

## XAFS Study for Chromium Species on Mesoporous Cr-Ti Mixed Oxides

Insuhk SUH, Masashi TANAKA, Fumitaka HAYASHI, Masakazu IWAMOTO\*  
Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

### Introduction

Through the wall ion exchange (WIE) method, sulfate anions in hexagonally mesostructured titanium oxysulfate (TS) are readily exchanged with P, As, and Se in aqueous solutions [1]. Recently, we found that the chromium ion-exchanged TS (Cr-TS) exhibited ordered pore structure of 2 nm and high surface area ( $S_{BET} > 400 \text{ m}^2 \text{ g}^{-1}$ ) upon calcination above 573 K [2]. The porous Cr-Ti mixed oxides were obtained by the adjustment of Cr amount to 1.3–1.9 mmol g<sup>-1</sup>. In this work, the state of chromium species on Cr-TS during the calcination was examined by using XAFS spectroscopy.

### Experimental

Parent TS was synthesized by the reported manner [3]. The chemical composition of TS is  $\text{TiO}(\text{HSO}_4)_{0.7}(\text{OH})_{1.9}(\text{C}_{19}\text{H}_{42}\text{N})_{0.6}\cdot\text{H}_2\text{O}$ . The WIE operation was carried out in an aqueous solution of  $\text{K}_2\text{CrO}_4$  with pH value of weak base (pH=8.63). The TS was dropped into the solution, stirred at room temperature for 2 h, filtered, and dried at 353 K. The calcination of Cr-TS obtained was performed at 473–673 K for 0–2 h in air. The XAFS spectra of Cr K-edge were recorded on beam line 7C of PF-KEK.

### Results and discussion

The XANES spectra of Cr-TS sample with Cr amount of 1.88 mmol g<sup>-1</sup> are shown in Figure 1A. For ion-exchanged sample, a sharp band at 5993 eV ascribed to the 1s-3d electronic transition of Cr(VI) species in tetrahedral geometry was observed. The spectrum was similar to that of  $\text{K}_2\text{Cr}_2\text{O}_7$  rather than that of  $\text{K}_2\text{CrO}_4$ . The band at 5993 eV decreased in intensity after calcination at 473 K and almost disappeared at 573 K, indicating the reduction of Cr(VI) to Cr(III). The spectrum of 573 K was almost same to that of  $\text{Cr}_2\text{O}_3$ . The band at 5993 eV reappeared after calcination at 673 K. The Cr-TS sample with Cr amount of 1.55 mmol g<sup>-1</sup> also showed same behavior of chromium during calcination, while Cr-TS with Cr of 0.56 mmol g<sup>-1</sup> did not show. The former sample had  $S_{BET}$  of 413 m<sup>2</sup> g<sup>-1</sup> and the latter one had 3 m<sup>2</sup> g<sup>-1</sup> and no mesoporosity. The spectra of both samples until calcination at 573 K were similar to those of Cr-TS with Cr of 1.88 mmol g<sup>-1</sup> ( $S_{BET}=441 \text{ m}^2 \text{ g}^{-1}$ ).

Figure 1B shows the Fourier transforms of  $k^3$ -weighted EXAFS spectra of Cr-TS. For the ion-exchanged Cr-TS, a band due to Cr(VI)-O bond of tetrahedral geometry appeared at 1.26 Å. By the calcination at 473 K, the band in the range of 1–2 Å became weak and broad. The weakening in intensity was responsible to the formation of  $\text{CrO}_3$  species with the disorder of the  $\text{CrO}_4$  tetrahedron. The broadening was

probably due to the formation of  $\text{Cr}_2\text{O}_3$  species with elongated Cr-O bond distance. The band at around 1.5 Å for 573 K-calcined Cr-TS was similar to that of  $\text{Cr}_2\text{O}_3$ , though the band at 2.52 Å due to Cr-Cr bond of  $\text{Cr}_2\text{O}_3$  in octahedral geometry was significantly small. This indicated that the small  $\text{Cr}_2\text{O}_3$  cluster produced. Therefore, the chromium species might be highly dispersed on Cr-TS. For the 673 K-calcined Cr-TS, the band at 1.50 Å became smaller than that of 573 K. It was suggested that the Cr(VI) species was reproduced by the calcination at 673 K as shown in Figure 1A and that the band due to the Cr(VI)-O bond would be overlapped with the Cr(III)-O bond.

From these results, we led the following things. When the amount of Cr is few, the chromium species is ion-exchanged with wall interior  $\text{HSO}_4^-$  of TS. As the amount of Cr increases, the chromium species on the wall surface increases. The chromium species exchanged as  $\text{Cr}_2\text{O}_7^{2-}$  is decomposed to  $\text{CrO}_3$  and then reduced to  $\text{Cr}_2\text{O}_3$  during calcination. By the calcination at higher temperature, the Cr(III) species on pore wall surface are re-oxidized to Cr(VI) species by oxygen in air. However, the Cr(III) species at pore wall inside retains. Therefore, it was concluded that the porous Cr-Ti mixed oxides with high surface area are obtained by the calcination of Cr-TS coating TS wall surface with the chromium species.

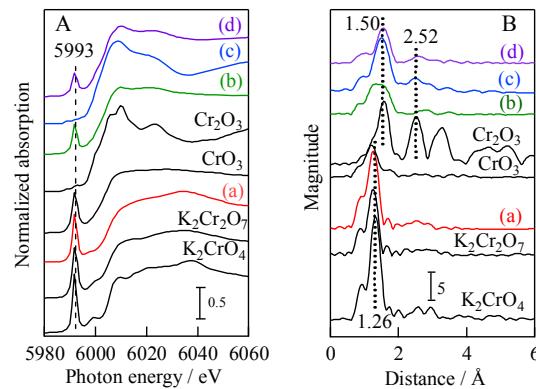


Figure 1: XANES spectra (A) and Fourier transforms of  $k^3$ -weighted EXAFS spectra (B) of Cr-TS with Cr amount of 1.88 mmol g<sup>-1</sup> after (a) ion exchange, (b) calcination at 473 K for 0 h, (c) 573 K 0 h, and (d) 673 K 2 h.

### References

- [1] H. Takada and M. Iwamoto, Ryusan to Kogyo 58, 29 (2005).
  - [2] I. Suh et al., Manuscript in preparation.
  - [3] M. Linden et al., Chem. Mater. 11, 3002 (1999).
- \* iwamoto@res.titech.ac.jp