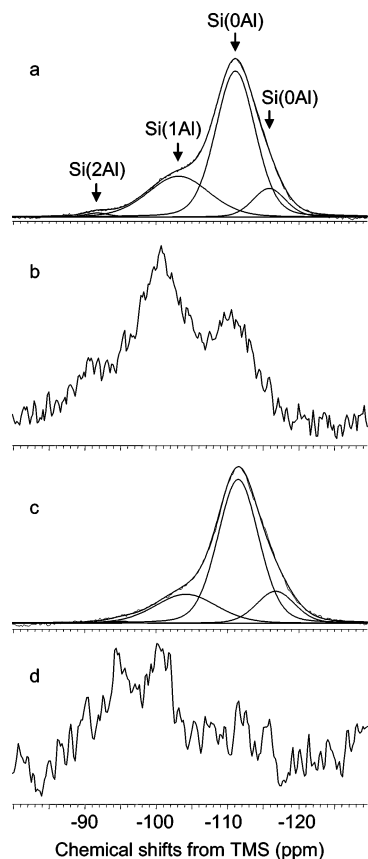
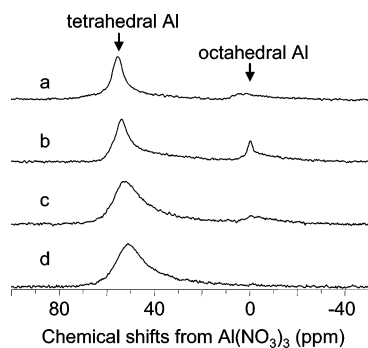**Figure 4.** Normal (a, c) and CP (b, d) ^{29}Si NMR spectra of CoBEA$_s$ (a, b) and CoBEA$_I$ (c, d) zeolites.

Figure 5. ^{27}Al NMR spectra of MOR$_{18}$ (a), HBEA$_{18}$ (b), CoBEA$_s$ (c), and CoBWEA$_I$ (d) zeolites.

in the zeolitic framework at tetrahedral coordination. The NMR spectra for MOR$_{18}$ and all BEA, except HBEA$_{12}$, samples exhibit an additional line at 0 ppm (Figure 5), which is assigned to extraframework aluminum in octahedral out-of-lattice positions. The relative concentration of Al in tetrahedral positions (Al$_T$ in Table 1) was calculated from the relative integrated line areas of the ^{27}Al NMR spectra (Figure 5). The lattice or framework Si/Al ratio is gained by dividing the bulk Si/Al ratio by Al$_T$ (fraction).[1] If a characteristic difference between Si/Al$_{fram}$ and Si/Al$_{NMR}$ exists (Table 1), it clearly indicates the presence of defect silanol groups in the zeolite. The difference between Si/Al$_{bulk}$ and Si/Al$_{fram}$ is the quantitative degree of dealumination. Because of dealumination of MOR$_{16}$, a rather high amount of octahedral aluminum was produced in MOR$_{18}$ and all of the beta zeolite samples, except HBEA$_{12}$, also contain extraframework aluminum (Figure 5).

SCHEME 1: Mordenite Twin (a, b) and Lone (c, d) Periodical Building Unts (PBUs)
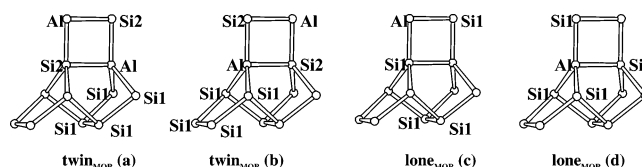
SCHEME 2: Beta Zeolite Twin2 (a), Twin1 (b), and Lone (c) Periodical Building Units (PBUs) in Thickened Lines
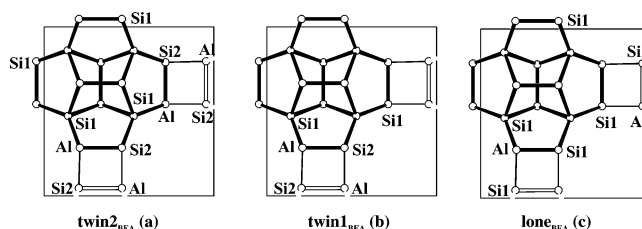
Discussion

The periodic building unit (PBU) of MOR (Scheme 1) is a 12-membered unit composed of two finite zigzag chains and a 4-membered ring, and the one of BEA (Scheme 2) is a tetragonal beta layer composed of 16-membered units connected through 4-membered rings.[30] Bodart et al.[22] suggested that two aluminum atoms are preferentially sitting in the four-membered rings of the mordenite structure in diagonal positions (twin$_{MOR}$ a and b); the configurations with only one Al atom (lone$_{MOR}$ c and d) are excluded. The two silicon atoms in the four-membered rings have Si(2Al) configurations, and the four Si atoms connected to the two Al atoms from outside the four-membered ring have Si(1Al) configurations (twin$_{MOR}$). Because of energetics reasons, Al should occupy the same positions in the four-membered rings of the beta zeolites (twin2$_{BEA}$ and twin1$_{BEA}$). The relative abundance of these sites is 3/4 in the BEA- and 1/3 in the MOR structure; consequently, all aluminum atoms should sit in the four-membered rings of the MOR and BEA zeolites in two-by-two positions in agreement with theoretical calculations.[12,13]

By calculating the theoretical compositions of MOR and BEA zeolites with the model above, we find that the following concentration relations result in Al$_T$ = Si(2Al) = Si(1Al)/2, and after decomposition through dealumination of these PBUs Al$_O$ = Si(OH)$_2$ = SiOH/2. It is well seen in Table 1 that the intensity ratios of Si(1Al) to Si(2Al) lines is much higher than two; therefore, the original "twin PBU only" suggestion[22] should be modified and configurations with "lone" Al atoms in the four-membered rings are also allowed (lone$_{MOR}$ and lone$_{BEA}$). The unit cell of BEA zeolite contains max 7 Al and min 57 Si atoms;[10] therefore, its 16-membered PBU involves less than 2 Al atoms; consequently, the mixture of 2 (twin2$_{BEA}$) and 1 (twin1$_{BEA}$) Al-containing "twin" PBUs are suggested beside the 1 Al atom containing lone PBU (lone$_{BEA}$).

Before calculation of different PBU concentrations, the measured ^{29}Si NMR lines should be resolved to signals originating from Si(nAl) and Si(OH)$_x$ lines. Silanol groups may be produced during preparation (e.g., template burning, calcination, etc.) and/or dealumination of the zeolites. Because only tetrahedral Al atoms containing zeolites may also include "original" defect sites (produced in the preparation procedure), in addition to twin and lone a third kind of PBU ("silicalite") without Al atoms should also be suggested because the disruption of Al−O−Si bonds precedes the splitting of Si−

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TABLE 2: Compositions Calculated for T12 Periodic Building Units (PBUs) of Mordenites[a]

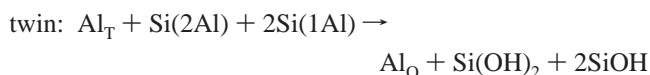| MOR	Σ Al + Si	Al_T	Al_O	Si site contribution				
				$Si(OH)_2$	$Si(2Al)$	SiOH	$Si(1Al)$	$Si(0Al)$
twin/atom	6p	p				p		2p	2p
tw.deal/at	6q		q	q		2q		2q
lone/atom	3(r − 2p)	(r − 2p)/4						r − 2p	7(r − 2p)/4
lo.deal/at	3(s − 2q)		(s − 2q)/4			s − 2q		7(s − 2q)/4
silic./atom	t − (7r − 6p)/4 −(7s − 6q)/4 + w + v			w		v		t − (7r − 6p)/4 −(7s − 6q)/4
Σ		(2p + r)/4	(2q + s)/4	q + w	p	s + v	r	t

[a] p = Si(2Al), q = Si(OH)₂ (dealuminated), r = Si(1Al), s = SiOH (dealuminated), t = Si(0Al), v = SiOH (original), w = Si(OH)₂ (original) concentrations.

TABLE 3: Compositions Calculated for T16 Periodic Building Units (PBUs) of Beta Zeolites[a]

zeolite	Σ Al + Si	Al_T	Al_O	Si site contribution				
				$Si(OH)_2$	$Si(2Al)$	SiOH	$Si(1Al)$	$Si(0Al)$
twin2/atom	8p	p				p		2p	4p
tw2.deal/at	8q		q	q		2q		4q
lone/atom	4(r − 2p)	(r − 2p)/4						r − 2p	11(r − 2p)/4
lo.deal/at	4(s − 2q)		(s − 2q)/4			s − 2q		11(s − 2q)/4
sil.2/atom	t − (11r − 6p)/4 −(11s − 6q)/4 + w + v			w		v		t − (11r − 6p)/4 −(11s − 6q)/4
Σ		(2p + r)/4	(2q + s)/4	q + w	p	s + v	r	t
twin1/atom	16p	p				p		2p	12p
tw1.deal/at	16q		q	q		2q		12q
lone/atom	4(r − 2p)	(r − 2p)/4						r − 2p	11(r − 2p)/4
lo.deal/at	4(s − 2q)		(s − 2q)/4			s − 2q		11(s − 2q)/4
sil.1/atom	t − (11r + 26p)/4 −(11s + 26q)/4 + w + v			w		v		t − (11r + 26p)/4 −(11s + 26q)/4
Σ		(2p + r)/4	(2q + s)/4	q + w	p	s + v	r	t

[a] See designations in Table 2.

O−Si bonds.[1] The following defect sites producing processes are taken into account:

twin: $Al_T + Si(2Al) + 2Si(1Al) \rightarrow$

$$Al_O + Si(OH)_2 + 2SiOH$$

lone: $Al_T + 4Si(1Al) \rightarrow Al_O + 4SiOH$

silicalite: $SiOSiOSi \rightarrow$

$$Si(OH)_2 + 2SiOH \text{ and/or } SiOSi \rightarrow 2SiOH \quad (2)$$

The silanol type defects should be eliminated from the ²⁹Si NMR line intensities in order to calculate the concentration of $Si(OH)_x$ sites. It was shown previously that the ²⁹Si NMR line at −105 ppm ("line1") includes Si(1Al) and SiOH intensities and the line at around −100 ppm ("line2") involves Si(2Al) and Si(OH)₂ signals. Substituting these defect-free line intensity values ($I_{linex} − I_{Si(OH)_x}$) and the real Si/Al$_{fram}$ ratios (gained from ²⁷Al NMR results) to eq 1, the following $2I_{Si(OH)_2} + I_{SiOH}$ concentrations (Table 1) can be calculated by eq 3

$$Si/Al_{fram} = 4/[\, 2(I_{line2} − I_{Si(OH)_2}) +$$

$$(I_{line1} − I_{SiOH})] \text{ (if } \sum I_{Si(nAl)} = 1)$$

$$2I_{Si(OH)_2} + I_{SiOH} = 2I_{line2} + I_{line1} − 4/Si/Al_{fram} \quad (3)$$

To calculate the quantity of silanol sites from the sum gained by eq 3, one should take an assumption to the ratios of SiOH to $Si(OH)_2$ concentrations. It is well seen from eq 2 that this

ratio should be higher than 2 if not only twin units are present. We assume that during dealumination the defect $Si(OH)_x$ groups are originated with equal probability from the Si(2Al) and Si-(1Al) configurations, which means that their ratios should not change remarkably during the process. The following intensity ratios are supposed:

$$Si(OH)_2/Si(2Al) = SiOH/Si(1Al) = Al_O/Al_T \quad (4)$$

The formulas used in the calculation of PBU compositions are shown in Table 2 for mordenites and in Table 3 for the beta zeolites. The Si(2Al) (p), Si(OH)₂ (deal) (q), Si(1Al) (r), and SiOH (deal) (s) concentrations are calculated with eqs 3 and 4 from the data shown in Table 1 normalized to Σ(Si + Al species) = 1. The Si(0Al), Si(OH)₂ (orig) (w), and SiOH (orig) (v) contents of silicalite PBUs are the differences of all Si(0Al) (t) and all $Si(OH)_x$ groups (Table 1 normalized) and those that are included in the twin and lone PBUs or produced during their decomposition. Two compositions are possible for beta zeolites with twin2, lone, and silicalite2 or twin1, lone, and silicalite1 PBUs (Table 3).

The suggested twin, lone, and silicalite PBU compositions are in accordance with the generally accepted view; accordingly, aluminum atoms occupy four-membered ring positions in the zeolite lattices.[11−13] Even these compositions do not harm the validity of the 2Al/5-ring avoidance rule of the connectivity-configuration matrixes method.[14,15]

The computed PBU compositions with formulas presented in Tables 2 and 3 are shown in Table 4. The ratio of lone PBUs

TABLE 4: MOR and BEA Zeolite Compositions (%) Assuming Perfect, Theoretical Twin (BEA: Twin2 or Twin1), Lone, and Silicalite PBUs

zeolite	PBU	PBU Al	PBU deal	Al_T	Al_O	Si(2Al)	Si(OH)$_2$	Si(1Al)	SiOH	Si(0Al)
MOR$_8$	twin	35.6	0	5.9	0	5.9	0	11.9	0	11.9
	lone	64.0	0	4.7	0			18.9	0	33.2
	silicalite	0.3					1.2 ↑		6.0 ↑	0.3
MOR$_9$	twin	40.3	0	6.7	0	6.7	0	13.4	0	13.4
	lone	43.2	0	3.6	0			14.4	0	25.2
	silicalite	16.5					0.1		0.5	16.0
MOR$_{10}$	twin	30.6	0	5.1	0	5.1	0	10.2	0	10.2
	lone	45.5	0	3.8	0			15.2	0	26.5
	silicalite	23.9					0.3		1.4	22.2
MOR$_{12}$	twin	25.2	0	4.2	0	4.2	0	8.4	0	8.4
	lone	42.6	0	3.6	0			14.2	0	24.9
	silicalite	32.2					1.0		5.3	25.8
MOR$_{16}$	twin	22.8	0	3.8	0	3.8	0	7.6	0	7.6
	lone	25.3	0	2.1	0			8.4	0	14.8
	silicalite	51.9					3.3		14.0	34.6
MOR$_{18}$	twin	15.0	0.9	2.5	0.1	2.5	0.1	5.0	0.3	5.3
	lone	22.0	1.3	1.8	0.1			7.3	0.4	13.6
	silicalite	60.1					0		0	60.1
HBEA$_{12}$	twin2	36.8	0	4.6	0	4.6	0	9.2	0	18.4
	lone	46.7	0	2.9	0			11.7	0	32.1
	silicalite	16.5					1.4		6.4	8.6
HBEA$_{18}$	twin2/1	0	0	0	0	0	0	0	0	0
	lone	61.4	20.7	3.8	1.3			15.4	5.2	56.5
	silicalite	17.8					0		2.4	15.4
CoBEA$_S$	twin2/1	4.9/9.8	0.7/1.4	0.6	0.1	0.6	0.1	1.2	0.2	2.8/8.4
	lone	58.1	8.2	3.6	0.5			14.5	2.1	45.6
	silicalite	28.0/22.4					0.3		7.6	20.1/14.5
CoBEA$_I$	twin2/1	4.2/8.3	0.1/0.1	0.5	0	0.5	0	1.0	0	2.1/6.3
	lone	68.8	0.8	4.3	0.1			17.2	0.2	47.9
	silicalite	26.2/22.0					0		0.6	25.6/21.4

always exceeds the concentration of twin units; therefore, the twin only assumption of Bodart et al.[22] must be modified. Silicalite units do not exist in the MOR$_8$ sample because the concentration of Si(0Al) is practically zero in this PBU. Therefore, presumably the original silanol groups are sitting preferentially in the decomposed lone units, far from the Al atoms in the MOR$_8$ zeolite. The presence of twin1 units is not possible in the most Al-containing beta zeolite (HBEA$_{12}$). Twin PBUs are not present in the HBEA$_{18}$ sample because of the lack of Si(2Al) in the structure. A general rule seems to be the higher stability of lone PBUs compared to the stability of twin units with changing Si/Al ratios.

The original defect sites can be clearly distinguished from those that are produced in the dealumination process. The MOR$_{16}$ sample contains a high amount (3.3 + 14.0%) of original defect groups. The ratio of twin to lone units is similar in the MOR$_{16}$ (0.9) and in dealuminated MOR$_{18}$ (0.7) zeolites. During dealumination of MOR$_{16}$ to MOR$_{18}$, both Al-containing PBUs decompose in a similar rate without preference. During dealumination of MOR$_{16}$ to MOR$_{18}$, all of the original defect groups decompose, and new dealuminated silanol groups form (0.1% Si(OH)$_2$ and 0.3 + 0.4% SiOH) from the twin and lone PBUs (Table 4).

Dealumination of the four-membered rings containing two Al atoms and two Si atoms in Si(2Al) configuration with four connecting Si atoms in Si(1Al) configuration should result in two Al$_O$ atoms with two Si(OH)$_2$ and four SiOH groups without any subsequent structural reorganization (eq 2). The dealumination process and the following restructuring of mordenites and beta zeolites can be different because all of the positions in the 4-membered rings are parts of the 12-membered rings in

the BEA-, but only half of them are situated in the 12- and another half of them in the 8-membered rings in the MOR structure. Because of this structure difference between MOR and BEA, the stability of the generated Si(OH)$_x$ groups and the formed hydroxyl nests may also be different.

As was already discussed in the Introduction, framework-related 3-fold-coordinated Al—OH intermediate species may exist in dealuminated zeolites,[6−8,18] which means a one-to-one SiOH/(3SiO)Al ratio. Indeed, the shoulder at ca. 30−40 ppm in the ^{27}Al NMR spectra (Figure 5c and 5d) suggests the presence of deformed tetrahedral atoms, that is, (SiO)$_3$AlOH, in the structure. In the hydrated state, water molecules are coordinatively bound to these (3SiO)Al species, leading to an equilibrium between tetrahedral and octahedral configuration, which is reflected in the ^{27}Al NMR spectra. The extraordinary sharpness of the octahedral line in the spectrum of HBEA$_{18}$ (Figure 5b) indicates a very high symmetry of this configuration. Exchange of the acidic protons of HBEA by cobalt ions results in an ionized tetrahedral configuration, which explains the conversion of octahedrally into tetrahedrally coordinated aluminum observed in the ^{27}Al NMR spectra (Figure 5 and Table 4) in accordance with the literature.[31]

By comparing mordenites and beta zeolites with similar Si/Al ratios (MOR$_{12}$ with HBEA$_{12}$ and MOR$_{18}$ with HBEA$_{18}$), we find that a distinct difference is the much higher silicalite PBU ratio in the MOR than in the BEA structure (32.2% and 60.1% compared to 16.5% and 17.8%, see Table 4). At the same time, MOR$_{12}$ and HBEA$_{12}$ contain original silanol sites in similar amounts (Table 4, 1.0% and 1.4% Si(OH)$_2$ as well as 5.3% and 6.4% SiOH, respectively). The main difference between the partially dealuminated MOR$_{18}$ and HBEA$_{18}$ samples is that

Distribution of Al in MOR and BEA Zeolites

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the latter structure does not contain twin PBUs and the mordenate has no original and only few dealuminated (0.8%, see Table 4) defect sites. The other difference is the presence of the aforementioned highly symmetric hydrated and hydroxyl group containing octahedral aluminum in the lattice of HBEA$_{18}$.

The difference in the mechanism of dealumination of MOR and BEA zeolites can be explained by their different structures. As was mentioned before, the lattice of BEA bears only 12-membered rings, and its more symmetric and open structure than that of MOR may favor the disruption of twin compared to lone PBUs and better stabilizes the conservation of both original and dealuminated defect sites.

Conclusions

The method of Bodart et al.[22] for determining aluminum siting and dealumination mechanism of mordenites was developed further. Besides the two or no Al atoms siting in the four-membered rings of periodical building units of mordenites and beta zeolites, we assumed that lone Al atoms may also be situated in these rings. The possible contribution of both Si-(2Al) configurations and defect Si(OH)$_2$ species to the line intensities originally attributed to Si(2Al) signals were also taken into account when calculating the PBU compositions. The only assumption taken for the distribution of silanol groups was that they are originating with equal probability from the Si(2Al) and Si(1Al) configurations during the dealumination process.

A detailed theoretical structure analysis of MOR and BEA lattices enabled us to achieve a deeper understanding of the origin of defect sites, the mechanism of dealumination, and ion-exchange through the ^{29}Si and ^{27}Al NMR analysis of Si and Al site contribution. We conclude that we are able to distinguish the Si(OH)$_x$ groups that are original defect sites or produced in a dealumination or calcination process. Mordenites contain silicalite PBUs at a higher ratio than beta zeolites at similar Si/Al ratios. The dealumination of mordenite resulted in the disappearance of original defect sites and the production of new silanol groups. The more symmetric structure of BEA than that of MOR preserves the presence of both kinds of defect sites better. The ion exchange of protons to cobalt ions effected the conversion of octahedrally into tetrahedrally coordinated aluminum in BEA zeolites. All of the studied zeolites contain lone Al sites in remarkable amount contrary to the exclusive two-by-two Al sitting in the theoretical structure of four-membered rings.

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