

Structural Analysis of the Active Sites of Fe-MFI Catalysts for Selective Catalytic Removal of Nitrous Oxide

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Introduction

Nitrous oxide (N₂O) is a strong green-house effect gas and can contribute to catalytic stratospheric ozone destruction. Recently we reported that the catalytic activity in N₂O reduction with CH₄ on Fe-MFI was dependent on the exchange level of Fe ion [1]. From the results of activity test and catalyst characterization, we suggested the presence of two types of Fe ion sites: mononuclear and binuclear Fe species. In this study, we characterized the structure of Fe species on Fe-MFI and discuss the nature of active sites of N₂O reduction on the basis of the relation between catalyst structure and performance.

Experimental

The zeolite-supported Fe-MFI catalyst was prepared by wet ion-exchange method [1]. The precursor of iron was FeSO₄·7H₂O (Wako). The Na form MFI zeolite was provided by TOSOH Co. (Si/Al₂ = 23.8). The loading amount of Fe is 0.35 and 2.8 wt%. The sample disk (0.5 mm, 10 mm ϕ) for EXAFS measurements was pretreated at 773 K with 11 kPa O₂ or N₂O for 0.5 h in a closed circulation reactor, respectively. After treatment, the sample disk was transformed to the measurement cell without exposing the sample disk to air. Iron *K*-edge EXAFS spectra were measured by transmission mode at liquid nitrogen temperature. After back ground subtraction, *k*³ weighted EXAFS functions were Fourier transformed into *R* space and the three or four-shell fitting were analyzed by curve fitting.

Results and Discussion

Figure 1(a) shows *k*³-weighted Fe *K*-edge EXAFS oscillations for 0.70 wt% Fe-MFI measured after treatment with O₂ or N₂O. It seems that the oscillation on 0.70 wt% Fe-MFI treated with O₂ is similar to that with N₂O. From the fitting results of EXAFS data [2], we could fit these spectra with the Fe-O₁ (OH species coordinated with Fe ion sites), Fe-O₂ (zeolite lattice), and Fe-Si shells. Therefore, it is expected that the Fe species over 0.70 wt% Fe-MFI can be isolated. Furthermore, the possibility of Fe-Fe bond over 0.70 wt% Fe-MFI can be ruled out because this catalyst contains almost exclusively Fe ions with lower reducibility from H₂-TPR and O₂-TPD results [1]. The comparison of the results between O₂ and N₂O treatments shows that the coordination number and the distance were almost the same values. This also indicates that only mononuclear Fe species are present over 0.70 wt% Fe-MFI catalyst.

In the case of 2.8 wt% Fe-MFI, the oscillation after the treatment with N₂O is different from that after O₂ treatment, especially, higher *k* region. From the fitting results of EXAFS data [2], we observed the contributions of the bridged oxygen species such as Fe-O-Fe and Fe-Fe bond after N₂O treatment. This behavior can be interpreted the presence of vacancy sites, which can be only fulfilled by bridged oxygen species after N₂O treatment. These are in good agreement with the results of O₂-TPD study [1]. Considering also other characterization results from H₂-TPR and O₂-TPD [1], it is strongly suggested that binuclear Fe species are formed on 2.8 wt% Fe-MFI. The coordination number of Fe-Fe is less than unity. This means that mononuclear Fe species also present over Fe-MFI. From the results of EXAFS analysis combined with other characterization, it is found that 2.8 wt% Fe-MFI contains binuclear and mononuclear Fe species, and 0.70 wt% Fe-MFI contains only a mononuclear Fe species.

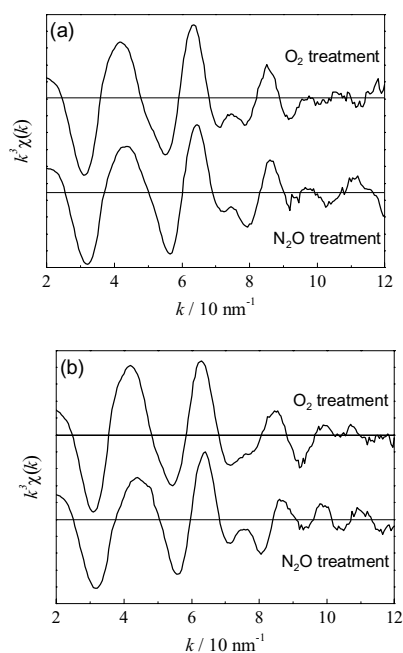


Fig. 1. *k*³-weighted Fe *K*-edge EXAFS for (a) 0.70 wt% Fe-MFI and (b) 2.8 wt% Fe-MFI.

References

- [1] M. Yoshida et al., *J. Catal.* 223 (2004) 454.
- [2] T. Nobukawa et al., *J. Catal.* 229 (2005) 374.

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