

Structural Analysis of the Active Sites of Fe-zeolite 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. Ion-exchanged Fe-BEA catalyst is the most efficient catalyst for the selective catalytic reduction (SCR) of N₂O with CH₄ in the presence of excess O₂ [1]. Although the active site is Fe ion species in the SCR reaction, the detailed structure of Fe ion species is unclear. In this study, in order to clear Fe ion structure, Fe *K*-edge EXAFS of Fe-BEA catalyst was measured after different conditions.

Experimental

The zeolite-supported Fe-BEA catalyst was prepared by wet ion-exchange method [1]. The precursor of iron was FeSO₄·7H₂O (Wako). The zeolite was provided by ZEOLYST Co. (Si/Al₂ = 25). The loading amount of Fe is 1.5 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 Fourier transforms of *k*³-weighted Fe *K*-edge EXAFS for Fe-BEA catalyst after O₂ or N₂O treatment. As can be seen in this figure, one peak with shorter bond length of 0.1-0.2 nm became small after N₂O treatment. On the other hand, the other peak with longer bond length of 0.2-0.3 nm became large after N₂O treatment.

Figure 1(b) and (c) show Fourier Filtered EXAFS data and calculated data after O₂ and N₂O treatment, respectively. The fitting results are listed in Table 1. It is found that Fourier Filtered EXAFS oscillation after N₂O treatment is different from that after O₂ treatment. After O₂ treatment, Fe-O₁, Fe-O₂, and Fe-Si bonds could be ascribed to O atoms of the OH species coordinated with Fe ion species, coordination of Fe species with zeolite lattice oxygen, and coordination of Fe species with zeolite lattice silicon, respectively. After N₂O treatment, we observed the Fe-Fe bond, which can be ascribed to binuclear Fe species, and increase of coordination number of Fe-O₁. This is due to bridging two Fe ions induced by

deposited oxygen during the N₂O treatment. From the CN value, the binuclear Fe species exist about half value of the total Fe ion on the catalyst. These results were in good agreement with other characterization results. Generally specking, binuclear species can be reduced easier than mononuclear one, therefore, formation of binuclear Fe species is important for the high activity of SCR reaction.

Table 1: Fe *K*-edge EXAFS fitting results for catalyst pretreated under different conditions.

Shell	CN	<i>R</i> / 10 ⁻¹ nm	σ / 10 ⁻¹ nm
O₂ treatment*			
Fe-O ₁	1.2 ± 0.1	1.88 ± 0.01	0.061 ± 0.014
Fe-O ₂	2.6 ± 0.2	2.05 ± 0.01	0.076 ± 0.009
Fe-Si	1.5 ± 0.3	3.23 ± 0.02	0.079 ± 0.025
N₂O treatment*			
Fe-O ₁	1.4 ± 0.1	1.88 ± 0.01	0.067 ± 0.012
Fe-O ₂	2.6 ± 0.1	2.03 ± 0.01	0.074 ± 0.008
Fe-Si	1.5 ± 0.3	3.23 ± 0.02	0.079 ± 0.026
Fe-Fe	0.5 ± 0.1	2.95 ± 0.01	0.059 ± 0.027

* Fourier Filtering range: 0.071-0.304 nm

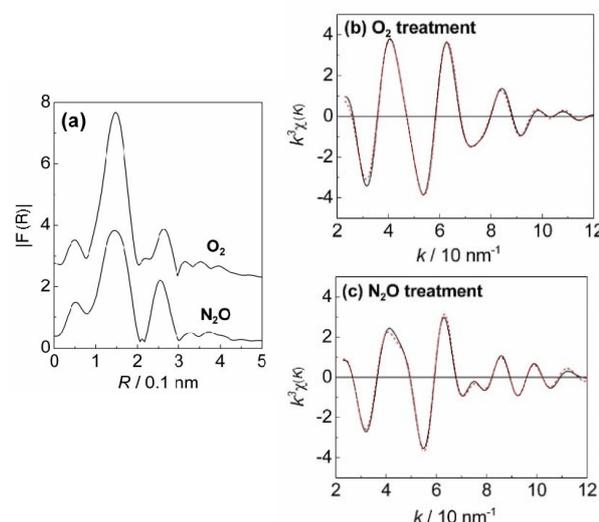


Fig. 1. (a): Fourier transforms of *k*³-weighted Fe *K*-edge EXAFS for Fe-BEA catalyst after O₂ and N₂O treatment. Fourier filtered EXAFS data (solid line) and calculated data (dotted line) after (b) O₂ and (c) N₂O treatment. Fourier transforms range: 23-120 nm⁻¹

References

[1] S. Kameoka et al., Chem. Commun. 745 (2000).

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