X-ray Absorption Fine Structure Analysis of the Local Environment of Fe in Fe/Al–MFI

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An MFI zeolite framework containing iron and aluminum has been prepared and characterized by X-ray absorption spectroscopy. Extended X-ray absorption fine structure analysis indicates that in the as-prepared zeolite Fe is present in the framework but migrates to extraframework sites upon thermal activation at elevated temperature. In the absence of framework Al, Fe forms small particles of Fe₃O₄. When Al is included in the zeolite, extraframework Fe associates with framework Al in a manner identical to that observed in Fe-exchanged H-ZSM-5. Therefore, the presence of framework Al in the MFI structure plays a critical role in stabilizing atomically dispersed Fe.

Introduction

A number of recent studies have shown that it is possible to synthesize a zeolite with an MFI framework structure, containing Fe within the framework.^{1–8} This material, which we will refer to as Fe–MFI, has also been described as Fe–silicalite in the literature. Removal of the templating agent used to form Fe–MFI and subsequent thermal pretreatment in both the absence and presence of steam can cause some or all of the framework Fe atoms to migrate to extraframework positions.^{2–11} Characterization of the Fe environment after template removal and thermal pretreatment suggests that Fe may be present as isolated and dimeric Fe grafted to the MFI framework.^{4,9,10} Steaming of Fe–MFI is reported to assist in the removal of Fe from the MFI framework and can result in small particles of Fe₂O₃ outside of the MFI crystals.^{5,7} It has recently been shown that the incorporation of Al into the MFI framework along with Fe results in a stabilization of the dispersion of Fe atoms upon their expulsion from the MFI framework during pretreatment.¹²

The catalytic activity of Fe–MFI and Fe/Al–MFI has been investigated for N₂O decomposition^{7,8,13–18} and the N₂O oxidation of benzene to phenol.^{19–23} Studies show that framework Fe atoms are not active for these reactions.^{7,14} In contrast, extraframework Fe produced during thermal pretreatment are active.^{7,8,22} Consistent with the observation that framework Al results in a stabilization of the dispersion of Fe atoms during thermal treatment, Fe/Al–MFI is reported to exhibit superior activity over the Fe–MFI analogue.^{14,20} Thermally pretreated Fe/Al–MFI²⁰ displays similar performance to that obtained with Fe–ZSM-5²⁴ prepared by exchange of the protons in H–ZSM-5 by Fe cations. For this reason it is particularly interesting to determine the local structure Fe atoms present in thermally pretreated Fe/Al–MFI.

In the present study, we report on the evolution of the local structure of iron in Fe/Al–MFI upon thermal treatment as

determined by EXAFS and XANES. For this work, three samples were made by a hydrothermal method in which the Fe/Al was varied. EXAFS and XANES were used to monitor the migration of Fe from framework to extraframework positions during thermal treatment. These results are compared to those of postsynthetically exchanged Fe–ZSM-5 reported in our previous study.²⁵ It will be shown that extraframework Fe in both samples possess remarkably similar structures. The role of framework Al in the dispersion of extraframework Fe will be discussed.

Experimental Methods

Materials Preparations. The samples in this study were made using either a hydrothermal synthesis in which Al and Fe were incorporated into the MFI structure during the crystallization of the framework, or by a postsynthetic exchange method in which Fe was exchanged into extraframework positions of H–ZSM-5. Hydrothermally synthesized samples were prepared by the fluoride synthesis route in the following manner.²⁶ Ammonium fluoride, tetrapropylammonium bromide, FeCl₃, aluminum nitrate (no aluminum nitrate was added in the synthesis of Fe/Al–MFI(∞)), and water were placed in Teflon-lined bomb reactors. The mixtures were stirred until all solids dissolved. Ludox LS-30 was then added to each mixture and the reactors were placed in an oven at 433 K for 7 days. The resulting materials were calcined in air at 823 K for 6 h after an 8 h ramp, also in air. The MFI products were then ion-exchanged with 1M ammonium nitrate, washed with deionized water, and dried overnight at 373 K. The samples were activated by calcining in air at 623 K and then heating in He at 1123 K for 6 h. Three samples were prepared, Fe/Al–MFI(0.38) and Fe/Al–MFI(1.02), in which both Fe and Al were included in the synthesis, and Fe/Al–MFI(∞), in which Fe but no Al was included (the number in brackets denotes the Fe/Al ratio for the sample).

Fe–ZSM-5 was prepared by solid-state exchange of H–ZSM-5 with FeCl₃. Na–ZSM-5 (Alsi-Penta, Si/Al = 25) was first converted to the ammonium form by aqueous exchange with ammonium nitrate. After drying, the resulting NH₄–ZSM-5 was transformed to H–ZSM-5 by calcination in air at 823 K for 8 h. The calcined H–ZSM-5 was then transferred

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to a glovebox and mixed with anhydrous FeCl_3 (Aldrich, 99.99%). The mixture was placed into a sealed reactor without exposure to air and the reactor was then heated from 298 to 583 K, the sublimation temperature of FeCl_3 . Upon cooling to room temperature, the sample was removed from the reactor and washed repeatedly with deionized water to remove Cl anions. The final product was dried in an oven at 383 K for 1 h. Three Fe–ZSM–5 samples were prepared with Fe/Al ratios of 0.33 and 0.80. These samples are denoted as Fe–ZSM–5(0.33) and Fe–ZSM–5(0.80), respectively.

X-ray Absorption Fine Structure Measurements. Prior to X-ray absorption measurements, the sample was pressed into a rectangular slot of a sample holder. The sample holder was then mounted in a cell, similar to that described by Jentoft et al.²⁷ Beryllium windows mounted at both ends of the cell permitted passage of the X-ray beam through the cell, while allowing the cell to be filled with gas or evacuated. After purging the cell in He, the samples were pretreated by heating in He at 773 K for 2 h 20 min and cooled to room temperature. The cell was then sealed and evacuated to prevent beam loss due to gas scattering.

XAFS measurements were conducted on beam lines 4–1 and 4–3 of the Stanford Synchrotron Radiation Laboratory (SSRL). The radiation was monochromatized using a Si(111) double-crystal monochromator and the incident beam was detuned by 15% at 7111.2 eV (the K-edge of Fe) using a piezo-electric translator in order to minimize contamination of higher harmonics. To minimize noise, the sample was cooled by attaching the cell to a dewar filled with LN_2 . The intensities of the incident and transmitted beams were monitored using separate ionization chambers, through which pure N_2 flowed. At least four scans were taken of each sample to obtain good signal-to-noise ratios (S/N). For each sample, a reference spectrum of Fe foil was recorded simultaneously so that the energy in the spectrum of the sample could be calibrated with respect to the K-edge energy of Fe metal, 7111.2 eV. The spectra of Fe foil, FeO, Fe_2O_3 , and Fe_3O_4 were collected for use as references. Boron nitride, which is nearly transparent to the X-rays, was used to dilute the reference compounds.

XAFS Data Analysis. EXAFS (extended X-ray absorption fine structure) data were analyzed using the UWXAFS 3.0 package²⁸ and the FEFF 8 code,²⁹ licensed from the University of Washington. The detailed procedure for data analysis is described elsewhere.^{25,30} The pre-edge background was removed by using a simple linear fit. The postedge background function was approximated with a piecewise spline that could be adjusted so that the low- R components of pre-Fourier transformed data $\chi(R)$ were minimized. The interference function of the EXAFS data could be obtained from $\chi(E) = [\mu(E) - \mu_0(E)]/\Delta\mu_0(E)$ above the absorption edge E_0 , where $\mu(E)$ is the absorption coefficient at energy E , $\mu_0(E)$ is the atomic-like absorption, and $\Delta\mu_0(E_0)$ is the jump at the edge. The scaled EXAFS function $k^3\chi(k)$ in momentum (k) space was Fourier transformed to obtain the radial structural function (RSF) in R space. A shell of interest in the RSF was back-Fourier transformed into momentum space. The Hanning windowsills window function was used to reduce the truncation effects from both forward- and inverse-Fourier transformations over a finite range. The reference materials used as standards for fitting the experimentally derived RSFs were generated with the FEFF 8 code and the Fourier-filtered data were fitted in momentum space. The amplitude reduction factor (S_0^2) was taken to be 0.76 for Fe, and was determined by fitting the experimental RSF of an Fe foil to that for metallic Fe generated with the FEFF 8 code.

Figure 1. Fe K-edge XANES of unactivated Fe/Al-MFI; (a) Fe/Al-MFI(0.38), (b) Fe/Al-MFI(1.02), and (c) Fe/Al-MFI(∞).

Figure 2. Fe K-edge XANES of activated Fe/Al-MFI; (a) Fe/Al-MFI(0.38), (b) Fe/Al-MFI(1.02), and (c) Fe/Al-MFI(∞).

Results and Discussion

XANES of Fe/Al-MFI. The XANES spectra recorded before and after activation are shown in Figures 1 and 2. Peaks observed in the XANES region of an XAFS experiment are due to electronic transition from an inner level to the outer unoccupied levels caused by X-ray absorption. These features give information about the local electronic structure and coordination environment around an absorber. The pre-edge feature ~ 10 eV below the Fe K-absorption edge appears because of a $1s \rightarrow 3d$ electron transition. While this electric-dipole transition is forbidden by parity considerations, it is observable experimentally due to electric quadrupole coupling.³¹ Unactivated Fe/Al-MFI shows an intense pre-edge peak regardless of the Fe/Al ratio and the intensity is the same for all samples. Bordiga et al.² and Berlier et al.³ have reported similar pre-edge features for Fe-MFI. Activation of the samples prepared in the present study at 1123 K causes a significant decrease in the pre-edge peak, as shown in Figure 2. The decrease in pre-edge intensity after activation is consistent with Fe leaving the noncentrosymmetric environment of the tetrahedral framework during activation and migrating to extraframework positions.^{32,33}

TABLE 1: Fe K-edge Energies of the Reference Materials and Fe/Al-MFI

	edge energy (eV) ^a	
Fe foil	7111.2	
FeO	7117.5	
Fe ₃ O ₄	7121.7	
Fe ₂ O ₃	7122.6	
Fe/Al-MFI(x)	unactivated	activated
x = 0.38	7122.2	7120.0
1.02	7122.4	7119.5
∞	7122.5	7122.2

^a precision ±0.1 eV. **Figure 3.** Fourier transforms of $k^3\chi(k)$ for unactivated Fe/Al-MFI; (a) Fe/Al-MFI(0.38), (b) Fe/Al-MFI(1.02), and (c) Fe/Al-MFI(∞). Fourier transforms of $k^3\chi(k)$ were conducted over the following ranges: (a) 1.95–11.55 Å⁻¹, (b) 1.95–10.70 Å⁻¹, (c) 1.95–11.60 Å⁻¹.

Supporting this conclusion is the observation that the intensity of the pre-edge peak of activated Fe/Al-MFI is very similar to that of He-pretreated Fe-ZSM-5 prepared by dry-exchange of H-ZSM-5.²⁵

Table 1 reports the Fe K-edge energy of unactivated and activated Fe/Al-MFI. The edge energy for several reference materials is also listed. The edge energy of unactivated Fe/Al-MFI is similar to that of Fe₂O₃, suggesting that the apparent oxidation state of Fe in unactivated Fe/Al-MFI is +3. Following activation, the edge energies for Fe/Al-MFI(0.38) and Fe/Al-MFI(1.02) decrease, suggesting that Fe is partially reduced. Following activation, the edge energy for Fe/Al-MFI(∞) decreases slightly, and now falls within the range reported for Fe₂O₃ and Fe₃O₄.

EXAFS of Fe/Al-MFI. The small oscillations in absorbance from 100 to 1000 eV above the absorption edge were isolated to produce the EXAFS function, $\chi(k)$ and the scaled EXAFS function $k^3\chi(k)$ was then Fourier transformed. Figure 3 shows the Fourier transforms of $k^3\chi(k)$ for each of the Fe/Al-MFI samples before activation at 1123 K. Unactivated Fe/Al-MFI has a principal peak at ~1.4 Å, corresponding to the contributions of oxygen in the lattice.^{1,3} This is consistent with the observation that the peaks at ~1.4 Å for each of the unactivated Fe/Al-MFI materials are nearly identical, irrespective of Fe and Al content. The Fourier-filtered EXAFS for Fe/Al-MFI(1.02) was fitted using a model consisting of an Fe absorber coordinated to four O atoms. The results of this fit are given in

TABLE 2: EXAFS Least-square Fitting Results for Fe/Al-MFI

treatment	Fe/Al	shell	N	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)	R-factor
unactivated	1.02	Fe-O	4.0*	1.78	0.0072	-14.7	0.0210
activated	0.38	Fe-O	2.7	2.12	0.0065	-0.19	0.0371
		Fe-Al	0.8	2.87	0.001*	1.49	
		Fe-O	2.0	3.13	0.001*	1.49	
		Fe-O	2.7	2.12	0.0062	0.26	0.0378
		Fe-Al	1.4	2.88	0.001*	6.76	
		Fe-Si	1.4	3.02	0.001*	6.76	
activated	1.02	Fe-O	3.6	2.06	0.0177	-2.74	0.0206
		Fe-Al	2.3	2.94	0.0095	7.00	
activated	∞	Fe-O	1.3*	1.88	0.0001	-6.02	0.0105
		Fe-O	4.0*	2.05	0.0065	-6.02	
		Fe-Fe	4.0*	3.01	0.0085	-7.82	
		Fe-Fe	8.0*	3.50	0.0057	-7.82	
		Fe-O	9.3*	3.69	0.0206	-6.02	
		Fe-Fe	1.3*	3.68	0.0008	-7.82	

*Fixed parameters.

Figure 4. Fourier transforms of $k^3\chi(k)$ for activated Fe/Al-MFI; (a) Fe/Al-MFI(0.38), (b) Fe/Al-MFI(1.02), and (c) Fe/Al-MFI(∞). Fourier transforms of $k^3\chi(k)$ were conducted over the following ranges: (a) 1.70–11.05 Å⁻¹, (b) 1.75–11.10 Å⁻¹, (c) 1.85–13.5 Å⁻¹.

Table 2. The Fe-O distance, 1.78 Å, is ca. 0.22–0.30 Å shorter than that reported for Fe-ZSM-5.²⁵ The Fe-O distance for unactivated Fe/Al-MFI reported in Table 2 is comparable to the values reported previously for Fe-MFI, 1.83 to 1.86 Å.^{1,3,6}

After activation, the Fourier transform of $k^3\chi(k)$ for each of the Fe/Al-MFI materials shows significant changes relative to the unactivated samples (see Figure 4). In the Fourier transform of $k^3\chi(k)$ of activated Fe/Al-MFI (Fe/Al = 0.38 and 1.02) the peak originally at 1.4 Å for the unactivated materials moves to 1.6 Å and a new peak appears at 2.5 Å. By contrast, the Fourier transform of $k^3\chi(k)$ for activated Fe/Al-MFI(∞), displays a very different pattern (see below).

The experimentally obtained EXAFS functions are compared in Figure 5 for activated Fe/Al-MFI and Fe-ZSM-5 at roughly comparable Fe/Al ratios. While not completely identical, the k^3 -weighted scattering functions are very similar for Fe/Al-MFI and Fe-ZSM-5. This same level of similarity is observed in the Fourier transforms of $k^3\chi(k)$ seen in Figures 6 and 7. In each case there are well-defined peaks observable at 1.6 and 2.5 Å (not phase corrected). The only significant difference is the shoulder ca. 3 Å in the Fourier transforms of $k^3\chi(k)$ for Fe/Al-MFI(0.38).

Figure 5. Experimental k^3 -weighted scattering functions, $k^3\chi(k)$, for Fe/Al-MFI (0.38) (solid line) and Fe-ZSM-5(0.33) (dashed line).

Figure 6. Fourier transforms of $k^3\chi(k)$ for Fe/Al-MFI (0.38) (solid line) and Fe-ZSM-5(0.33) (dashed line). Fourier transforms of $k^3\chi(k)$ were conducted over the following ranges: (a) 1.70–11.05 $\text{\AA}^{-1}$, (b) 1.75–11.10 $\text{\AA}^{-1}$.

In our previous work with postsynthetic-exchanged Fe-ZSM-5, it was concluded that the peak at 1.6 $\text{\AA}$ was the result of Fe–O backscattering.²⁵ For the peak at 2.5 $\text{\AA}$ three possibilities were considered: Fe–Al backscattering, Fe–Fe backscattering, or a combination of Fe–Al and Fe–Fe backscattering. To this end, quantum chemical calculations were performed to determine the geometries for several possible isolated and di-iron species associated with framework Al. Density functional theory calculations were carried out using the B3LYP functional and the 6-31G** basis set. The Fourier transform of $k^3\chi(k)$ for

Figure 7. Fourier transforms of $k^3\chi(k)$ for Fe/Al-MFI(1.02) (solid line) and Fe-ZSM-5(0.80) (dashed line). Fourier transforms of $k^3\chi(k)$ were conducted over the following ranges: (a) 1.70–11.05 $\text{\AA}^{-1}$, (b) 1.75–11.20 $\text{\AA}^{-1}$.

each of these structures was then simulated using the FEFF 8 code. It was determined that all three cases result in peaks at 2–3 $\text{\AA}$ in the Fourier transforms of $k^3\chi(k)$ that are indistinguishable if only the magnitude of the function is considered. However, the imaginary portion of the Fourier-transformed data provides additional information. The ability to identify the backscattering element contribution to a given peak by observing the imaginary part of the Fourier-transformed data is supported by the recognition that this function is a characteristic of the absorber-backscatterer pair, independent of the distance between the absorber and the backscatterer or the coordination number of the backscatterer.³⁰ Comparison of the imaginary part of the Fourier transforms of $k^3\chi(k)$ for Fe–Al backscattering, Fe–Fe backscattering, or a combination of Fe–Al and Fe–Fe backscattering revealed that Fe–Al and Fe–Fe backscatterers result in easily distinguishable imaginary parts of the RSF. It was also discovered that a combination of Fe–Al and Fe–Fe backscatterers resulted in an imaginary part of the RSF that was nearly identical to the case of Fe–Fe. Comparison of the magnitude and imaginary part of the experimental RSF for postsynthetic exchanged Fe-ZSM-5 with the three model cases resulted in a close match to the Fe–Al case. Based on this analysis, it was concluded that the peak at 2.5 $\text{\AA}$ in the Fourier transform of $k^3\chi(k)$ of postsynthetically exchanged Fe-ZSM5 is due to Fe–Al scattering. Figure 8A shows the magnitude (solid line) and imaginary part (dashed line) of the Fourier transform of $k^3\chi(k)$ for Fe/Al-MFI(0.38), while Figure 8B shows the corresponding plots for Fe-ZSM-5(0.33). Comparison of these figures reveals that the magnitude and imaginary part of the Fourier transform of the peak in $k^3\chi(k)$ at 2.5 $\text{\AA}$ are nearly identical for both cases. Based on this similarity, the peak at 2.5 $\text{\AA}$ in the Fourier transforms of $k^3\chi(k)$ of Fe/Al-MFI(0.38) and Fe/Al-MFI(1.02) is assigned to Fe–Al backscattering.

We propose two possibilities for the origin of the shoulder peak at 3 $\text{\AA}$ for Fe/Al-MFI(0.38), Fe–O and Fe–Si scattering. Fe–Fe and Fe–Al scattering are eliminated because, as discussed above, simulations of Fe–Fe and Fe–Al backscattering have been found to result in peaks at shorter distances ca. 2.5 $\text{\AA}$.²⁵ Furthermore, Fe–Fe backscattering is eliminated because the iron concentration in the Fe/Al-MFI(0.38) is quite

Figure 8. Fourier transforms of $k^3\chi(k)$ for (a) Fe/Al-MFI(0.38) and (b) Fe-ZSM-5(0.33). The magnitudes of the Fourier-transformed data are plotted as solid lines and imaginary parts of the Fourier transformed data are plotted as dashed lines.

TABLE 3: Comparison of Interatomic Distances for Fe/Al-MFI and Fe-ZSM-5

R ($\text{\AA}$)	Fe/Al-MFI (0.38)	Fe/Al-MFI (1.02)	Fe-ZSM-5 (0.33)	Fe-ZSM-5 (0.80)
Fe-O	2.12	2.06	2.14	2.11
Fe-Al	2.87	2.94	2.90	2.82

low, at 0.38 wt % Fe and the Fourier transform of $k^3\chi(k)$ for the more iron-concentrated material (Fe/Al-MFI(1.02)) in Figure 8A does not show a shoulder in the Fourier transform of $k^3\chi(k)$ near 3 $\text{\AA}$. Therefore, we exclude the possibility that this shoulder is due to backscattering from a neighboring Fe atom.

With the aid of the identification for the peaks at 1.6 $\text{\AA}$ and 2.5 $\text{\AA}$ in Fe-ZSM-5, we adopted one Fe-O and one Fe-Al scattering for the two main peaks in the Fourier transforms of $k^3\chi(k)$ of Fe/Al-MFI(0.38) and Fe/Al-MFI(1.02).²⁵ To fit the shoulder of the second peak for Fe/Al-MFI(0.38), we also considered the scattering from oxygen or silicon through separate EXAFS least-squares fits. The results are shown in Table 2. The goodness of the two fits for Fe/Al-MFI(0.38) are similar and thus, it is difficult to determine the source of the shoulder. The total coordination number for the peaks at 2.5–3.15 $\text{\AA}$ is 2.8 in both fits. In the fit where a silicon shell was considered, the Fe-Al and Fe-Si coordination numbers are both 1.4, half of the total coordination number, since the Al and Si around the iron have very similar potentials.

Both fits for Fe/Al-MFI(0.38) and the fit for Fe/Al-MFI(1.02) have an Fe-O shell at 2.06–2.12 $\text{\AA}$ with an Fe-O coordination number of 2.7 for Fe/Al-MFI(0.38) and 3.6 for Fe/Al-MFI(1.02). For Fe/Al-MFI(0.38), both fits have an Fe-Al shell at 2.87–2.88 $\text{\AA}$ with an Fe-Al coordination number that varies with the type of shells fitted as described above. Fe/Al-MFI(1.02) has an Fe-Al shell at 2.94 with a coordination number of 2.3. Fe-Al coordination numbers greater than 1 were also observed for Fe-ZSM-5 and were attributed to the contribution of multiple scattering by oxygen or silicon atoms to the peak at 2.5 $\text{\AA}$.²⁵ Comparison of the interatomic distances for the first two shells for Fe/Al-MFI(0.38) and Fe/Al-MFI(1.02) are made with those of Fe-ZSM-5(0.33) and Fe-ZSM-5(0.80) in Table 3. Very close agreement is found for the Fe-O shell with an interatomic distance within 2.06–2.14 $\text{\AA}$ for all samples. Similarly, all samples display Fe-Al distances within 2.82–2.94 $\text{\AA}$. The similarity of the Fe-O and Fe-Al distances among these samples suggests similar struc-

Figure 9. (A) Experimental EXAFS $\chi(k)$ for activated Fe/Al-MFI(∞) (solid line) and bulk Fe_3O_4 (dotted line), and (B) Fourier-filtered EXAFS functions of activated Fe/Al-MFI(∞) (solid line) and its least-squares fit (dots).

tures. The Fe-O and Fe-Fe bond distances are also in good agreement with quantum chemical calculations of the structure for an isolated Fe cation bonded to the charge-exchange site at framework Al atoms. For such a structure the calculated Fe-O bond distance is 1.99 $\text{\AA}$ and the Fe-Al bond distance is 2.85.³⁴

The structure of the material with no Al, Fe/Al-MFI(∞), changed considerably after activation, as shown in Figure 4c. The Fourier transforms of $k^3\chi(k)$ are clearly different from those of unactivated Fe/Al-MFI and the activated materials with Al. Figure 9A compares the experimental EXAFS function for the sample with that of bulk Fe_3O_4 . The spectra are almost identical. Because of this similarity, we fit the experimental results using a theoretically generated Fe_3O_4 standard. For the fit, six shells were fit up to a distance of ca. 3.5 $\text{\AA}$. We fixed coordination numbers as average values for two different irons in an octahedral and a tetrahedral coordination.³⁵ The experimental

Fourier-filtered $k^3\chi(k)$ and its fit are shown in Figure 9B. The fitting results are also included in Table 2. The distances between atoms are identical to those given by Krylov et al.,³⁵ confirming that the activated Fe/Al-MFI(∞) with no Al has the inverse spinel structure of Fe₃O₄.

Conclusions

Iron in unactivated Fe/Al-MFI resides in tetrahedral positions within the MFI framework. However, after thermal activation XANES and EXAFS measurements suggest that Fe migrates to extraframework sites. When Al is included in the structure, the resulting extraframework Fe associates with framework Al in a manner identical to that observed for Fe-ZSM-5. Thermal activation of Fe/Al-MFI prepared without Al results in extraframework Fe with a structure similar to Fe₃O₄. Therefore, aluminum in the MFI framework plays a critical role in the stabilization of isolated Fe.

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