

XAFS study of iron titanate catalyst for NH₃-SCR of NO_x

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Introduction

Iron titanate catalyst (FeTiO_x) is a potential candidate for the substitution of V₂O₅-WO₃ (MoO₃)/TiO₂ catalyst for NH₃-SCR of NO_x to eliminate NO_x from stationary and mobile sources.^[1] To investigate the microstructure of active phase in this novel catalyst, XRD, Raman spectra and FTIR *etc.* have been applied, indicating that the active phase is mainly iron titanate crystallite. XAFS is a useful tool to characterize the local structure of such kind of catalytic material, thus XANES and EXAFS study have been performed systemically in this study.

Experimental

The XAFS of Fe, Ti K-edges and S K-edge were recorded in a transmission mode on BL-7C beam line and in a fluorescence mode on BL-9A beam line at PF, KEK, Japan. Data were analyzed using the REX2000 program. The XANES of S K-edge were normalized by edge height and then the first-order derivatives were determined to compare the variation of absorption edge energies.

Results and discussion*Influence of calcination temperature on microstructure*

XANES results indicate that the coordination structures of both Fe and Ti species were transformed from severely distorted octahedron to more symmetrical octahedron after high temperature calcination, which is closely associated with the increasing of crystallization degree. From EXAFS results, although the high temperature calcination resulted in the severe change of the second coordination shells, the Fe-O-Ti or Ti-O-Fe structure was still present in well crystallized catalyst, continuing to perform high catalytic activity in the SCR reaction.^[2]

Influence of sulfation on microstructure

New EXAFS oscillations of Fe K-edge in FeTiO_x catalyst occurred after sulfation at some k values (Fig. 1A), which may be attributed to Fe-O-S oscillations. As shown in Fig. 1B, for the fresh catalyst, the first peak in R space was attributed to Fe-O bond and the second peak to Fe-O-Ti bond. For Fe₂(SO₄)₃, the first peak was also attributed to Fe-O bond but with larger bond distance than that in FeTiO_x, and the second peak was attributed to Fe-O-S bond also with larger bond distance than that of Fe-O-Ti. After sulfation, the Fe-O bond distance in FeTiO_x catalyst showed some increase. At the same time, another shoulder peak appeared at a longer distance than that of Fe-O-Ti bond, indicating the formation of some Fe-O-S structure. Obviously, no change was observed for EXAFS oscillations of Ti K-edge in FeTiO_x catalyst after sulfation

(Fig. 1C). Accordingly, both Ti-O and Ti-O-Fe bonds in R space also showed no obvious variation after sulfation, and no new peak attributed to Ti(SO₄)₂ species appeared (Fig. 1D). These results imply that sulfate species was mainly formed on iron sites during the sulfation process. As the S K-edge XANES spectra shown in Fig. 1E, not only the pre-edge peak intensity but also the absorption edge energy of S K-edge in FeTiO_x after sulfation were identical to those of Fe₂(SO₄)₃, implying again the formation of sulfate species on iron sites. Fig. 1F shows the difference between the spectra of Fe K-edge EXAFS oscillations in FeTiO_x catalysts before and after sulfation, with the red dots corresponding to the calculated EXAFS oscillations of Fe-O-S bond in Fe₂(SO₄)₃ using FEFF. Good curve fitting results were obtained, validating the formation of Fe-O-S structure again.^[3]

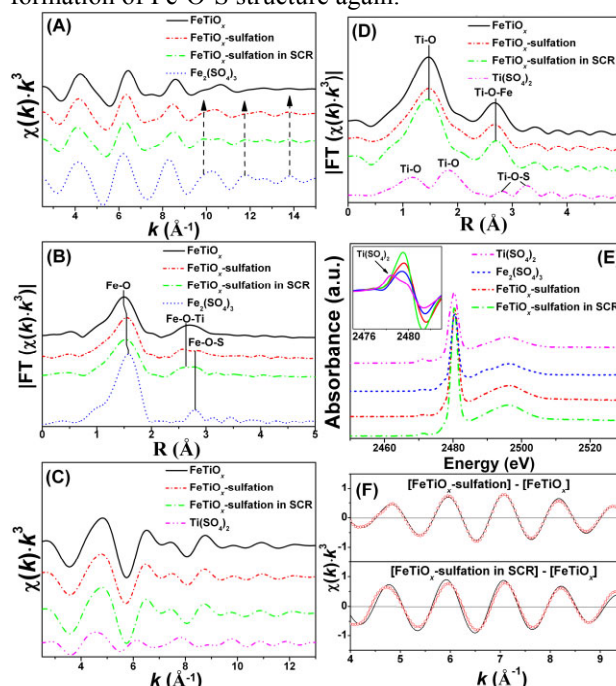


Fig. 1. XAFS results: (A) $k^3 \cdot \chi(k)$ of Fe K-edge; (B) FT of $k^3 \cdot \chi(k)$ of Fe K-edge; (C) $k^3 \cdot \chi(k)$ of Ti K-edge; (D) FT of $k^3 \cdot \chi(k)$ of Ti K-edge; (E) XANES of S K-edge and first-order derivatives (inset); (F) difference between Fe K-edge EXAFS oscillations in FeTiO_x catalysts before and after sulfation in SO₂ + O₂ and SCR condition.

References

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