

## Determination of the specific microstructure of iron titanate catalyst for NH<sub>3</sub>-SCR of NO<sub>x</sub> by XAFS method

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### Introduction

In our previous study, we have successfully developed a novel and environmental-friendly iron titanate (FeTiO<sub>x</sub>) catalyst prepared by conventional co-precipitation method, which showed high activity, N<sub>2</sub> selectivity and H<sub>2</sub>O/SO<sub>2</sub> durability for the selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub> (NH<sub>3</sub>-SCR) in the medium temperature range (200-400 °C).<sup>[1-4]</sup> This FeTiO<sub>x</sub> catalyst is promising to be used in the deNO<sub>x</sub> process for flue gas and diesel engine exhaust for environmental protection. We deduced that the iron titanate crystallite with specific Fe-O-Ti structure, but not aggregated Fe<sub>2</sub>O<sub>3</sub> oxide particles, was the real active phase in NH<sub>3</sub>-SCR reaction. However, no direct evidence was obtained using XRD, UV-vis DRS, TEM and Raman spectroscopy *etc.* due to the poor crystallinity of this catalyst both in the bulk phase and on the surface. In order to understand in-depth the structural nature of the active phase in this FeTiO<sub>x</sub> catalyst for further catalyst redesign and activity improvement, more powerful characterization method for determining the local structure of catalytic materials should be applied, such as the XAFS method. In this study, using XANES and EXAFS combined with theoretical calculation, the specific microstructure of FeTiO<sub>x</sub> catalyst will be systematically determined.<sup>[5]</sup>

### Experimental

The XAFS of Fe, Ti K-edges were recorded in a transmission mode on BL-7C beam line at PF, KEK, Japan. Data were analyzed using the REX2000 program. The geometry optimization of TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>TiO<sub>5</sub> crystals using DFT were carried out using Dmol3 module in Materials Studio software package.

### Results and discussion

The NH<sub>3</sub>-SCR activity at low temperatures over catalysts prepared by different precursors and methods decreased in the following sequence: FeTiO<sub>x</sub>-Ti(SO<sub>4</sub>)<sub>2</sub> >> Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> > FeTiO<sub>x</sub>-TiCl<sub>4</sub>. New highly active species with specific structure should be formed in the most active FeTiO<sub>x</sub>-Ti(SO<sub>4</sub>)<sub>2</sub>. As confirmed by XANES, well crystallized Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> exists in Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> catalyst, and FeTiO<sub>x</sub>-Ti(SO<sub>4</sub>)<sub>2</sub> catalyst possessed octahedrally coordinated Fe<sup>3+</sup> and Ti<sup>4+</sup> species with severe structure

distortion which were mainly from iron titanate crystallite. As for FeTiO<sub>x</sub>-TiCl<sub>4</sub> catalyst, only half of the Fe<sup>3+</sup> species in this catalyst was in the form of active iron titanate crystallite, and accordingly the low temperature NH<sub>3</sub>-SCR activity over FeTiO<sub>x</sub>-TiCl<sub>4</sub> catalyst was much lower than that over FeTiO<sub>x</sub>-Ti(SO<sub>4</sub>)<sub>2</sub> catalyst but higher than that over Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> catalyst. The XANES results and DFT calculation also confirmed the presence of electronic inductive effect between Fe<sup>3+</sup> and Ti<sup>4+</sup> species, which effectively reduced the electron density around the Fe<sup>3+</sup>, thus leading to the enhancement of NO adsorption, oxidation ability and finally the low temperature NH<sub>3</sub>-SCR activity.

Fig. 1 depicts the Fourier transform of filtered  $k^3$ -weighted EXAFS oscillations of Fe-K and Ti-K edges into R space. Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> catalyst has similar coordination peaks of Fe-K and Ti-K edges as those of hematite Fe<sub>2</sub>O<sub>3</sub> and anatase TiO<sub>2</sub>, respectively. As suggested by XANES results, FeTiO<sub>x</sub>-TiCl<sub>4</sub> catalyst shows peaks in the second coordination shells similar to those of Fe<sub>2</sub>TiO<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub> and rutile TiO<sub>2</sub>. However, these peaks are much smaller due to the coexistence of iron titanate crystallite. For FeTiO<sub>x</sub>-Ti(SO<sub>4</sub>)<sub>2</sub> catalyst, the intensity of the second coordination peaks of both Fe and Ti was rather low, implying a crystallite state of this sample again. It is noteworthy that only one single peak appeared for the second coordination shells of both Fe and Ti species in FeTiO<sub>x</sub>-Ti(SO<sub>4</sub>)<sub>2</sub> catalyst, which was totally different from those of reference samples and the other two catalysts.

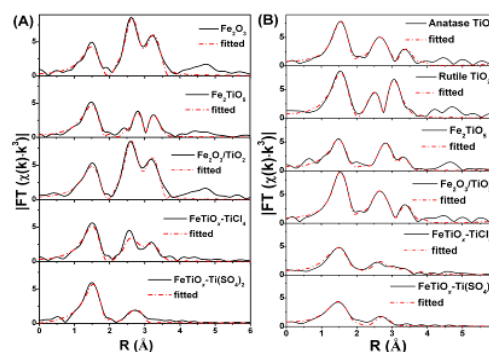
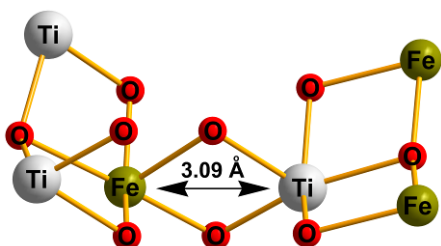


Fig. 1. Fourier transforms of filtered  $k^3 \cdot \chi(k)$  into R space of (A) Fe-K and (B) Ti-K edges in different samples.

The single peak in the second coordination shells of  $\text{FeTiO}_x\text{-Ti}(\text{SO}_4)_2$  catalyst can be assigned to  $\text{Fe}^{3+}\text{-O-Ti}^{4+}$  linkage suggested by the XANES results. The curve fitting results indicate the  $\text{Fe}^{3+}\text{-O-Ti}^{4+}$  distance as  $3.09 \pm 0.04 \text{ \AA}$ , which agrees well with the edge shared Fe-O-Ti and Ti-O-Fe structures. Compared to the edge shared Fe-O-Ti structure in well crystallized  $\text{Fe}_2\text{TiO}_5$  reference sample, the bond distances of Fe-O-Ti and Ti-O-Fe in this catalyst is  $0.09 \text{ \AA}$  shorter. This is also probably related with the nano effect of  $\text{FeTiO}_x\text{-Ti}(\text{SO}_4)_2$  catalyst in poor crystallinity, of which the catalyst surface possessed a large proportion of unsaturated coordination atoms with shorter average bond distances. The stronger interaction between  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  species in this catalyst induces the shift of Fe-K absorption edge to higher energy than that of  $\text{Fe}_2\text{TiO}_5$ .  $\text{Fe}^{3+}$  species must be more positively charged on the catalyst surface and is probably responsible for its highest  $\text{NH}_3\text{-SCR}$  activity. After curve fitting, the coordination numbers of Fe-O-Ti and Ti-O-Fe bonds are 2.6 and 2.0, indicating again the small particle size or crystallite phase of iron titanate species in this catalyst.

In order to further confirm the size of the crystallite domains of iron titanate species in  $\text{FeTiO}_x\text{-Ti}(\text{SO}_4)_2$  catalyst, the Fe-K EXAFS and Ti-K EXAFS were calculated by FEFF8.4 code using iron titanate crystallite with different atom numbers as models. Besides of the Fe-O and Ti-O coordination peaks in the first shell, only Fe-O-Ti and Ti-O-Fe coordination peaks in the second shell were observed when the atom numbers in the iron titanate crystallite were set to 15, which was mainly due to the inclusion of  $\text{Fe}^{3+}\text{-O-Ti}^{4+}$  linkages with edge shared oxygens in the adopted model. These results are consistent with the EXAFS data of  $\text{FeTiO}_x\text{-Ti}(\text{SO}_4)_2$  catalyst, in which the only Fe-O-Ti and Ti-O-Fe coordination peaks in the second shell were also observed. However, further increasing the atom numbers to 27 resulted in the appearance of another two shoulder peaks in the second coordination shells of Fe and Ti species, which were mainly due to the inclusion of  $\text{Fe}^{3+}\text{-O-M}$  and  $\text{Ti}^{4+}\text{-O-M}$  ( $\text{M} = \text{Fe}$  or  $\text{Ti}$ ) linkages with corner shared oxygens. These results clearly suggest that the crystallite domains of iron titanate species in  $\text{FeTiO}_x\text{-Ti}(\text{SO}_4)_2$  catalyst were mainly composed by *ca.* 15 atoms, which is in well agreement with the very small particle size of iron titanate crystallite that was concluded from EXAFS curve fitting results.



**Fig. 2.** Proposed model of homogeneous edge shared  $\text{Fe}^{3+}\text{-}(\text{O})_2\text{-Ti}^{4+}$  structure in iron titanate catalyst.

Based on XANES and EXAFS results, a structure model of iron titanate catalyst  $\text{FeTiO}_x\text{-Ti}(\text{SO}_4)_2$  derived from  $\text{Ti}(\text{SO}_4)_2$  precursor is proposed, as shown in Fig. 2. In this model, the edge shared Fe-O-Ti structure can be denoted as  $\text{Fe}^{3+}\text{-}(\text{O})_2\text{-Ti}^{4+}$ , where  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  species are connected with two edge shared oxygen atoms with shorter Fe-Ti bond distance than that in well crystallized  $\text{Fe}_2\text{TiO}_5$ . This special structure is in crystallite state, *i.e.* iron titanate with very small particle size. In other words, the active phase in  $\text{FeTiO}_x\text{-Ti}(\text{SO}_4)_2$  catalyst is macroscopically disordered but microscopically ordered. In this active phase,  $\text{Fe}^{3+}$  and  $\text{Ti}^{4+}$  species was strongly linked through edge shared fashion, and the electron density around the  $\text{Fe}^{3+}$  species is effectively reduced by the surrounding  $\text{Ti}^{4+}$  ions, which is beneficial to the enhancement of NO adsorption, oxidation ability and thus the low temperature  $\text{NH}_3\text{-SCR}$  activity. The presence of  $\text{Fe}^{3+}\text{-}(\text{O})_2\text{-Ti}^{4+}$  structure in  $\text{FeTiO}_x\text{-Ti}(\text{SO}_4)_2$  catalyst may also be responsible for its high resistance to  $\text{SO}_2$  poisoning due to the low decomposition temperature of sulfate species on  $\text{Ti}^{4+}$ . In the future study, we can stabilize this structure onto some catalyst supports with large surface areas for practical use, such as the  $\text{deNO}_x$  process for flue gas in coal-fired power plants and diesel engine exhaust for environmental protection.

### References

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