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Determination of Fe-substituted sites in the MFI structure by Fe K-edge EXAFS

N. Matsubayashi *, H. Shimada, M. Imamura, T. Sato, K. Okabe, Y. Yoshimura, A. Nishijima

National Institute of Materials and Chemical Research, 1-1, Higashi, Tsukuba, Ibaraki, 305 Japan

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Abstract

The local structure around iron in the MFI structured ferrisilicate was investigated by the Fe K-edge extended X-ray absorption fine structure (EXAFS) method to identify the Fe substituted sites in the framework. After removal of the intense first neighbor Fe–O peak, the second and further peaks in the Fourier transformed EXAFS spectra of the MFI structured ferrisilicate were analyzed by comparing the experimentally-obtained spectra with the simulated ones for twelve Si sites in the MFI framework. The results suggest that a few of the twelve Si sites in the framework are selectively substituted by Fe.

Keywords: EXAFS; MFI ferrisilicate

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1. Introduction

Synthetic zeolites are extensively applied to sorbents, ion exchangers, catalysts and catalyst supports. In particular, much attention has been paid to the MFI structured zeolites in the field of catalysis because of the peculiar cross-linked cages with ten-membered rings which are the origin of the high selectivity for the gasoline fraction in the methanol-to-gasoline (MTG) reaction [1]. The isostructural ferrisilicate is also an interesting material because iron is atomically dispersed in the MFI framework [2]. From catalytic view point, the MFI structured ferrisilicate, having weaker acid sites than the isostructural aluminosilicate, provides high selectivity for light olefins.

In spite of lots of investigations on the ZSM-5 zeolites, the aluminum-substituted sites in the framework have not been well determined. Furthermore, almost no information has been given on the Fe-substituted sites in the framework of the MFI ferrisilicate. The authors have previously studied the crystallization of the MFI ferrisilicate by versatile techniques, such as FT-IR, TG, XRD and extended X-ray absorption fine structure (EXAFS) [3,4]. In the present study, the EXAFS method has been applied to the investigation of local structure around Fe in the MFI framework. The discussion has been extended to the determination of the Fe-substituted sites.

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* Correspondence author.

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2. Experimental

Appropriate amounts of colloidal silica, ferric nitrate, tetrapropylammonium(TPA) bromide, sodium hydroxide and distilled water were mixed together to form a ferrisilicate gel having the following molar ratios; $SiO_2/Fe_2O_3 = 60$, $SiO_2/TPABr = 10$, $SiO_2/OH = 10$. The gel was subsequently autoclaved at 433 K. The completely and partially crystallized ferrisilicate samples were taken out of the cooled autoclave at several stages during the hydrothermal reaction. In this report, the samples are specified by the synthesis periods of 2–60 h. The crystallinity of the each sample was evaluated by the XRD peak intensity corresponding to a spacing of $d(501)$.

The Fe K-edge XAFS measurements were performed in the transmission mode at the BL-7C of the Photon Factory, National Laboratory for High Energy Physics with a Si(111) double crystal monochromator at about 20 K under a vacuum of 10^{-2} Pa. The samples were pressed into pellets with 10–20 vol.-% of dry methylcellulose as a binder under a dry nitrogen atmosphere.

All the EXAFS analyses were performed in r-space by Fourier transformation. Prior to Fourier transformation, each EXAFS spectrum was transformed to normalized $\chi(k)$ by the method developed by one of the authors [5]. Low frequency noises of the obtained $\chi(k)$ which give ghost peaks within 1.5 Å^{-1} were removed by subtracting the inverse Fourier transform of the peaks within 1.5 Å^{-1} in the Fourier transform from original $\chi(k)$ spectra. The hamming window function was used over the full range of data ($k = 2.35–19.45$ Å^{-1}) in the Fourier transform. It was confirmed by synthesized data that the procedure did not distort the Fourier transforms. Finally, the spectra in r-space were obtained by Fourier transformation of the $\chi(k)$ of a range of $k = 2.8–14.8$ Å^{-1} with a hamming window width of 10% of the range on both sides. The phase shift correction during the Fourier transformation was done using the phase shift functions for Fe–O and Fe–Si obtained by FEFF [6] calculation.

3. Results and discussion

Fig. 1 shows the Fourier transforms of the Fe K-edge EXAFS of the ferrisilicate samples in each stage of hydrothermal reaction together with the spectra of α-FeO(OH) and Fe_2SiO_4. The intensity of the nearest peak at 1.8 Å attributed to the nearest Fe–O scattering slightly increases with hydrothermal reaction time up to 16 h and then drastically increases between 16 and 16.5 h. From the XRD intensities, the crystallization was found to be completed in a short period of 30 min after 16 h induction period [3]. Thus, the notable increase in the Fe–O peak intensity is ascribed to the fact that the Fe atoms in the ferrisilicate are atomically dispersed in the tetrahedral MFI framework.

Fig. 2 shows the Fe K-edge XANES spectra of the ferrisilicate after 16 and 16.5 h of reaction periods with the spectrum of α-FeO(OH). The peak at 7110 eV corresponding to 1s → 3d

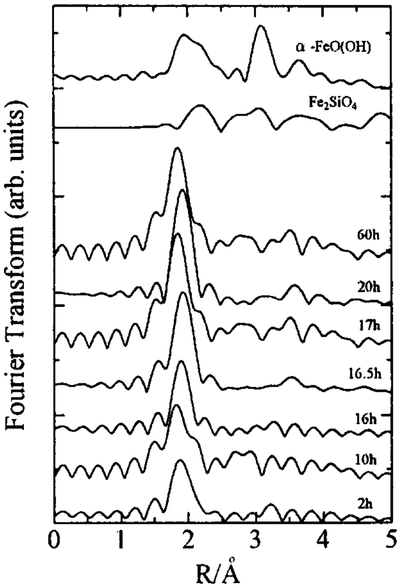

Fig. 1. Fourier transforms of Fe K-edge EXAFS spectra of Fe zeolite during the hydrothermal reaction (2, 10, 16, 16.5, 17, 20, 60 h as synthesis period) with those of α-FeO(OH) and Fe_2SiO_4.

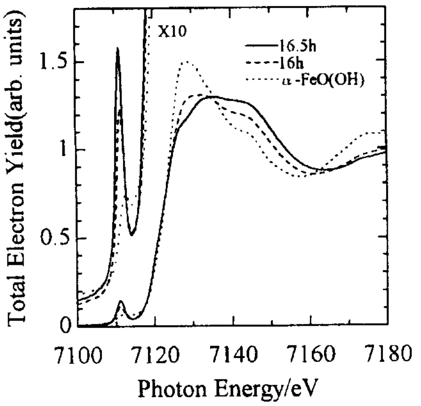

Fig. 2. Fe K-edge XANES spectra at reaction periods of 16 and 16.5 h with the spectra of α-FeO(OH).

transition is enhanced in tetrahedral coordination. The peak at 7128 eV is characteristic of octahedral coordination such as α-FeO(OH). Thus, the XANES features of 7100–7150 eV show that the structure around Fe is changed from octahedral coordination to tetrahedral coordination during the crystallization. That is to say, most of Fe atoms are incorporated into the framework during the crystallization. This result is in good agreement with the previous result showing that more than 80% of Fe atoms are in the framework by XRD, IR, NH_3-TPD and other techniques [3].

The second and further neighbor peaks in the Fourier transformed spectra involve interesting information on the ferrisilicate configuration which may indicate the Fe-substituted sites. These peaks, however, are weak and overlapped with the ripple peaks from the intense Fe–O peak even in the spectra of well-crystallized samples.

To focus on the second and further peaks in Fig. 1, the nearest Fe–O peaks at 1.8 Å were removed by Fourier filtering with full range hamming window, as shown in Fig. 3. By this procedure the influence of the ripple peaks from the nearest Fe–O peak was completely removed. In Fig. 3, the phase shift function of Fe–Si was used instead of Fe–O in Fig. 1 for the phase shift correction.

Weak peaks appear at 3.1 Å in the spectra of all the ferrisilicate samples. We assign these peaks to Fe–(O)–Si scattering, although the distance is too close to the distance of Fe–(O)–Fe (3.06 Å) in α-FeO(OH) [6] to distinguish them. A new peak appears at 3.6 Å in the spectra of the ferrisilicates with synthesis time longer than 16.5 h corresponding to the completion of crystallization. This change is due to the change of the local structure around Fe from Fe–O–Fe into Fe–O–Si, consistent with the notable increase of the nearest Fe–O peak between 16 h and 16.5 h in Fig. 1. The distance of 3.6 Å, however, is too large to be assigned to Fe–(O)–Si bonding in the MFI crystal.

The peaks at 3.6 Å is very likely resulted from the multiple scattering. Thus, as a next step we have employed simulation analysis of the EXAFS spectra using the FEFF program by Rehr et al. [7], in which the multiple scattering effect is well considered.

The atomic coordinates used in the simulation were obtained by substituting Si by Fe in the crystal structure of TPA ZSM-5 zeolite obtained by single crystal X-ray diffraction [8]. The numbering of the Si sites (*T*: to be indi-

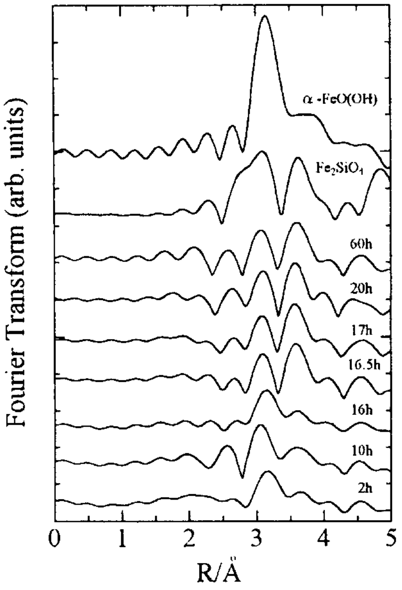

Fig. 3. Fourier transforms removed the contribution of the peaks at 1.8 Å in Fig. 1.

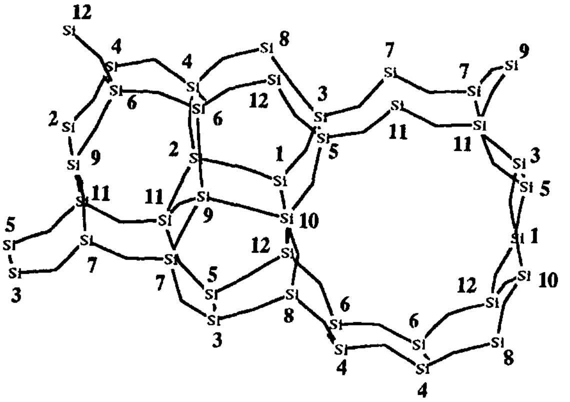

Fig. 4. ZSM-5 framework structure showing the Si-site numbering used.

cated hereafter) is shown in Fig. 4. The Fe–O distances in the distorted tetrahedron were elongated by 0.28 Å, compared with the Si–O distances in the aluminosilicate ZSM-5 structure, to fit the simulated EXAFS to the experimental data of the ferrisilicate (16.5 h). Other atomic coordinates were assumed to be the same as those in the aluminosilicate ZSM-5 structure. In the FEFF calculation, Debye temperature and amplitude reduction factor were adopted as fitting parameters to fit the simulated EXAFS to the experimental data. As the result, the Debye temperature and the reduction factor were fixed, respectively, at 800 K and unity for calculation on all the *T* sites of the MFI framework.

Fig. 5 shows Fourier transforms of the EXAFS for each of twelve *T* sites and the average of all the simulated data by FEFF, together with the experimental of the ferrisilicate (16.5 h). In all the Fourier transforms, the nearest Fe–O peaks at 1.8 Å have been removed in the same way as in Fig. 3. All the simulated data exhibit intense peaks at about 3 Å corresponding to Fe–(O)–Si scattering in the MFI crystal. Thus, the peak at 3.1 Å in the experimental data is attributed to Fe–(O)–Si scattering. The peak shift from 3 to 3.1 Å is due to the substitution of Si by Fe. The shift is much smaller than expected from the Fe–O elongation from 1.58 to 1.86 Å. By an XRD measurement [9], the *d*(084) spacing changes from 1.990 to 1.993 Å with 1% substitution of Si by Fe. Considering the small change of the lattice parameter, the Fe substitution is relaxed by quite local distortion of the Fe–O–Si bonding.

By comparing the experimental EXAFS with the simulated data on all the sites, the iron substituted sites can be discussed. If iron substi-

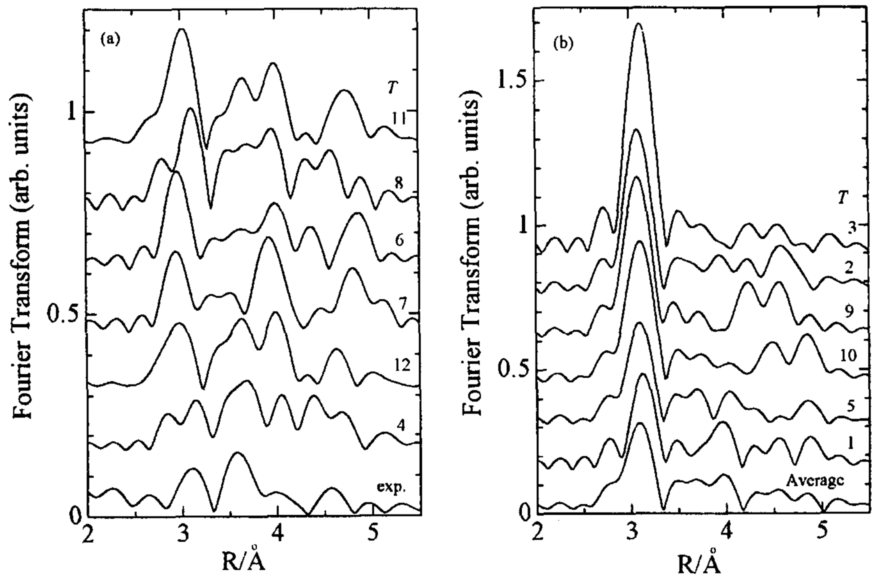

Fig. 5. Fourier transforms of EXAFS data simulated for twelve *T* sites and their average by FEFF with that of experimental data of 16.5 h. (a) with a weaker peak around 3 Å and (b) with a stronger peak around 3 Å.

tutes all the *T* sites randomly, the experimentally obtained spectra will agree with the averaged spectrum shown in the bottom of Fig. 5b. It should be noted that the Y-axis of Fig. 5b is scaled as about 70% of that of Fig. 5a. The peak at 3.1 Å in the experimental data, however, is much weaker than that in the averaged data. This suggests that iron substitutes several sites shown in Fig. 5a which give weaker peaks at 3.1 Å than those in Fig. 5b. Comparing the whole spectral characteristics, particularly the intensity of the peak at 3.1 Å and the features at 3.6, 4 and 4.6 Å, the experimentally obtained spectrum show resemblance to the simulated data for *T*4 and *T*12.

As described previously, the peak observed at 3.6 Å in the experimental EXAFS was not assigned to any single scattering of Fe–(O)–Si. Similar features are observed at about 3.6 Å in the simulated spectra for *T*4 and *T*12, which do not have Si atoms at the distance. This indicates that the peaks at about 3.6 Å are assigned to the multiple scattering involving the nearest Fe–O in tetrahedral coordination. Comparing the experimental EXAFS and the simulated ones for *T*4 and *T*12, the peaks at 4 and 4.6 Å correspond to the scatterings by the second and third nearest silicon, though these peaks may include contribution from the scattering by O and multiple scattering. The peak at 4 Å in the experimental spectrum is weaker than those of *T*4 and *T*12. This fact indicates larger structural distortion around Fe of the analyzed sample than those in the simulated spectra of the structure simulated on *T*4 and *T*12. The disagreement between the experimental and the simulation comes from the assumption in the present model that the configuration of second and further neighbor atoms is same as that of ZSM-5. Considering all the above results, iron is most likely to substitute selectively *T*4 and/or *T*12 sites in the MFI framework. More detailed analysis by optimization of three dimensional structure in the simulation will be necessary to ensure the above discussion.

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