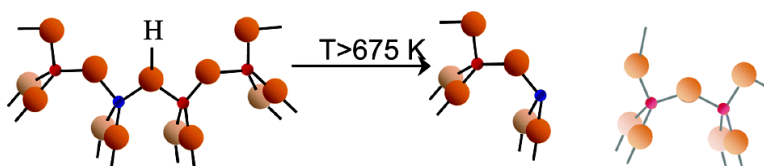


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## Three-Coordinate Aluminum in Zeolites Observed with In situ X-ray Absorption Near-Edge Spectroscopy at the Al K-Edge: Flexibility of Aluminum Coordinations in Zeolites

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**Abstract:** Application of in situ X-ray absorption near-edge spectroscopy (XANES) at the Al K-edge provides unique insight into the flexibility of the aluminum coordinations in zeolites as a function of treatment or during true reaction conditions. A unique, previously not observed, pre-edge feature is detected in zeolites H-Mordenite and steamed and unsteamed H-Beta at temperatures above 675 K. Spectra simulations using the full multiple scattering code Feff8 identify the unique pre-edge feature as three-coordinate aluminum. The amount of three-fold coordinated aluminum is a function of temperature and pretreatment of a zeolite: a steamed zeolite Beta contains more three-coordinate aluminum than an unsteamed sample. No clear differences between zeolites H-Mordenite and H-Beta were observed. Octahedrally coordinated aluminum forms in zeolites H-Mordenite and H-Beta at room temperature in a stream of wet helium. This octahedrally coordinated aluminum is unstable at temperatures higher than 395 K, where it quantitatively reverts to the tetrahedral coordination.

### Introduction

Zeolites are cage-like porous structures based on a framework of silicon, oxygen, and aluminum atoms. In the last fifty years, zeolites are undisputed as excellent catalysts for a wide variety of reactions. In oil refinery, they play a dominant role, and more recently, zeolites are replacing mineral acids as green catalysts.<sup>1</sup> New zeolitic structures continue being discovered, showing that the world of zeolites is thriving.<sup>2–5</sup> This makes it very surprising that structure–activity relations are very often lacking, although detailed crystal structures are well-known.<sup>6</sup> Zeolites are always activated to provide optimum activity and selectivity. These steps or reaction conditions involve perturbation of the framework, and dealumination may occur, creating different aluminum states and changing the texture of the material.

In many reactions, the aluminum atom in the framework is associated with active sites, in both Brønsted and Lewis acid catalyzed reactions. In Brønsted acid catalyzed reactions, a proton, which is charge-balancing the negative charge on the framework induced by the presence of aluminum, is the major

catalytic species. In Lewis catalyzed reactions, both framework and extraframework aluminum species (EFAl) have been suggested as active sites. As methods that can directly probe aluminum coordinations are limited, the structure of these sites remains an open question. In many reports, the presence of a three-coordinate aluminum species is proposed<sup>7–12</sup> and held responsible for Lewis activity. However, often the assumptions are based on indirect methods, and in many cases, its presence is speculative. In general,<sup>27</sup>Al MAS NMR spectroscopy is the preferred method to determine aluminum coordination in zeolites, and its use is widespread. It provides detailed quantitative information (if used correctly) with very high resolution using multiple quantum magic-angle spinning (MQMAS).<sup>13,14</sup> A disadvantage of <sup>27</sup>Al MAS NMR is its problematic use in nonstandard conditions, due to the quadrupolar nature of the aluminum nucleus. Normally, samples are hydrated in a controlled environment to decrease the quadrupolar interactions, thereby enhancing the aluminum visibility.<sup>15</sup> Moreover, the spinning of a sample at high spinning speeds is required for

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obtaining quantitative and high-resolution spectra, limiting the possibilities of measuring a sample at reaction temperatures in the presence of reactants. Moreover, at a high temperature during dehydration, the quadrupolar interactions become increasingly higher, generally leading to increasing loss of resolution or even of the complete signal in the spectra.<sup>16,17</sup> Thus, although quantitative reports on dried zeolitic samples exist, performing <sup>27</sup>Al MAS NMR experiments at nonstandard conditions is a difficult task.<sup>17,18</sup> Clearly, there is a need for a method to determine the aluminum coordination at nonstandard conditions.

Therefore, we turned to X-ray absorption spectroscopy (XAS). XAS is an element-specific technique that provides detailed information about the local structure of the element under investigation.<sup>19</sup> The near-edge spectra of aluminum oxidic compounds with a different first coordination sphere show distinct characteristics.<sup>20–26</sup> Characteristic features for four-, five-, and six-coordinated aluminum have been described, and theoretical insight into the origin of these features has been given using full multiple scattering calculations.<sup>27,28</sup>

An in situ low-energy X-ray absorption fine structure (ILEXAFS) setup has been developed<sup>29,30</sup> for the determination of the coordination of aluminum in zeolites. Using this setup, the aluminum coordinations can be determined at a temperature up to 475 K in the presence of water and up to 1000 K in a vacuum. Although the resolution in an XAFS experiment may not be as high as achievable in an optimized NMR experiment, it enables the direct detection of aluminum coordinations at nonambient conditions. Previous experiments with the ILEXAFS setup have shown that, in acidic zeolites, a transformation of tetrahedrally coordinated aluminum to the octahedral coordination occurs at room temperature in the presence of water,<sup>31</sup> also observed in H–Y zeolite by <sup>27</sup>Al MAS NMR.<sup>32</sup> The XANES measurements show that the octahedral coordination is unstable at temperatures above 400 K, where it reverts back to the tetrahedral coordination.

In this study, the temperature range is extended to a higher temperature (975 K). First, the hydrated state of the sample in

a normal <sup>27</sup>Al MAS NMR experiment is mimicked in the ILEXAFS setup. The changes in the aluminum coordination in zeolites Mordenite and Beta were studied as a function of temperature and the presence of water in the gas phase. In addition, the influence of steaming on the changing aluminum coordinations has been followed. At specific treatment conditions, a three-fold coordinated Al species is detected.

## Experimental Section

**XAS Measurements.** Al K-edge XAS measurements have been performed at the SRS, Daresbury (UK), Station 3.4. The synchrotron was operating at 2.0 GeV with an average current of 120 mA. A double crystal scanning monochromator mounted with YB<sub>66</sub> crystals was used. Measurements were performed in the ILEXAFS setup<sup>29,30</sup> that enables treatment of the sample during measurement. Two different setups have been used. The in situ cell consists of a small sphere with two openings that are sealed with thin X-ray transparent duracoated beryllium windows. The entrance window is 7 μm thick with an oval shape (12 × 8 mm<sup>2</sup>), and it is supported on a grid; the exit window (13 μm thickness, diameter of 23 mm) is integrated with the fluorescence detector, which is a continuously flushed gas proportional counter (GPC). These fragile windows limit the maximum temperature, but a continuous gas flow can be maintained. Omitting the windows and using a GPC with its own protective window enables measurements at temperatures up to 1000 K in a vacuum. Samples are pressed into a self-supporting wafer and positioned on the sample holder. The intensity of the incoming photon beam (*I*<sub>0</sub>) is measured by the total electron yield signal of a fine copper or gold mesh. The X-ray energy is calibrated using an aluminum foil, setting the energy at the first maximum of the first derivative to 1560 eV.

**Samples and Treatments.** Macrocrystalline zeolite Beta (1–2 μm) was prepared according to Kunkeler et al.<sup>33</sup> The as-synthesized Beta was thoroughly washed, ion exchanged, carefully calcined, and ion exchanged to obtain NH<sub>4</sub>-Beta, as previously outlined.<sup>34</sup> Heating in dry nitrogen at 725 K produced H-beta. The Si/Al ratio of this sample was 11.6. Zeolite H-BetaSt was obtained by steaming zeolite NH<sub>4</sub>-Beta in 39 mbar water partial pressure for 3 days at temperature 825 K as previously reported.<sup>48</sup>

Zeolite Mordenite Na-LZM-5 (obtained via BP Amoco, Si/Al = 7) was ion exchanged to obtain NH<sub>4</sub>-Mordenite. Calcination in air at 725 K produced H-Mordenite. Both zeolites were checked with XRD, <sup>27</sup>Al MAS NMR, and N<sub>2</sub> physisorption and showed high crystallinity and 100% tetrahedrally coordinated aluminum in the NH<sub>4</sub> forms.

The Al K-edge XANES measurements were performed in two temperature regimes, low and high temperature. A stream of helium saturated with water at room temperature flowed over the samples during measurement in the low-temperature regime. Al K-edge XANES measurements were performed at regular temperature intervals to a maximum of 475 K. The high-temperature measurements were performed in a vacuum (*P* < 10<sup>-4</sup> mbar). Al K-edge XANES measurements were performed at regular temperature intervals to a maximum of 975 K.

**Feff8 Calculations.** Interpretation of the XANES spectra is performed using the ab initio self-consistent field full multiple scattering code, Feff8.<sup>35,36</sup> The output of a calculation includes the X-ray absorption spectrum and the density of states. Full multiple scattering calculations reproduce Al K-edge XANES spectra very accurately.<sup>27,28</sup> In these papers, the spectra of compounds with four- and six-coordinated

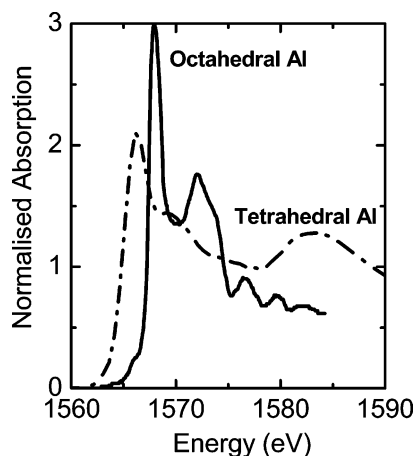
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**Table 1.** Local Structure of Aluminum in  $\text{HAlSi}_{28}\text{O}_{78}$  Clusters Used in the Full Multiple Scattering Calculations

Al coordination	structure
I. tetrahedral	as in zeolite Y
II. trigonal	one oxygen bond <sup>a</sup> lengthened to 2.2 Å three oxygens unchanged
III. trigonal	one oxygen neighbor removed <sup>b</sup> three oxygens unchanged
IV. trigonal	one oxygen neighbor removed <sup>b</sup> planar trigonal, Al–O = 1.75 Å

<sup>a</sup> The oxygen atom containing the hydrogen atom. <sup>b</sup> The hydrogen atom is also removed.

**Figure 1.** Typical Al K-edge XANES spectra for aluminum in tetrahedral (as in  $\text{NH}_4$ -Beta zeolite, dashed line) and octahedral coordination (as in corundum, crystalline  $\text{Al}_2\text{O}_3$ , solid line).

aluminum with known crystallographic structures have been replicated with great detail.

It is known that multiple scattering within a radius of 15 Å affects the shape of the spectra.<sup>27,28</sup> A cluster ( $\text{HAlSi}_{28}\text{O}_{78}$ ) of about 20 Å in diameter was taken from the crystallographic structure of zeolite Y.<sup>6</sup> This size is sufficient to reproduce the characteristic features present in the spectrum of a tetrahedrally coordinated aluminum atom in a zeolite. The aluminum atom is positioned in the center of the cluster.

The structure of a three-coordinate aluminum is unknown. Therefore, the structure of three-coordinate aluminum is mimicked by distorting the tetrahedrally coordinated aluminum in the  $\text{HAlSi}_{28}\text{O}_{78}$  cluster in several ways and observing the changes in the spectral features calculated with Feff8. Table 1 provides the local structures of the three-fold coordinated aluminum, embedded in the  $\text{HAlSi}_{28}\text{O}_{78}$  cluster, that are used in the calculations.

The input parameters are among others the atomic coordinates of the atoms in the cluster and the choice of potential. The Hedin–Lundqvist potential is used in this study. Multiple scattering paths with a maximum of eight legs are calculated in the self-consistent field, full multiple scattering calculations.

## Results

Figure 1 shows typical Al K-edge XAFS spectra for a tetrahedrally and octahedrally coordinated aluminum atom, respectively. The spectrum of a tetrahedral aluminum oxide is that of an  $\text{NH}_4$ -Beta zeolite that has according to <sup>27</sup>Al MAS NMR only framework tetrahedral aluminum. The spectrum of corundum (crystalline  $\text{Al}_2\text{O}_3$ ) is given as an example of an octahedral aluminum. The octahedral aluminum is distorted, and the aluminum has two different Al–O bond distances. Obvious differences in the spectra are visible, of which the most important ones are listed in Table 2. Previously, we have shown

**Table 2.** Characteristic Features in Al K-Edge XANES of Different Aluminum Coordinations

coordination	edge position (eV)	whiteline intensity	split whiteline (eV)	characteristic peaks <sup>a</sup> (eV)	pre-edge
tetrahedral	1566	low	yes	20 and 70	no
(distorted) octahedral	1568	high	4	50	small
square planar <sup>b</sup>		medium	no		large

<sup>a</sup> Indicative of Al–O bond length. <sup>b</sup> Nitrogen coordinates to aluminum.

that exact aluminum coordinations can be determined in samples with mixed aluminum coordinations.<sup>21,34</sup> In Table 2, the characteristics of other coordinations are given as well. In general, the edge position (taken as the maximum in the first derivative) varies with coordination number, being the highest for octahedral aluminum and the lowest for tetrahedral aluminum. For a spectrum of a tetrahedrally coordinated aluminum, a broad peak at about 20 eV above the absorption edge is visible. This peak is characteristic for an aluminum–oxygen bond length of around 1.65–1.75 Å, which is typical for a tetrahedral aluminum. This broad band originates from the multiple scattering in the first aluminum oxide coordination sphere in tetrahedral geometry.

Spectra of octahedrally coordinated aluminum show a high intensity of the edge peak, which consists of a doublet separated by 4 eV (Figure 1). A different octahedral coordination sphere gives a different relative intensity of these two peaks.

The spectrum of a square-planar-coordinated aluminum (like chloroaluminum phthalocyanine<sup>37</sup>) shows a sharp intense pre-edge. This is caused by a transition into the nonbonding  $p_z$  type orbitals. A square-planar aluminum coordination, however, is not common in aluminum oxide and silicon–aluminum oxide framework structures. The high flexibility of a zeolitic framework arises from the flexibility of the T–O–T angles in silica–alumina frameworks, which are much more flexible than the O–T–O angles in the rather rigid tetrahedra.<sup>38,39</sup>

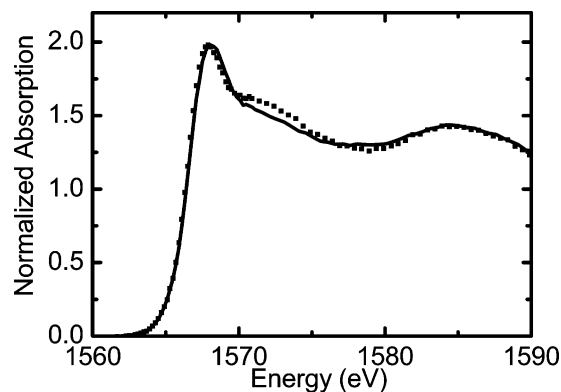
**Aluminum K-Edge XANES at Low Temperature.** Figure 2 shows the Al K-edge XANES spectra of H-Mordenite in a wet helium stream measured at room temperature (squares) and at 395 K (solid line). The squares represent the measured points, showing the good signal-to-noise ratio in the spectra. The sample measured at 395 K shows the characteristic features of tetrahedrally coordinated aluminum. The spectrum measured at room temperature shows a higher intensity at 1570–1575 eV, which has previously been assigned to the presence of a small amount of octahedrally coordinated aluminum.<sup>21,27</sup> A normalization method<sup>27</sup> gives an estimate of the amount of octahedrally coordinated aluminum in the spectrum, here about 10%. Heating this sample to 395 K removes the higher intensity from the spectra, indicative of a transformation of octahedral to tetrahedral aluminum. Previously, we have shown the presence of octahedrally coordinated aluminum in zeolites H-Y and H-Beta,<sup>29,31</sup> measured at room temperature in wet conditions. The environment of the sample during measurement are similar to those of a standard <sup>27</sup>Al MAS NMR measurement, and the results of

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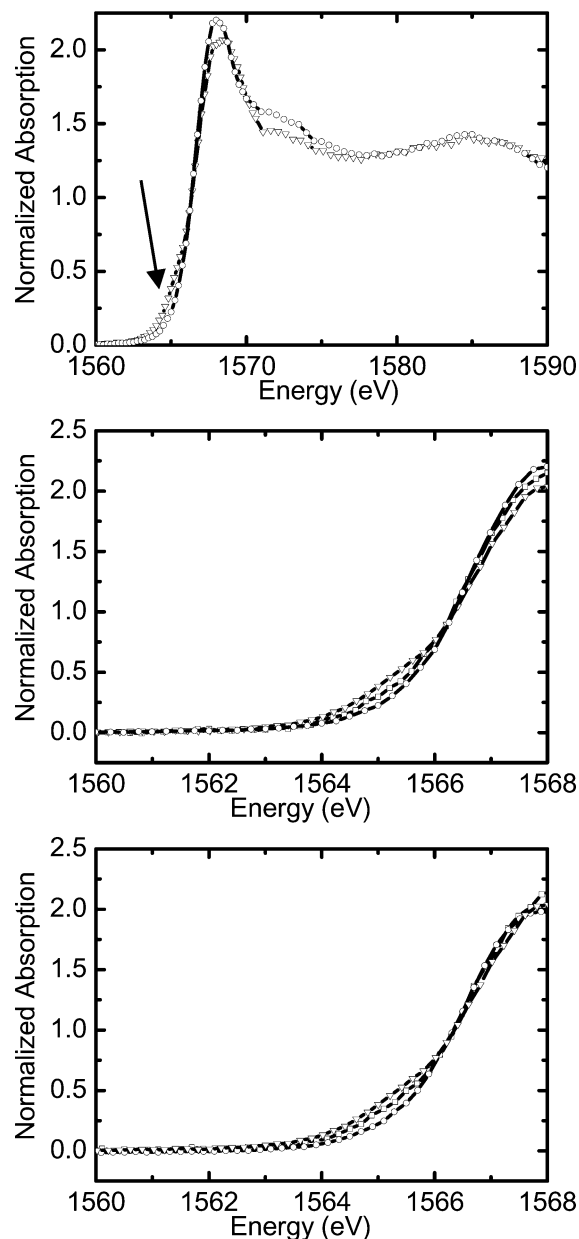


**Figure 2.** Al K-edge XANES spectra of zeolite H-Mordenite taken at room temperature (■) and at 395 K (—). The spectra are taken in a flow of wet helium. The difference in the spectra is due to the presence of a small amount of octahedrally coordinated aluminum in the spectrum taken at room temperature.

both measurement methods were fully comparable. The octahedral to tetrahedral transformation as a function of temperature is also observed for zeolites H-Beta and H-Y.<sup>31</sup> At a small water partial pressure, a transformation of the octahedral aluminum in these zeolites to the tetrahedral coordination occurs at temperatures above 395 K. At room temperature, the reverse transformation takes place.

**Aluminum K-Edge XANES at High Temperature.** Figure 3a shows the Al K-edge XANES spectra of zeolite H-Mordenite measured in a vacuum at room temperature (circles) and at 975 K (triangles). The tetrahedral aluminum features are dominantly visible in both spectra. The higher intensity at 1570–1575 eV is characteristic of the presence of octahedrally coordinated Al in the sample measured at room temperature. A small pre-edge feature is visible (marked by an arrow) in the spectrum of the sample measured at 975 K. In Figure 3b, the energy range near the absorption edge is enlarged and a spectrum measured at 675 K (squares) is compared to those measured at room temperature (circles) and at 975 K (triangles). The low-energy feature appears at temperatures around 675 K, gradually increasing with temperature. Figure 3c compares the spectra taken at 975 K (triangles) with that taken after cooling to room temperature in a vacuum (squares) and after the addition of a small partial pressure of water to the sample (circles). The intensity of the low-energy feature decreases after cooling, but it is slightly more intense than in the spectrum measured at 675 K. It completely vanishes after the addition of water. Meanwhile, the characteristic features of an octahedrally coordinated aluminum appear (not shown), confirming the presence of octahedral aluminum in acidic Mordenite in wet conditions at room temperature.

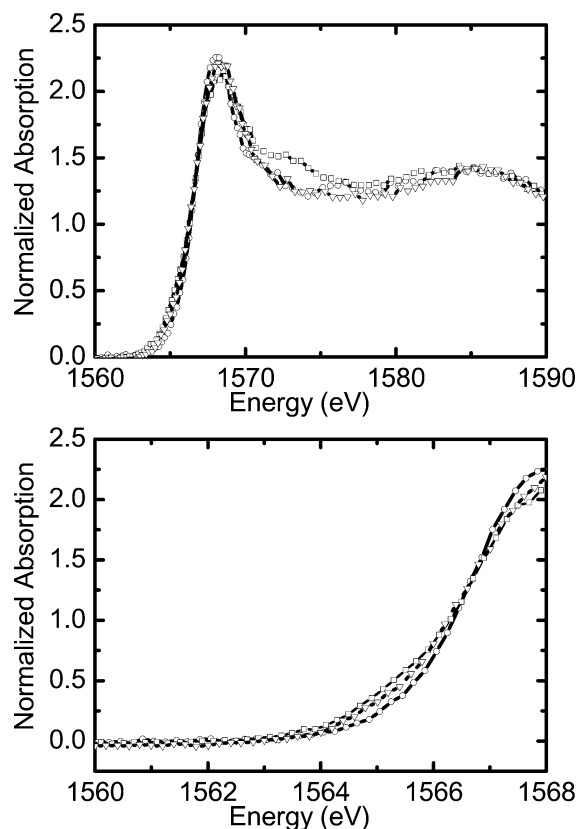
Figure 4a shows the spectra of NH<sub>4</sub>-Beta measured at room temperature (circles) and at 975 K (triangles), compared to the spectrum of BetaSt measured at 975 K (squares). Differences in the spectra are visible in the range 1570–1575 eV, where the steamed sample shows enhanced intensity. Clearly, octahedrally coordinated aluminum is present at 975 K in the steamed sample. In Figure 4b, the edge region is enlarged, and the low-energy feature is visible for both samples measured at 975 K, though the intensity is larger in the case of the steamed zeolite Beta. Clearly, the intensity of the low-energy feature varies with treatment to the zeolite prior to the measurement. The low-energy feature disappears from the spectra after



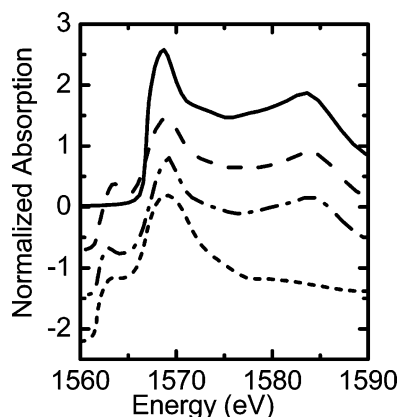
**Figure 3.** (a) Al K-edge XANES spectra of zeolite H-Mordenite taken at room temperature (○) and at 975 K (▽). The spectra are taken in a vacuum. The pre-edge feature, assigned to three-coordinate aluminum, is marked with an arrow. (b) Al K-edge XANES spectra of zeolite H-Mordenite taken at room temperature (○), at 675 K (□), and at 975 K (▽). The spectra are taken in a vacuum. Different quantities of three-fold coordinated aluminum are discernible in the spectra. (c) Al K-edge XANES spectra of zeolite H-Mordenite taken in a vacuum at 975 K (▽) and at room temperature after the heat treatment (□) and in a flow of wet helium at room temperature (○).

exposing the heated samples to air. The presence of traces of water in the gas phase causes also the appearance of the features characteristic of octahedrally coordinated aluminum.<sup>31</sup>

**Full Multiple Scattering Calculations.** Figure 5 shows the theoretical XANES spectra (calculated with Feff8) of the clusters as listed in Table 1. The spectrum of the tetrahedrally coordinated aluminum (solid line) shows the characteristic features as mentioned in Table 2. A sharp edge with a shoulder at 1573 eV and a broad peak at about 1585 eV can be observed. Lengthening the bond length of one of the oxygen neighbors



**Figure 4.** (a) Al K-edge XANES spectra of zeolite  $\text{NH}_4$ -Beta taken in a vacuum at room temperature ( $\circ$ ) and at 975 K ( $\nabla$ ). The squares ( $\square$ ) represent the spectrum of ex situ steamed zeolite Beta taken at 975 K. All spectra are taken in a vacuum. (b) Enlargement of the near-edge region of the spectra in part a.



**Figure 5.** Theoretical Al K-edge XANES spectra of aluminum in a tetrahedral coordination (I in Table 1, solid line), in a trigonal coordination (II in Table 1, dashed line), in a trigonal coordination (III in Table 1, dashed dotted line), and in a planar trigonal coordination (IV in Table 1, dotted line).

to 2.2 Å shows essentially a similar spectrum (long dashed line), except for the appearance of a large pre-edge feature. The broad peak is shifted a little to higher energy, and the sharp edge with its small shoulder is still dominantly discernible. The multiple scattering in the first aluminum oxide coordination sphere remains largely present in this trigonal coordination. Deleting one oxygen neighbor (dotted dashed line) also indicates the presence of a large pre-edge feature, further maintaining the characteristic features of tetrahedrally coordinated aluminum. However, after the exclusion of one oxygen neighboring atom

and distortion of the remaining three oxygen atoms to a planar trigonal coordination, the spectrum changes dramatically (dotted line). The large pre-edge feature is still visible; however, the broad component at about 1585 eV has completely disappeared, because tetrahedral geometry is no longer present. The DOS of all these spectra indicate that the origin of the pre-edge feature is the presence of a mixed nonbonding s,p,d orbital, which is empty due to the unsaturated nature of the aluminum coordination. The presence of the pre-edge feature, indicative of a nonbonding (Al)p-orbital, evidences three-fold coordination of the aluminum atom in the structures (II, III, and IV) presented in Table 1. In structure II, the bond to the oxygen atom with the extremely long aluminum oxygen bond length of 2.2 Å is being broken. A Feff8 calculation on a structure with a distorted tetrahedral coordination in dried acidic zeolites<sup>40</sup> showed no evidence of this pre-edge structure. In this tetrahedral aluminum, three short Al–O bond lengths of 1.68 Å and one long bond length of 1.83 Å are suggested based on quantum chemical calculations. This is confirmed by experimental Al K-edge XANES spectra on acidic zeolites in a completely dry environment that do not show a pre-edge feature,<sup>31</sup> indicating a persisting tetrahedral coordination in acidic zeolitic samples. Reported spectra of compounds containing aluminum in various tetrahedral coordinations do not show the pre-edge feature,<sup>20–24,27,28</sup> indicating that the pre-edge feature is commonly not observed.

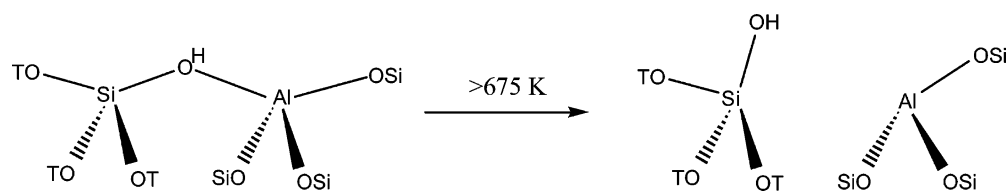
The energy position of the pre-edge feature in the calculated spectra (Figure 5) is lower than that in the experimental spectra. A manual shift of the Fermi-level greatly improves the agreement between the theoretical and experimental spectra (spectra not shown).

## Discussion

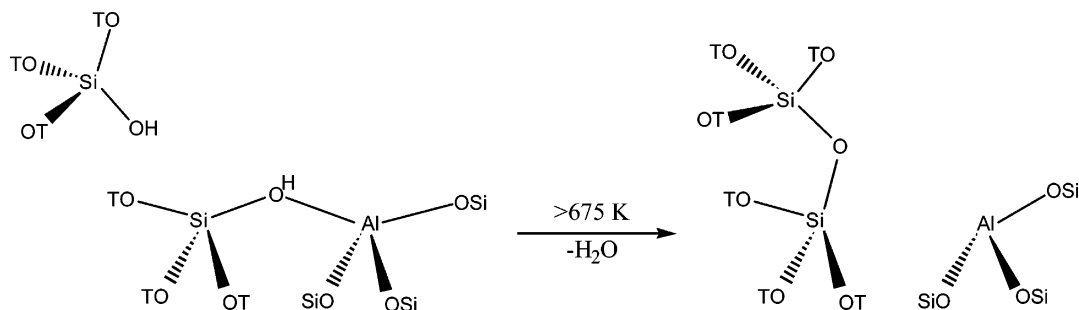
**Three-Coordinate Aluminum in Zeolites.** Zeolites H-Mordenite and H-Beta (steamed and unsteamed) show the presence of a unique pre-edge feature in the Al K-edge XANES spectra when heated to temperatures above 675 K in a vacuum (Figures 3 and 4). This feature is indicative of the presence of a nonbonding p orbital and thus of a three-fold coordinated aluminum oxide species. The assignment is based on full multiple scattering calculations using the Feff8 code. A deviation from the tetrahedral geometry forming a three-fold coordinated aluminum shows a large pre-edge peak in the simulated spectra. Actual structures that may cause the pre-edge feature are presented below. The amount of three-coordinate aluminum is a function of temperature: A significant amount of three-coordinate aluminum is formed at temperatures higher than 675 K. Increasing the temperature to 975 K increases the amount of three-coordinate aluminum. This species is stable after cooling the sample down to room temperature, although the amount diminishes. A direct comparison of the amount of three-fold coordinated aluminum in steamed and unsteamed zeolite Beta (Figure 4a and b) shows that the steamed sample contains more three-coordinate aluminum species at 975 K. The creation of defect sites during the steaming process likely enhances the formation of this three-coordinate aluminum. Three-fold coordinated aluminum is not observed at room temperature without any heat treatment.

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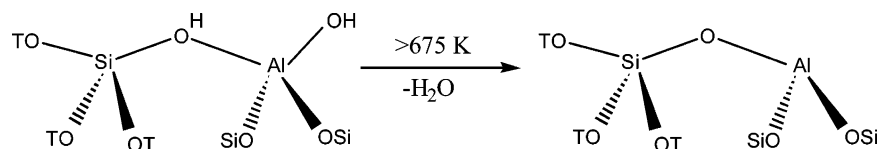
Scheme 1



Scheme 2



Scheme 3



The amount of three-coordinate aluminum is difficult to estimate from the spectra. A comparison of the intensity of the pre-edge feature in the samples with the intensity in the calculated spectra suggests that the amount is at most 10% of the total aluminum content. Currently, only the relative amounts in different samples can be estimated as shown previously. The quantification of these species is a subject of further research.

#### Structure of 3-Fold Coordinated Aluminum in Zeolites.

The mechanisms of dehydroxylation and dealumination in zeolites are not well understood. Although the exact structure of the aluminum species that may cause a pre-edge feature in Al K-edge XANES spectra is therefore difficult to envision, several plausible structures are presented. (i) In the absence of defect sites near the Brønsted acid site, the weakest aluminum oxygen bond may be broken at the very high temperature, without complete dehydroxylation (Scheme 1).

Scheme 1 represents the occurring mechanism according to the first trigonal coordination in Table 1. The weakest aluminum oxygen bond that bears the proton is broken, and an extremely long Al–O distance is present. However, this scheme is expected to be reversible after cooling the sample to room temperature, restoring the original Al–O(H) bond, making the transition of the distorted tetrahedral to three-fold coordination reversible. This is in clear contradiction with the spectroscopic observations (Figure 3), which were not completely reversible.

The reaction in Scheme 1 may be directly followed by dehydroxylation, and in a subsequent step, extraction of aluminum from the framework may occur.<sup>10</sup> The structure and nature of the extraframework aluminum remains unclear. This extraction of framework aluminum is expected to be a function of the aluminum position in the framework.

(ii) A second mechanism that may lead to the formation of three-fold coordinated aluminum is via direct dehydroxylation at or in the neighborhood of a defect site. It is known that

dehydroxylation of Brønsted acid protons occurs at temperatures higher than 775 K.<sup>41</sup> In Scheme 2, a bridging hydroxyl group is dehydroxylated with a nearby Si–OH group, releasing water. In Scheme 3, a defect site on the aluminum atom causes the irreversible formation of three-fold coordinated aluminum.

In both Schemes, water is released making the transition irreversible in a vacuum. However, the presence of water at room temperature may induce the reversible reactions. Although at this moment it can only be determined that the amount of three-fold coordinated aluminum in zeolites is low, this low amount suggests that defect sites play a role during the transition to three-fold coordinated aluminum. This favors Schemes 2 and 3 above Scheme 1 which should cause a higher fraction of aluminum to change coordination. This can also explain the higher amount of three-fold coordinated aluminum in steamed zeolite Beta compared to the nonsteamed zeolite Beta. During synthesis of this zeolite Beta, special care was taken to keep the number of defect sites low, by first performing calcination in ammonia at 675 K and, after ion exchange with sodium chloride, calcination in 1% ozone in oxygen at 400 K, before calcination at 675 K.<sup>34</sup> This may explain the similar amount of three-coordinate aluminum in zeolites Beta and Mordenite (Figures 3 and 4).

#### Effect of H<sub>2</sub>O on the Aluminum Coordination in Zeolites.

Three-coordinate aluminum is not stable in the presence of water or to exposure to air at room temperature (Figure 3c). Traces of water in the gas phase cause the low-energy feature to disappear, showing the (strong) Lewis acid character of this species. Meanwhile, the presence of water creates a fraction of octahedrally coordinated aluminum. The octahedral content varies between 10 and 25% for different H-zeolites, the highest amount found in H-Beta. The formation of octahedral aluminum

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occurs already at room temperature.<sup>31,32</sup> The presence of this octahedrally coordinated species has been well documented for zeolite H-Beta,<sup>42–46</sup> but it is also reported for other zeolites.<sup>31,32,47</sup> It is generally assumed that this octahedral species is attached to the framework and that partial hydrolysis of the framework took place. The coordination is reverted to tetrahedral after an ion exchange with alkali ions or after the absorption of a strong base like ammonia and pyridine.<sup>42,48</sup> The latter procedure is generally performed at a temperature of 375–400 K. Interestingly, it is shown here for zeolite H-Mordenite that the octahedral–tetrahedral transformation also occurs, at temperatures higher than 395 K, even at low water partial pressure. This has also been shown for zeolites H-Y and H-Beta,<sup>31</sup> suggesting that the low stability of the octahedral framework aluminum with temperature is a general behavior in zeolites. The transformation of three-coordinate aluminum to a tetrahedral coordination and the simultaneous formation of octahedrally coordinated aluminum (Figure 3c) could be linked processes. Partial hydrolysis of the tetrahedral framework aluminum at high temperature (Schemes 2 and 3) could create a species that acts as an acceptor site for water molecules to complete an octahedral coordination by formation of Al–OH and bridging Al–O(H)–Si species. The partial hydrolysis of the tetrahedral aluminum enables the aluminum atom to adopt the more bulky octahedral coordination in the rigid silica–alumina zeolitic framework. The structure of octahedrally coordinated aluminum that is partially attached to the framework is often suggested to coordinate to water and hydroxonium ions; however, it is more likely that water molecules dissociate and form Al–OH and Al–O<sup>H</sup>–Si species.<sup>49</sup> However, the intensity of the pre-edge feature in H-Mordenite at 975 K is very similar to that of H-Beta measured at the same temperature, while the amount of octahedrally coordinated aluminum at room temperature is somewhat higher in H-Beta. As the Si/Al ratios for these zeolites are different, a systematic study of the influence of the Si/Al ratios and the number of defect sites on the amount of three- and six-coordinated aluminum should establish any relationship between these two coordinations. The relation remains an open question until the detailed local structures of both the octahedrally and the three-fold coordinated aluminum have been elucidated.

**Reported Claims for Three-Fold Coordinated Aluminum in Zeolites.** Many reports in the literature have suggested the presence of three-coordinate aluminum in zeolites. A variety of techniques have been used, such as <sup>27</sup>Al MAS NMR,<sup>7,8,9</sup> ESR,<sup>10</sup> XPS,<sup>11</sup> IR,<sup>12,46</sup> and so forth, and often, only an indirect indication for three-fold coordinated aluminum is provided.<sup>10–12</sup> In most cases, these methods were not applied in situ and samples were not treated or they were pretreated in a different manner (for example, hydration in the case of <sup>27</sup>Al MAS NMR) before data collection at room temperature or lower. In some

cases, equally severe heat treatments comparable to those in this study were given to the samples.

Our Al K-edge XANES measurements (for example, on H-Mordenite in Figure 3c) make clear that with techniques (such as <sup>27</sup>Al MAS NMR and XPS), where a sample is hydrated or exposed to air and measured without further treatment, no three-coordinate aluminum associated with the low-energy feature can be detected. The exposure to air or water directly annihilates the three-fold coordinated aluminum species observed in this study. More advanced NMR methods are necessary to enable detection of the three-coordinate aluminum at the same conditions employed in this study, although in this type of experiment the high resolution of the “normal” spectra is absent.<sup>17,18</sup> Often, in fully dehydrated samples, a total loss of signal in <sup>27</sup>Al MAS NMR spectra is observed. In any case, without the unambiguous determination of the NMR parameters (notably, the isotropic chemical shift) of broad peaks in <sup>27</sup>Al MAS NMR spectra, no conclusive assignment of peaks to three-coordinate aluminum can be made. It has been suggested that three-fold coordinated aluminum<sup>50,51</sup> causes a “broad hump” in <sup>27</sup>Al MAS NMR spectra in zeolites USY, ZSM5, Mordenite, and MCM-22. This broad hump was observed in both dehydrated and rehydrated samples; however, no isotropic chemical shifts were reported, due to the invisibility of this species in multiple quantum NMR<sup>50</sup> or due to the impossibility of determining the isotropic chemical shift using <sup>1</sup>H/<sup>27</sup>Al TRAPDOR NMR.<sup>51</sup> These studies claim that dehydroxylation had caused the irreversible formation of three-coordinate aluminum and that it is still present after rehydration. This is in clear contrast to the species observed in our Al K-edge spectra. In our steamed zeolite Beta, no three-fold coordinated aluminum is observed when measured at room temperature. Only a heat treatment induces three-coordinate aluminum, for steamed and unsteamed zeolite samples. Moreover, <sup>27</sup>Al MAS NMR in combination with multiple quantum NMR on USY<sup>52,53</sup> and steamed Beta<sup>48</sup> samples have shown that all aluminum in hydrated samples is accounted for in the spectra without the observation of three-fold coordinated aluminum. This suggests that, at standard NMR conditions, that is, in a hydrated state, no three-coordinate aluminum is present, at least not the Lewis acid aluminum site observed in this study.

It has been suggested that, in a dehydrated sample H-ZSM5, most of the tetrahedrally coordinated aluminum is converted into some kind of intermediate state between three- and four-coordinated aluminum.<sup>9</sup> Our Al K-edge spectra that are measured at high temperatures (Figures 3 and 4) clearly indicate that the aluminum is dominant in the four-coordinated state even at temperatures up to 975 K.

A series of infrared (IR) studies after the adsorption of probe molecules on treated zeolites have shown the presence of a variety of sorption sites.<sup>54,55</sup> IR spectra, measured at 77 K, show a weak feature at about 2230 cm<sup>-1</sup> after the adsorption of CO on zeolites after heating the zeolites in a vacuum (*T* > 675 K). This feature has been ascribed to the presence of highly

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unsaturated cationic aluminum,<sup>55</sup> and it is suggested to be three-fold coordinated.<sup>54</sup> The high wavenumber observed in the IR spectra is ascribed to the strong Lewis acid character of the adsorption site. The amount of this feature is a function of zeolite and the pretreatment of the zeolite.<sup>54,56</sup> This behavior is in full agreement with our in situ Al K-edge XANES measurements showing a clear dependence of the three-coordinate aluminum species as function of treatment (Figure 4). The suggestion of three-coordinate aluminum based on the indirect detection with IR spectroscopy at 77 K after the adsorption of CO as a probe molecule is confirmed by the direct detection of this species with in situ Al K-edge XANES. A very high frequency (VHF) band at about 3782 cm<sup>-1</sup> observed by IR spectroscopy in mildly dealuminated or at high-temperature calcined zeolite samples has been assigned to a hydroxyl group attached to three-coordinate aluminum attached to the framework.<sup>46</sup> A correlation of its intensity with that of a T–O–T vibration band at 885 cm<sup>-1</sup> and the Lewis acid behavior of this site have also been reported.<sup>57,58</sup> The proposed structure is a three-coordinate aluminum attached to two O–Si species, and a hydroxyl group completes the tricoordination. This structure can be formed after the first dehydroxylation step of the species in Scheme 1. However, no agreement on the assignment of this VHF band is present in the literature, and moreover, the adsorption of water diminished its intensity significantly but not completely.<sup>46</sup> Further research must be performed before a definite correlation between the observations from different spectroscopic methods can be made.

In situ Al K-edge XANES opens up possibilities of measuring the aluminum coordinations at a variety of pretreatment conditions and temperatures. Moreover, the determination of the

aluminum coordination during reaction conditions of a variety of reactions can be assessed. In principle, solid–gas and solid–liquid conditions can be handled during an Al K-edge XAS experiment. The present study clearly shows that the aluminum coordination in zeolites is a strong function of the exact measuring condition such as temperature and the presence of water.

## Conclusions

Al K-edge XANES is very suitable for the detection of aluminum coordinations in zeolites at nonambient conditions. The results show an extreme sensitivity of the aluminum coordination on the exact conditions of measurement. At temperatures above 675 K, a small part of tetrahedral coordinated aluminum in H-Zeolite transforms into a three-coordinate species, identified by a small pre-edge feature in the Al K-edge XANES spectra. This species is stable after cooling to room temperature, and the amount is a function of zeolite and the steaming treatment of the zeolite. Exposure to water or air at room temperature results in the removal of this species; at the same time, octahedrally coordinated aluminum is formed. No three-fold coordinated aluminum is detected in steamed zeolite Beta that is measured at room temperature after exposure to air.

In acidic zeolites, a transformation of part of the tetrahedral aluminum atoms to an octahedral coordination occurs at room temperature after the admission of a small water partial pressure. This framework connected octahedral aluminum is unstable at temperatures higher than 395 K, where it adopts a tetrahedral coordination.

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