

Fe K-edge XAFS Study of Fe-MFI Metallosilicates for NO Decomposition Catalysts with CH₄

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Introduction

Fe-modified zeolites have been reported for application of deNO_x catalysts. For example, Fe/H-MFI shows a high catalytic activity for selective catalytic reduction (SCR) of NO or N₂O with hydrocarbons. In this case, catalytically active species are Fe ions, and the ions supported on the zeolites are not stable structurally for the reaction. In case of metallosilicate-type materials, Fe ions can be stabilized in MFI-zeolite framework. The MFI-type metallosilicates with Fe³⁺ in the framework have been reported by several workers, and it is applied to the catalyst with red-ox activity. Recently, Wu et al. reported that Fe³⁺-substituted Al³⁺-mordenites are synthesized under template-free condition.¹ We recently synthesized the Fe³⁺-substituted Al-mordenites with high crystallinity. In our previous study, Fe-incorporated MOR catalysts synthesized by hydrothermal synthesis shows high activity for NO-SCR. The local structure of Fe ions in the Fe-substituted mordenite (FeMOR) catalysts were evaluated by K-edge XAFS. In this report, we applied Fe K-edge XAFS for characterization of Fe-substituted MFI metallosilicates (synthesized as described below), which shows higher activity for NO-SCR than FeMOR. In addition, the stability of the local Fe³⁺ structure for NO-CH₄ reaction is also evaluated.

Experimental

The metallosilicates of Fe-substituted MFI zeolites were prepared by the hydrothermal synthesis. In brief, Fe-mordenites with several ratio of Fe/(Fe+Al) were synthesized at 343 K for 7 days from the Na₂O-Fe₂O₃(and/or Al₂O₃, Ga₂O₃)-SiO₂-H₂O system with the tetrapropylammonium bromide as a template. Detail of the synthesis is similar to that of FeMOR, described in other paper.² Each Fe content is denoted as Fe_NMFI (N = Fe/(Fe+Al) [%]), and molecular ratio of silica/alumina (= Si/(Fe+Ga+Al)₂) is 72 in whole samples. Microporous properties of the synthesized samples with high crystallinity have been confirmed by means of XRD, Raman, and N₂-isotherm (at 77 K). The XAFS measurement was carried out at the BL-10B station of the KEK-PF in a transmission mode at room temperature. Data analysis of EXAFS was carried out by the method described elsewhere.³

Results and discussion

Fig. 1 shows Fe K-edge XANES of FeMFI and FeGaMFI before/after the NO-CH₄ reaction. In case of

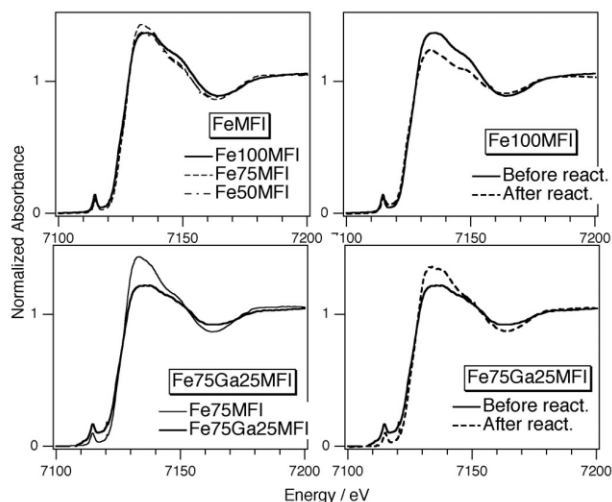


Figure 1 Fe K-edge XANES of FeMFI samples before/after NO-CH₄ reaction at 873 K.

FeMFI, XANES spectra in all Fe ratios are almost due to tetrahedral Fe³⁺ with T_d symmetry. This result indicates the incorporation of Fe ions in MFI-zeolite framework. By co-existence of Ga in FeMFI (FeGaMFI), mixture of tetrahedra and FeOOH-like octahedra may be present from XANES spectra. It indicates the distortion of Fe symmetry by co-substitution of Ga³⁺. On these samples, order of NO-SCR activity is; Fe₇₅Ga₂₅MFI > Fe₁₀₀MFI > Fe₇₅MFI > Fe₅₀MFI. These result suggests that incorporated Fe³⁺ ions act as active species, and Ga co-substitution enhance the activity of Fe³⁺ species. After NO-CH₄ reaction at 873 K, structural change can be shown by XANES in both FeMFI and FeGaMFI. For FeMFI, distortion of Fe³⁺-tetrahed is brought about to form C_{3v}-like octahedra. On the other hand, Fe species in FeGaMFI shows nearly T_d-symmetric tetrahedra after the reaction. The feature of structural change during the reaction is definitely different from FeMFI. In addition, result of the tendency of the structural change is supported by that of FT-EXAFS. From these results, T_d-symmetric Fe³⁺ species in MFI framework act as the active species, and its stability relates to the catalytic activity for NO-SCR.

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- 3 T. Tanaka et al., *J. Chem. Soc. Faraday Trans. 1*, **84**, 2987 (1988).

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