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Local Structure of Aluminum in Zeolite Mordenite as Affected by Temperature

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The local aluminum structure in zeolite mordenite was studied at temperatures up to 1000 K in a vacuum by Al K-edge X-ray absorption near-edge structure (XANES) spectroscopy. The interatomic aluminum–oxygen distances and the number of coordinating oxygen atoms were determined by Fourier transform analyses of experimental Al K-edge XANES spectra and the fits of the nearest oxygen atoms contributions, using a limited number of variables. The values of fixed parameters for Fourier transform and fit are established from the spectrum of Na–mordenite, considered the reference compound for the studied zeolites H–mordenites, which was also used to test the accuracy and the stability of the determined structural parameters. To reveal the aluminum coordination in H–mordenite at various temperatures, the Fourier transform peak of the coordinating oxygen polyhedron was fitted first with a single-shell model, and the obtained structural information was refined by the fits, on the basis of the most plausible models for the aluminum coordination environment. The choice of such models for each temperature was performed according to the qualitative predictions on the aluminum local atomic structure provided by the preedge data analysis and ²⁷Al magic angle spinning (MAS) NMR experiments. By this method, the presence of sixfold aluminum atoms, aside from the fourfold ones, in H–mordenite at room temperature was revealed quantitatively, and the concentrations of these mixed coordinations were determined; the structural distortion of the oxygen tetrahedron around aluminum in dehydrated H–mordenite at $T = 575$ K was found to be strong, and the corresponding Al–O distances for this distortion were obtained; for H–mordenite at 985 K, the presence of threefold coordinated aluminum atoms, aside from the fourfold ones, was revealed, and an estimate of the amount of threefold aluminum was given.

I. Introduction

Zeolites find wide application as catalysts, catalyst supports, ion exchangers, and (selective) sorbents.¹ They are microporous materials and consist of silicon and aluminum atoms, tetrahedrally coordinated with oxygen. Charge balance requires a positive charge for each aluminum atom. When a proton is the charge-compensating cation, the zeolite contains a Brønsted acid site (BAS), which shows Brønsted catalytic activity. The BAS is a hydroxyl group bridging one aluminum and one silicon atom. The Brønsted catalytic site is, therefore, associated with tetrahedrally coordinated aluminum. Theory predicts three short aluminum–oxygen bonds and one longer aluminum–hydroxide bond.^{2–4} This has been confirmed by ²⁷Al MAS NMR⁵ and in situ Al K-edge X-ray absorption spectroscopy (XAS) measurements of dehydrated samples.^{6,7}

Prior to use, zeolite catalysts are activated, which often involves heat treatments and/or acid or base leaching.¹ Dealumination of the zeolite also results in catalyst activation and stabilization. During these processes, Lewis acid sites form. In contrast to BAS, the structure of Lewis acid sites is unknown. At temperatures above 700 K, dehydroxylation of the zeolite framework occurs; the temperature, however, depends on many factors such as the type of zeolite and their Si/Al ratio.^{8,9}

To understand zeolitic catalytic behavior and the processes during activation, a detailed structural characterization of these

materials must be made under treatment conditions (e.g., high temperature) or during a catalytic reaction. Classical methods have generally failed to provide structural data on the aluminum coordination under these conditions, although progress has been made with ²⁷Al NMR.^{10,11} Recent instrumental developments enable the determination of the local aluminum structure in zeolites under well-defined conditions using XAS.^{12,13} With this method, the local structure of BAS in zeolites was established to consist of three short Al–O bonds and one long Al–OH bond in the dehydrated state, as mentioned above. Moreover, it was shown that the aluminum coordination is flexible and depends on the measurement conditions.^{14,15} A unique preedge feature in Al K-edge spectra of H–mordenite was observed at temperatures above 675 K. This feature was ascribed to the presence of a small amount of threefold coordinated aluminum.¹⁴ Moreover, acidic zeolites, activated at temperatures above 625 K and exposed to a humid environment at room temperature, form octahedrally coordinated aluminum.^{14–16} Octahedrally coordinated aluminum is normally detected in activated acidic zeolites using conventional ²⁷Al MAS NMR.^{17,18}

We studied the local aluminum structure of catalytically important zeolite mordenite at temperatures up to 1000 K in a vacuum by Al K-edge X-ray absorption near-edge structure (XANES) spectroscopy. The interatomic aluminum–oxygen distances (R) and the number (N) of coordinating oxygen atoms were determined by the Fourier transform (FT) analysis of experimental Al K-edge XANES, as described in refs 19 and 20. The FT peak of the first shell (oxygen polyhedron) around

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the aluminum atom in H-mordenite at different temperatures is fitted first with a single-shell model under the limited number of variables, and the obtained structural information is refined then by the fits, on the basis of the most plausible models for the aluminum coordination environment. The choice of such models for each temperature is made according to the qualitative predictions on the aluminum local atomic structure provided by the preedge data analysis and ^{27}Al MAS NMR experiments. The accuracy and the stability of the determined structural parameters are tested by applying the method used to Al K-edge XANES in zeolite Na-mordenite, which can be considered the reference compound for the studied zeolites, H-mordenites. By this method, the presence of sixfold aluminum atoms, aside from the fourfold ones, in H-mordenite at room temperature (RT) is revealed quantitatively, and the concentrations of these mixed coordinations are determined; the structural distortion of the oxygen tetrahedron around aluminum in dehydrated H-mordenite at $T = 575$ K is found to be strong, and the corresponding Al–O distances for this distortion are obtained; for H-mordenite at 985 K, the presence of threefold coordinated aluminum atoms, aside from the fourfold ones, is revealed and an estimate of the amount of threefold aluminum given.

II. Experimental Section

Al K-edge XANES spectra were recorded at the Al K-edge at 1560 eV at station 3.4 of the SRS, Daresbury (U.K.), in the ILEXAFS setup.^{12,13} In this setup, XAS spectra can be measured at various temperatures in the presence of a gas or in a vacuum. Fluorescence yield was detected with a gas proportional counter, integrated with the in situ cell. The I_0 signal was measured by the drain current from a copper mesh. Station 3.4 has a double crystal monochromator, equipped with YB66 crystals. The synchrotron was operating at 2.0 GeV with an average current of 120 mA.

NH_4 -mordenite was obtained by repeated ion exchange with NH_4NO_3 of Na-mordenite (LZM-5). H-mordenite was obtained by calcination of NH_4 -mordenite at 725 K overnight. Prior to the measurement, samples were heat-treated in the ILEXAFS in situ cell to temperatures given below. All the measurements were performed in a vacuum.

III. Data Analysis Method

To perform the FT analysis of Al K-edge XANES in zeolites, the function $\chi(k)$, which contains the structural information of the local aluminum environment, was extracted from the experimental Al K-absorption cross-sections (σ^{exper}), presented in Figure 1 for all temperatures studied, by the expression $\chi(k) = \sigma^{\text{exper}}(k)/\sigma_{\text{at}}(k) - 1$, where k is the photoelectron's wavenumber. In this expression, the factorized "atomic" part of the absorption cross-section $\sigma_{\text{at}}(k)$ was obtained from the experimental spectrum according to ref 20. The procedure used consists of the following steps: at first, the convolution of $\sigma^{\text{exper}}(k)$ with the Lorentz function under the large, nonphysical value of its energy width (G) is performed, which suppresses the $\chi(k)$ oscillations and converts the expression $\sigma^{\text{exper}}(k) = \sigma_{\text{at}}(k)[1 + \chi(k)]$ into the parity $[\sigma^{\text{exper}}(k)]_{\text{convoluted}} = [\sigma_{\text{at}}(k)]_{\text{convoluted}}$, that is, the $[\sigma_{\text{at}}(k)]_{\text{convoluted}}$ — the convoluted or "smeared" $\sigma_{\text{at}}(k)$ is obtained from the experimental XANES spectrum by this step. The final step of the procedure is the recovery of $\sigma_{\text{at}}(k)$ from the $[\sigma_{\text{at}}(k)]_{\text{convoluted}}$ under the used G value. The validity of this procedure and the accuracy of the corresponding code were tested (i) via the extraction of $\sigma_{\text{at}}(k)$ from theoretical functions $\sigma^{\text{th}}(k)$, simulated with various $\sigma_{\text{at}}(k)$, (ii) by the values of interatomic distances, which were determined in agreement

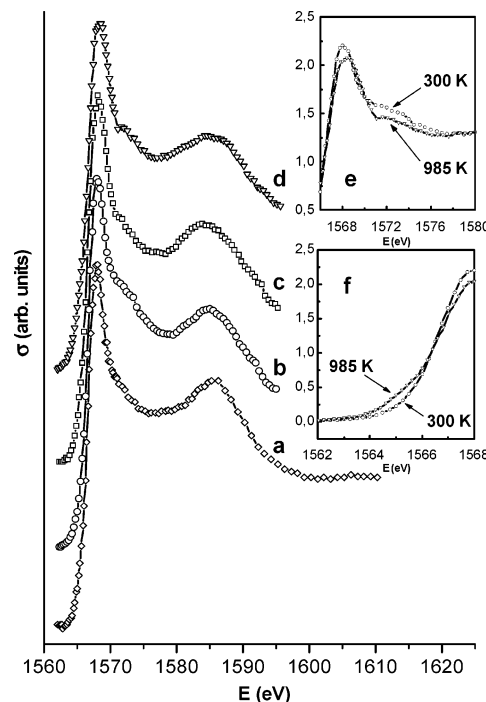


Figure 1. Experimental Al K-edge XANES spectra of mordenites: (a) Na-mordenite at 300 K and H-mordenite at (b) 300 K, (c) 575 K, and (d) 985 K. Inserts show the enlarged preedges (f) and the excess intensity at ~ 1573 eV (e) in Al K-edge XANES of H-mordenite for the temperatures $T = 300$ and 985 K.

with the available diffraction data for a wide number of studied reference compounds^{19–21} using the obtained functions $\sigma_{\text{at}}(k)$, as well as by the values of other fit parameters, determined by $\sigma_{\text{at}}(k)$ in physically reasonable limits for these parameters.

The contributions of the photoelectron single-scattering processes of the second and more distant shells (the middle-range order or MRO contribution in $\chi(k)$) and of the multiple-scattering (MS) processes to the K-XANES formation in minerals and glasses, as well as the influence of these processes on the values of the structural parameters R and N , determined by the method used, were studied in refs 19 and 20. It was revealed that the MRO term in $\chi(k)$ is the main source of inaccuracy in the R and N values of the first shell. However, the effect of MRO and MS terms on the accuracy of R and N becomes negligible for strongly disordered and amorphous materials, when the k_{min} value is set to an energy above the first main edge features in the spectrum.²¹ This clearly simplifies the FT analysis of XANES, because the FT procedure can be applied directly to the experimental $\chi(k)$ over the chosen k interval, without subtracting the MRO term.¹⁹ For the studied compounds, the effect of the MRO and MS terms is negligible within the chosen k interval, if the resulting function $F(R)$ of the FT of experimental XANES appears to be in agreement in a wide R -range with the corresponding function, obtained via the fit, on the basis of the account of the coordinating polyhedron only. To confirm this for Al K-edge XANES of zeolites and to test the accuracy of the R determination, the method is applied in section IV.A. to the spectrum of Na-mordenite. In this compound, aluminum is tetrahedrally coordinated to four oxygen atoms at a similar distance.²²

The FT of $\chi(k)$ and the R -space fit of the first oxygen shell contribution into the FT resulting function $F(R)$ over the range $0.5 < R < 3.5$ Å were performed with the FEFFIT code.²³ The photoelectron scattering amplitudes and phase shifts for the FT analysis were calculated by the method of Hartree–Fock (HF)

MT potential generation,²⁴ which provides the value of interstitial potential (MT zero) $E_{\text{MT}} = 1558$ eV for four-coordinated aluminum, the same as was used for Al K-edge XANES in minerals.²⁵ For six-coordinated aluminum, the E_{MT} value shifted 2 eV to higher energy,²⁵ which is in agreement with experimental spectra.^{26–29} This shift was taken into account in the analysis of the XANES spectra that contain both tetrahedral (Td) and octahedral (Oh) aluminum (section IV.B.1.). The photoelectron scattering amplitudes were calculated at an Al–O distance of $R_{\text{Al–O}} = 1.87$ Å, which is the average of typical $R_{\text{Al–O}}$ for four-coordinated aluminum (~ 1.73 Å) and six-coordinated aluminum (~ 2.0 Å). An FT analysis of contributions of Al–O pairs with different $R_{\text{Al–O}}$ distances using these scattering amplitudes revealed that they are suitable for the structural analysis of compounds with Al–O distances varying from 1.67 to 2.2 Å.

Within the HF MT potential model, the E_{MT} value is used to determine the photoelectron k -scale with $k = [0.2625(E - E_{\text{MT}})]^{1/2}$, and the traditional fit parameter E_0 can be excluded from the number of variables. The possibility of decreasing the number of varied parameters is important for the FT analysis of Al K-edge XANES, because the ΔR and the short Δk ranges, used to fit the first shell contribution in $F(R)$, limit the number of independent variables, $N_{\text{idp}} = (2 \cdot \Delta k \cdot \Delta R / \pi) + 1$, to three or four.³⁰ Therefore, the quantitative analysis of the complicated aluminum coordination in zeolites was performed with no more than three or four variables, while fixing the other parameters, and using the most plausible models for the local aluminum environment, predicted by other experimental techniques. Combinations of mixed polyhedron coordinations and split polyhedrons are assumed. The most likely model was chosen by comparing the obtained values of χ^2 or reduced χ^2 values.³⁰ The fixed values of the fit input parameters (the reduction factor S_0^2 for photoelectron intrinsic losses, Debye–Waller (DW) parameter σ^2 (when it is not varied) and Γ to account for extrinsic losses, core hole width, and experimental energy resolution³¹) are taken from appropriate reference or data in the literature. For example, the photoelectron extrinsic losses, core hole width, and experimental energy resolution were accounted for by the exponential form $\exp(-0.2625 \cdot \Gamma \cdot 2R/k)$,³¹ where $\Gamma = \Gamma_{\text{exper}} + \Gamma_{\text{h}} + \Gamma_{\text{el}}$. In the latter expression, Γ_{exper} is the energy parameter (in electronvolts) for the experimental resolution and Γ_{h} and Γ_{el} the energy widths of the core hole and the excited electron states, respectively. This exponential can also be given as $\exp(-2R/\lambda_{\text{eff}})$, with the effective mean free path length λ_{eff} for the photoelectron of $1/\lambda_{\text{eff}} = 0.2625(\Gamma_{\text{exper}} + \Gamma_{\text{h}})/k + 1/\lambda_{\text{el}}$. For aluminum compounds, Γ_{h} and the electron mean free path length $\lambda_{\text{el}}(k) = k/(0.2625\Gamma_{\text{el}})$, which is approximately constant in the k -interval used, were taken from ref 32. The obtained $\lambda_{\text{eff}}(k)$ value is similar to that provided by the FEFF8.2 package³³ and was used for the fit performed by FEFFIT.²³

IV. Results

IV.A. FT Analysis of Al K-edge XANES in Na–Mordenite. Zeolite H–mordenite is obtained from Na–mordenite by repeated ion exchange with NH_4NO_3 , replacing extra-framework Na^+ cations for NH_4^+ , with subsequent removal of NH_3 through heating. Therefore, Na–mordenite can be used as the reference compound for the FT analysis of Al K-edge XANES in H–mordenites, which permits the following: (i) the establishment of FT input and fit fixed parameters, chosen to minimize the number of fit variables for H–mordenite and (ii) the testing of the stability of the interatomic Al–O distances determination

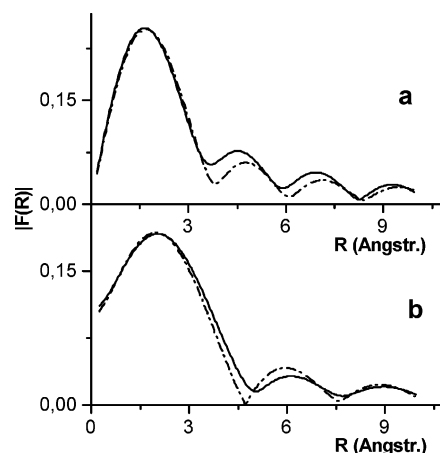


Figure 2. FT magnitudes $|F(R)|$ for experimental $\chi(k)$ (solid curves) and best obtained fits (dashed curves) of Na–mordenite. The FT is performed over two Δk ranges: (a) $2.0 < k < 3.5$ Å^{−1} and (b) $2.0 < k < 3.1$ Å^{−1} (see text for details).

by applying an FT to Al-XANES over the k -interval with $k_{\text{min}} = 2.0$ Å^{−1}, excluding the first main edge features at energies up to ~ 1575 eV. Figure 2 enables a comparison of the FT magnitude $|F(R)|$ of $\chi(k)$, extracted from the experimental Al K-edge XANES of Na–mordenite with the corresponding function for the single-shell fit model of the nearest oxygen contribution. To avoid overloading the figures, the corresponding imaginary parts $\text{Im}F(R)$ are not presented. However, only simultaneous agreement for $|F(R)|$ and $\text{Im}F(R)$ provides R -factors of fit smaller than 0.001.

The single-shell fit, performed with fixed values of the parameters $E_{\text{MT}} = 1558$ eV, $\Gamma = 1.5$ eV, and the fixed reduction factor $S_0^2 = 1.0$, gives values for $R_{\text{Al–O}}$, N , and σ^2 (Table 1). The goodness of the fit is characterized by the values of R -factor = 0.0004 and $\chi^2 = 0.3$. The coordination number of $N = 5.7$ is then used to provide an amplitude reduction factor of $S_0^2 = 0.7$ to obtain $N = 4.0$. This S_0^2 value lies within the physically reasonable limits of about 0.7–0.9 for these compounds.³¹

The FT performed over two Δk -ranges from $k_{\text{min}} = 2.0$ to $k_{\text{max}} = 3.5$ Å^{−1} and from $k_{\text{min}} = 2.0$ to $k_{\text{max}} = 3.1$ Å^{−1} revealed the stability of the determined structural parameters for this Δk variation. Thus, the R and N values, which are the integral characteristics of the fitted curves, are as follows: $R = 1.728$ Å, $N = 4.0$ (set by $S_0^2 = 0.7$) for the fit with $k_{\text{max}} = 3.1$ Å^{−1} (Figure 2b) and $R = 1.725$ Å, $N = 3.95$ (under the same $S_0^2 = 0.7$) for the fit with $k_{\text{max}} = 3.5$ Å^{−1} (Figure 2a). The changes in R are ≤ 0.005 Å and the changes in N are $\leq 2\%$. Therefore, the most limited data range available for H–mordenite (Figure 1) is expected to provide equally accurate results.

Presented in Figure 2 are the comparisons of $|F(R)|$ functions, obtained via FT of experimental Al K-edge XANES in Na–mordenite and via the fit based on the single-shell model for aluminum coordination, which shows their agreement in the extended R -range. The same agreement for both $|F(R)|$ and $\text{Im}F(R)$ is obtained in H–mordenites for the fits performed with models for coordinating oxygens only, which is illustrated in Figure 3 for the temperature $T = 575$ K. This agreement unambiguously indicates that, for the studied zeolites, the effect of the MRO and MS terms is negligible under the value used of $k_{\text{min}} = 2.0$ Å^{−1}, chosen to exclude the energy region of the first main edge crest features. This choice of k_{min} also permits the minimization of possible inaccuracies in the $\sigma_{\text{at}}(k)$ function.

The adequacy of the values of the fixed parameters used and the stability of the determined fitting parameters were tested

TABLE 1: Structural Parameters $R_{\text{Al-O}}$, N , and σ^2 for Na–Mordenite from FT Analysis of Al K-edge XANES^a

T (K)	$R_{\text{Al-O}}$ (Å)		N			σ^2 (Å ²)	reduced χ^2 χ_{ν}^2
	Al K-XANES	ref 22	Al K-XANES $S_0^2 = 1.0$	Al K-XANES $S_0^2 = 0.7$	ref 22		
300	1.73	1.73	5.71	4.0	4.0	0.005	0.3

^a Performed under the fixed values of parameters $E_{\text{MT}} = 1558$ eV and $\Gamma = 1.5$ eV.

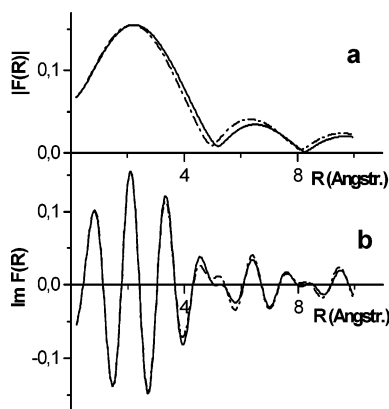


Figure 3. (a) FT magnitudes $|F(R)|$ and (b) imaginary parts $\text{Im}F(R)$ of Al K-edge XANES in H–mordenite at 575 K (solid curves) and of the (3 + 1) model for oxygen tetrahedron distortion (dash-dotted curves).

on the reference sample Na–mordenite by varying the values of the fixed parameters in physically reasonable ranges ($\Gamma = 1$ –2.0 eV, $E_{\text{MT}} = 1558 \pm 1.5$ eV, $\sigma^2 = 0.004$ –0.006 Å² (when σ^2 is not varied)) and observing the changes in values of the fitted parameters S_0^2 , N and R . The following points were observed: (a) the value of the interatomic Al–O distance $R_{\text{Al-O}}$ for this reference zeolite, (b) the lack of dependence of the obtained N and R values on the possible variations of the Δk interval used for FT (this point is a sensitive criterion for the adequacy of the Γ and σ^2 values used), and (c) the values of the DW parameter σ^2 (when it is varied) for the Al–O pair, which are expected to be in the range of about 0.004 to 0.007 Å² at 300 K.³⁴ The above deviations from the established values of the fixed parameters showed minor divergences in the values of S_0^2 , N , R , and σ^2 (when varied). Thus, the divergences in R -values are less than the resolution that can be obtained by the FT analysis of K-edge XANES, confirming the stability of the determined R -values. The results obtained by Al K-edge XANES in the reference zeolite Na–mordenite justify the results of the papers^{20,21} that the FT analysis of K-edge XANES in disordered and amorphous compounds yields inaccuracies in interatomic distances R -determination of ± 0.005 Å ($\sim 1\%$) and in N -determination of $\sim 5\%$ (for the last value, the appropriate reference compounds are needed). It must be noted that the experimental errors (high-frequency noise) have no effect on the uncertainties in the fitted parameters because of the high signal/noise ratio in the XANES energies region, in contrast to extended X-ray absorption fine structure (EXAFS) analysis.

In zeolites, several aluminum species are often present, and moreover, the polyhedron may be significantly distorted.^{2–7} To accurately determine structural disorder, anharmonicity in atomic thermal motion must be taken into account. The influence of anharmonicity in zeolites is estimated from the Al K-edge XANES spectrum of Na–mordenite, because there is limited compositional disorder for this reference compound. The $\chi(k)$ of Na–mordenite was fitted using a cumulant expansion of the DW factor in a power series of k .³⁵ This is the expansion about $k = 0$, and hence, it is accurate for the XANES region (low k

values). With this approach, the fit of the coordinating oxygen contribution in $F(R)$ was performed with three variables: σ^2 (C_2 cumulant for harmonic approximation) and cumulants C_3 and C_4 to account for the anharmonicity effects. $R_{\text{Al-O}}$, N , and the values of the other input fit parameters are fixed. The values for $C_3 = 0.0001$ and $C_4 = 0.0003$ are more than 10 times smaller than σ^2 , which hardly changed. This indicates that at RT the effect of anharmonicity in atomic motion on the asymmetry of the first shell's Fourier peak can be neglected. Before extrapolation of this conclusion to higher temperature, a similar analysis of the spectra at the corresponding temperatures must be carried out. However, it is expected that, for the XANES analysis of zeolites, the anharmonicity effects at the elevated temperatures can also be neglected, because their effect on the phase of $\chi(k)$ is not significant at low k , contributing only $\sim 1\%$ to the total phase up to $k = 6$ Å^{−1}.³⁵ The errors in the coordination numbers due to the presence of these effects will usually be larger than those in the interatomic distances.

IV.B. Al Coordination Environment in H–Mordenites.

IV.B.1. H–Mordenite at Room Temperature. Octahedrally coordinated aluminum is often found in acidic zeolites after exposure to water.^{15,16,18} The octahedral aluminum reverts to a tetrahedral coordination after treatment with ammonia, or after ion exchange with alkali ions,¹⁷ or after heating to temperatures above 400 K in a vacuum.^{14,15} The room-temperature XANES spectrum of H–mordenite (Figure 1) shows an excess intensity at about 1573 eV, which is characteristic of octahedrally coordinated aluminum.^{25–29} This confirms the presence of octahedrally coordinated aluminum as measured by ²⁷Al MAS NMR on a similar sample of H–mordenite.¹⁸ To quantitatively determine the presence of six-coordinated aluminum, aside from the four-coordinated one, as well as to obtain the relative amounts of these mixed aluminum coordinations, first, a fit with a single-shell model of the oxygen contribution in the FT was performed, followed by a fit of a two-shell model. In the two-shell model, the oxygen contribution (fitting function $\chi(k)$) is represented by the sum of two terms

$$\chi(k) = C\chi_1(k) + (1 - C)\chi_2(k) \quad (1)$$

where χ_1 is the contribution of the tetrahedrally coordinated aluminum with an Al–O distance of $R_{\text{Al-O}} \equiv R_1$, C is the concentration of such atoms, and χ_2 the contribution of the octahedrally coordinated aluminum with an Al–O distance of $R_{\text{Al-O}} \equiv R_2$. The fit based on this model was performed by taking into account the energy shift of ~ 2 eV between the E_{MT} values for four- and six-coordinated aluminum (vide supra).

At first, the fit based on the single-shell model, which assumes the presence of only one type of aluminum coordination (Td coordinated aluminum), was performed with two variables, N and R , using the value $\sigma^2 = 0.005$ Å² and the values of other FT and fit fixed parameters established for the model zeolite Na–mordenite. The fit yields the values $N = 3.2$, which is smaller than the average of any possible two-shell model with Td and Oh coordinated aluminum and $R_{\text{Al-O}} = 1.72$ Å, with the R -factor = 0.065 and $\chi_{\nu}^2 = 17.7$ (Table 2). At the same

TABLE 2: Fit Models Used for Al K-edge XANES Analysis of H-Mordenite at Elevated Temperature (*T*) and Structural Parameters for Aluminum Coordination Environment Determined by These Models

<i>T</i> (K)	single-shell fit			fit based on the models for aluminum coordination environment			
	<i>N</i>	$R_{\text{Al-O}}$ (Å)	reduced χ^2 χ_v^2	model	reduced χ^2 χ_v^2	Al-O distance (Å)	percentage of tetrahedral aluminum, <i>C</i> (%)
300	3.2	1.72	17.7	mixture of Td and Oh	0.5	$R_1(\text{O}_4) = 1.72$ $R_2(\text{O}_6) = 2.15$	88
				Td split as (3 + 1)	1.5		
				Td split as (2 + 2)	1.7		
575	3.7	1.75	3.5	Td split as (3 + 1)	0.2	$R_{1,1}(\text{O}_4) = 1.71$ $R_{1,2}(\text{O}_4) = 1.91$	100
				Td split as (2 + 2)	0.5		
				Td split as (1 + 3)	0.7		
985	3.9	1.73	0.5	mixture of threefold and Td aluminum	0.14	$R_1(\text{O}_4) = 1.73$ $R_2(\text{O}_3) = 1.69$	90–95
				Td split as (3 + 1)	0.2		
				Td split as (2 + 2)	0.2		

time, the fit with the varied σ^2 resulted in the large, nonphysical for RT, value of $\sigma^2 = 0.023 \text{ \AA}^2$.

The poor single-shell fit quality for H-mordenite at RT compared to the reference Na-mordenite, which was obtained under the same values of FT and fit fixed parameters for both compounds, indicates the presence of strong dispersion in Al–O distances for coordinating oxygen atoms. This assumption arises from the previous $\chi(k)$ simulations for a distorted oxygen polyhedron around the metal atom, which revealed that, when the difference in metal–oxygen distances exceeds $\sim 0.25 \text{ \AA}$, a single-shell model will not provide the average values of structural parameters for this polyhedron, and the fit based on the two- or three-shell models must be used.²¹ The expected distribution of Al–O distances in H-mordenite at RT can be the result (i) of the mixture of Td and Oh aluminum coordinations, as predicted by ²⁷Al MAS NMR experiments and by the qualitative analysis of XANES features, or (ii) of the structural distortions within the tetrahedron, under the assumption of pure four-coordinated aluminum. Therefore, to improve the fit quality, the two-shell model for the aluminum coordination environment, which takes into account the mixture of tetrahedrally and octahedrally coordinated aluminum in H-mordenite at RT, was considered first.

The fit based on this model was performed by the expression (1) for the fitting function $\chi(k)$ using three variables R_1 , R_2 , C , the value $\sigma^2 = 0.005 \text{ \AA}^2$, and the values of other FT and fit fixed parameters established for the reference Na-mordenite. This fit, characterized by good quality with R -factor = 0.0005 and $\chi_v^2 = 0.5$, gave a tetrahedral content of 88% with $R_{\text{Al-O}} = 1.72 \text{ \AA}$ and an octahedral content of 12% with $R_{\text{Al-O}} = 2.15 \text{ \AA}$ (Table 2). The results of the two-shell model are in good agreement with ²⁷Al MAS NMR data on a similar sample of H-mordenite, which also showed mixed aluminum coordination with 84% tetrahedrally and 16% octahedrally coordinated aluminum¹⁸ at RT.

To reveal the adequacy of the model with the mixture of Td and Oh aluminum coordinations, the fit quality obtained by it was compared to that obtained for the pure Td aluminum coordination in assumption of coordinating tetrahedron's distortions, according to the following most plausible models for the distribution of long and short Al–O distances: (3 + 1) and (2 + 2). These models were realized using the expression for χ_1 (which represents the Td aluminum coordination) written as

$$\chi_1(k) = \chi_{1,1}(k) + \chi_{1,2}(k) \quad (2)$$

where $\chi_{1,1}$ and $\chi_{1,2}$ are the contributions of oxygen atoms located

at distances $R_{\text{Al-O}} \equiv R_{1,1}$ and $R_{\text{Al-O}} \equiv R_{1,2}$, respectively. The fit was performed with the two-shell Td models (3 + 1) and (2 + 2) for the split of the coordinating oxygen tetrahedron, using variables $R_{1,1}$ and $R_{1,2}$ and the values of FT and fit fixed parameters established for the reference Na-mordenite. The fit resulted in worse quality compared to the mixture of Td and Oh aluminum coordinations (Table 2), which is characterized by the values of the R -factor = 0.0014 and $\chi_v^2 = 1.5$ and 1.7, respectively, for the considered tetrahedron distortion models (3 + 1) and (2 + 2).

The results of the performed fits for the compared models of the aluminum local environment revealed the advantage of the model with the mixture of Td and Oh coordinated aluminum in H-mordenite at RT. The aluminum–oxygen bond length of $R_{\text{Al-O}} = 1.72 \text{ \AA}$ obtained by this model for the tetrahedral coordination is very similar to that found in Na-mordenite. The bond length of $R_{\text{Al-O}} = 2.15 \text{ \AA}$ in the octahedrally coordinated aluminum is longer than expected on the basis of the aluminum–oxygen bond lengths in reference compounds with nondistorted octahedral coordination of aluminum, which is on the order of 2.0 \AA .²⁶ For low-*Z* elements, a metal–oxygen distance of 2.1 \AA is found for Mg–O in Mg compounds with six-coordinated Mg.³⁶ The unexpectedly long Al–O distance of $\sim 2.15 \text{ \AA}$ may originate from distortions in the octahedron in H-mordenite at 300 K. However, the fit with the limited number of variables (due to the short Δk interval used for FT of Al K-edge XANES) is less accurate and detailed for such a complicated radial distribution of Al–O distances of a mixture of simultaneously distorted tetrahedral and octahedral coordinations.

IV.B.2. H-Mordenite at 575 K. Heating zeolite mordenite to 575 K dehydrates the sample completely; at even higher temperatures, dehydroxylation occurs.⁸ A reversal of octahedral coordination to tetrahedral at temperatures above 400 K had been reported.^{14,15} Therefore, only tetrahedrally coordinated aluminum is expected for the sample measured at 575 K. This is confirmed by the lack of additional intensity at $\sim 1573 \text{ eV}$ in the Al K-edge XANES spectrum and by the FT analysis of Al K-edge XANES of H-mordenite measured at 575 K. The FT resulting function $F(R)$ was first fitted using a single-shell model with variables N , R , the value of $\sigma^2 = 0.096 \text{ \AA}^2$, and the values of other FT and fit fixed parameters established for the reference Na-mordenite. The σ^2 value used was obtained by extrapolating the value of $\sigma^2 = 0.005 \text{ \AA}^2$, found for Na-mordenite at room temperature, and using linear temperature dependence³⁴ in the studied temperature range up to $\sim 1000 \text{ K}$. A coordination number of $N = 3.7$ and an average Al–O distance of $R = 1.75 \text{ \AA}$ were found (Table 2) via this fit characterized by the values

of R -factor = 0.007 and $\chi^2_v = 3.5$. It must be noted that the single-shell fit with the three variables N , R , and σ^2 resulted in the same values of the structural parameters, illustrating the stability of the obtained values and justifying the presence of mostly four-coordinated aluminum in H-mordenite at $T = 575$ K.

To reveal the distortions in the oxygen tetrahedron, the most probable two-shell model for χ_1 was represented by eq 2, which describes the sum of two shells: the first, $\chi_{1,1}$, corresponds to three oxygens at shorter Al–O distance $R_{\text{Al-O}} \equiv R_{1,1}$ in the Al–O(–Si) entity; the second shell, $\chi_{1,2}$, matches the one oxygen with elongated bond length $R_{\text{Al-O}} \equiv R_{1,2}$ in the Al–OH(–Si) unit. The fit was performed with two variables, $R_{1,1}$ and $R_{1,2}$, a fixed value of $\sigma^2 = 0.0096 \text{ \AA}^2$, and other FT and fit fixed parameters established for the reference Na–mordenite. In addition to the two-shell model (3 + 1) for the distortion of the oxygen tetrahedron, alternative split models, such as (2 + 2) and (1 + 3) (the latter with $R_{\text{Al-O}}$ for one atom $\leq R_{\text{Al-O}}$ for three atoms) were studied to account for the tetrahedral distortions. The (3 + 1) model with three oxygen atoms located at $R_{\text{Al-O}} = 1.71 \text{ \AA}$ and one oxygen atom at $R_{\text{Al-O}} = 1.91 \text{ \AA}$ gave an R -factor = 0.0003 and $\chi^2_v = 0.2$, which is significantly smaller than those of the other compared models (Table 2). To illustrate the fit quality, the magnitude of $|F(R)|$ and the imaginary part $\text{Im}F(R)$ of the FT of the Al K-edge XANES in H-mordenite at 575 K are compared to the corresponding functions of the (3 + 1) model (Figure 3).

The structural parameters reveal quantitatively the strongly distorted nature of the tetrahedral aluminum associated with the Brønsted acid site, even for the limited data range.^{2–7} Bonding of the acidic proton weakens the aluminum–oxygen bond and elongates it. Consequently, the other three oxygen bonds are strengthened, which is reflected in a shortening of the aluminum–oxygen bond. This may, however, be beyond the limit of detection.

IV.B.3. H–Mordenite at 985 K. In the Al K-edge XANES spectrum of H-mordenite measured at 985 K, a small preedge feature (Figure 1) was observed.¹⁴ In addition to the tetrahedrally coordinated aluminum, this feature illustrates the presence of a small amount of threefold coordinated aluminum formed during dehydroxylation. It was observed at temperatures above 675 K, and its intensity increased at higher temperatures. In the near-edge spectrum, no evidence of other aluminum coordinations was found.

The Al–K-edge XANES spectrum was Fourier transformed and the analysis of $F(R)$ was started with the single-shell fit model for the oxygen atoms around the aluminum atom. The fit was performed with variables N and R , using $\sigma^2 = 0.016 \text{ \AA}^2$, which was theoretically obtained for 985 K via the linear extrapolation of its RT value and the values of other FT and fit fixed parameters established for the reference Na–mordenite. This fit model gave $N = 3.9$ and $R_{\text{Al-O}} = 1.73 \text{ \AA}$ with an R -factor = 0.0005 and $\chi^2_v = 0.5$ (Table 2). The stability of the obtained structural parameters was confirmed including σ^2 into the number of variables. The good fit quality, obtained even by the single-shell model for the aluminum local environment, indicates the small presence of other possible aluminum coordinations, as well as the absence of strong distortions in the coordinating oxygen tetrahedron.

To reveal the small presence of threefold coordinated aluminum, aside from the fourfold one in H-mordenite at 985 K (as predicted by the analysis of the preedge in Al K-XANES), a fit model based on eq 1 which accounts for a mixture of three- and fourfold coordinated aluminum was used. In this model,

the χ_2 term in eq 1 under the fixed $N_2 = 3$ corresponds to the three-coordinated aluminum ($R_{\text{Al-O}} \equiv R_2$) and χ_1 under the fixed $N_1 = 4$ to the fourfold coordination ($R_{\text{Al-O}} \equiv R_1$) with concentration C . The fit performed by this model with variables R_1 , R_2 , and C gave for four-coordinated aluminum $R_{\text{Al-O}} = 1.73 \text{ \AA}$ with concentration $C = 90\text{--}95\%$. The remaining threefold coordinated aluminum has an Al–O distance of $R_{\text{Al-O}} = 1.69 \text{ \AA}$ (Table 2). Although a slightly shorter distance is expected for threefold coordinated aluminum, compared to tetrahedrally coordinated, the difference between the expected and obtained Al–O distances for threefold aluminum is about the resolution that can be obtained by the approach used. The fit quality is characterized by the values of R -factor = 0.0002 and $\chi^2_v = 0.14$, which are better than those obtained under the assumption of the presence of only pure Td aluminum coordination.

To justify the uniqueness of the conclusion on the mixture of threefold and fourfold coordinated aluminum in H-mordenite at 985 K, the alternative refinement of the single-shell fit model was considered, on the basis of the assumption of the presence of pure four-coordinated aluminum only, with the distortions in the coordinating oxygen tetrahedron. These tetrahedral distortions were simulated by the two most plausible split models (3 + 1) and (2 + 2) for χ_1 . The fit with these models was realized by eq 2, where $\chi_{1,1}$ matches the oxygen atoms with bond length $R_{\text{Al-O}} \equiv R_{1,1}$ and $\chi_{1,2}$ matches the oxygen atoms with $R_{\text{Al-O}} \equiv R_{1,2}$. The obtained fit's quality is characterized by the same values for both models (3 + 1) and (2 + 2) of R -factor = 0.0004 and $\chi^2_v = 0.2$, which are worse than those for the mixture of threefold and fourfold coordinated aluminum. At the same time, the identification of the possible distortions in the coordinating oxygen tetrahedron, which are small as predicted by the single-shell fit results, under the mixture of three- and fourfold coordinated aluminum, is expected to be unreliable because of the short experimental data range and, as a consequence, the limited number of varied parameters.

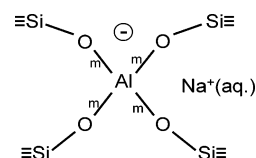
V. Summary and Conclusions

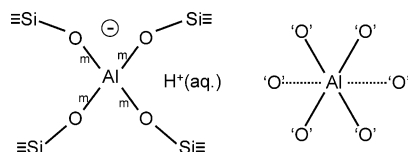
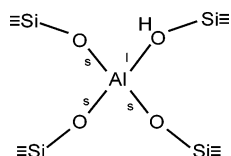
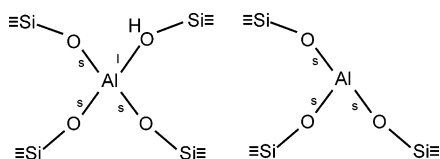
Fourier transform analyses of Al K-edge XANES spectra of zeolite mordenite, which were measured under well-defined conditions, provide a detailed picture of the structure of the Brønsted acid site and the changes in aluminum coordination. The schemes of the FT analysis of XANES can be especially useful when limited data ranges are available, because a high time resolution needed to be achieved, but also in case of overlapping edges.

Scheme 1 shows the tetrahedrally coordinated framework of aluminum in Na-mordenite, which is used as the reference compound. This coordination is dictated by the zeolite structure derived from XRD and is also generally observed in ^{27}Al MAS NMR and Al K-edge EXAFS measurements.³⁷

After ion exchange to NH_4 -mordenite and calcination at 725 K, a combination of tetrahedral and octahedral aluminum is observed (Scheme 2). Octahedral aluminum is often observed in acidic zeolites with ^{27}Al MAS NMR.^{38–41} It has been shown that, in acidic zeolites heated in an inert environment, the coordination of some tetrahedrally coordinated aluminum

SCHEME 1: Tetrahedrally Coordinated Aluminum in Na–Mordenite



SCHEME 2: Tetrahedrally and Octahedrally Coordinated Aluminum in Hydrated H-Mordenite**SCHEME 3: Strongly Distorted Tetrahedrally Coordinated Aluminum in Dehydrated H-Mordenite****SCHEME 4: Tetrahedrally and Threefold Coordinated Aluminum in H-Mordenite at $T = 985$ K**

changes to octahedral after cooling to room temperature and exposure to a humid environment. ^{27}Al MAS NMR is generally measured on samples exposed to a humid atmosphere, thus creating the octahedrally coordinated aluminum. The Al K-edge XAS measurements, however, are performed in a vacuum, after the samples are exposed to the humidity of the air. About 10% of octahedrally coordinated aluminum in H-mordenite was still observed in the XANES data¹⁴ and is revealed quantitatively by the performed FT analysis of Al K-edge XANES. The octahedral aluminum formed in air is stable after evacuation.

At temperatures higher than 400 K, no octahedrally coordinated aluminum was observed. Complete dehydration of the sample creates the bridging hydroxyl groups, which are the BAS. The FT analysis of Al K-edge XANES showed a highly distorted tetrahedral coordination of the dehydrated H-mordenite (Scheme 3) and gave the values of three short (1.71 Å) and one long (1.91 Å) Al–O distance. The proton is localized on one oxygen atom, which consequently elongates the corresponding Al–O bond. Theory has calculated this elongation of the Al–OH bond.^{2–4} Meanwhile, the other three Al–O bonds are predicted to shorten. However, the FT XANES analysis did not indicate significant shortening, probably because the shift is within the limits of accuracy. Previous Al K-edge EXAFS analyses of ZSM5 and Y structures also indicated very similar distortions in their acidic state.^{6,7} ^{27}Al NMR also demonstrates a strongly distorted tetrahedrally coordinated aluminum atom in the dehydrated state.^{5,10} Moreover, in a true in situ experiment, it was shown that the tetrahedral aluminum site responds to the adsorption of reactive intermediates during oligomerization of ethylene. A partial relaxation of the distortion was observed.¹⁴

Finally, Scheme 4 shows the structures derived at extremely high temperatures. The FT analysis of Al K-edge XANES reveals that the dominant aluminum coordination is tetrahedral, and a small fraction of about 5–10% threefold coordinated aluminum is observed. Dehydroxylation probably occurs, and the zeolite structure starts to collapse. Threefold coordinated aluminum was identified also by a unique pre-edge feature in the near-edge. This coordination is only observed at high temperature or after cooling to room temperature under vacuum. As soon as the zeolite is exposed to a humid atmosphere, the

threefold coordinated aluminum disappears, and octahedrally coordinated aluminum is formed. The good fit quality, obtained even by the single-shell model for the aluminum local environment, indicates a very small dispersion of Al–O distances for coordinating oxygen atoms. Therefore, the possible structural distortions of the coordinating oxygen tetrahedron at 985 K, if they occur, are significantly less than when measured at 575 K. The extremely high temperature probably causes high proton mobility, making the oxygen tetrahedron more symmetric.

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