

## XAFS study on mesoporous Cr and Ti mixed oxides prepared by wall ion exchange method

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### Introduction

Through the wall ion exchange (WIE) method, sulfate anions in hexagonally mesostructured titanium oxysulfate (TS) are readily exchanged with several oxyanions of P, As, Se, and Cr in aqueous solutions [1]. Recently, we found that the Cr-exchanged TS (Cr-TS) exhibited ordered pore structure and high surface area upon calcination. The surface area of the Cr-TS gradually increased with increasing the Cr content in the range of 0.54-1.29 mmol g<sup>-1</sup> of Cr. The maximum surface areas were 400 m<sup>2</sup> g<sup>-1</sup> or more at 1.29-1.67 mmol g<sup>-1</sup>. In this work, to elucidate the formation mechanism of mesoporous structure, the states of chromium on Cr-TS were investigated by using XAFS spectroscopy.

### Experimental

Parent TS was prepared by the reported manner [2]. The chemical composition of TS is TiO(HSO<sub>4</sub>)<sub>0.7</sub>(OH)<sub>1.9</sub>(C<sub>19</sub>H<sub>42</sub>N)<sub>0.6</sub>·H<sub>2</sub>O. The WIE was performed at room temperature in an aqueous solution of K<sub>2</sub>CrO<sub>4</sub> at weak basic condition (pH=8.6). The TS was added into the solution, stirred for 2 h, filtered, and dried at 353 K. The Cr-TS were calcined at 673 K for 2 h in air. The XAFS spectra of Cr K-edge were recorded on beam line 9C of PF-KEK.

### Results and discussion

Figure 1 shows the XANES spectra of Cr reference compounds and various Cr-TS samples. A sharp peak at 5993 eV was observed for all ion-exchanged Cr-TS samples. This peak is ascribed to Cr(VI) in tetrahedral geometry [3]. The spectra of Cr-TS were similar to that of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> rather than that of K<sub>2</sub>CrO<sub>4</sub>. On the basis of this result, we could consider that the tetrahedral Cr ions dimerized during ion exchange to form Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> species. After calcination (Figure 1b), a peak at 6010 eV assigned to Cr(III) appeared. It should be noted that Cr-TS samples with 0.74 and 1.67 mmol g<sup>-1</sup> of Cr also exhibited a sharp peak of Cr(VI) at 5993 eV. Therefore, it was suggested that the formation of mesoporous structure of Cr-TS was dependent on the amount of Cr(VI).

The Fourier transform of *k*<sup>3</sup>-weighted EXAFS spectrum for each Cr-TS sample is shown in Figure 2. A band at 1.24 Å due to Cr-O bond of tetrahedron CrO<sub>4</sub> appeared on the spectra of all ion-exchanged Cr-TS samples (Figure 2a), which were similar to those of K<sub>2</sub>CrO<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. In contrast, the spectra of calcined Cr-TS showed two bands at 1.50 and 2.40 Å. These bands were reported to be due to Cr-O and Cr-Cr bond of Cr<sub>2</sub>O<sub>3</sub>, respectively [4]. However, the magnitude of

second band at 2.40 Å was weak for calcined Cr-TS, indicating that Cr species were highly dispersed. The pre-edge peak of Cr(VI) was observed on the spectra of calcined Cr-TS with 0.74 and 1.67 mmol g<sup>-1</sup> (Figure 1b) but the band of Cr-O in CrO<sub>3</sub> was not appeared at near 1.0 Å (Figure 2b), which were not understood yet.

In summary, introduced Cr ions in Cr-TS existed as Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> species and part of those were converted into Cr<sub>2</sub>O<sub>3</sub>-like species upon calcination. The amount of remained Cr(VI) was correlated with the formation of mesoporous structure of Cr-TS. Additional study is needed to elucidate the effect of Cr species on the formation of mesoporous structures.

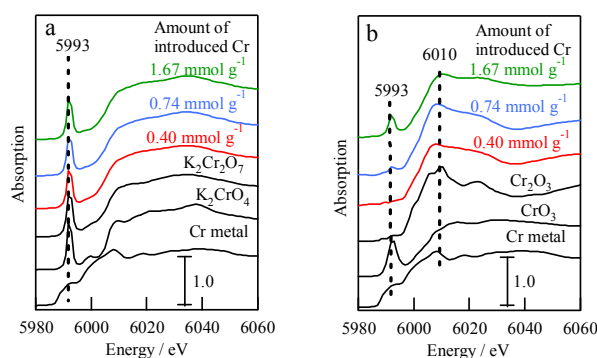


Figure 1: XANES spectra of Cr-TS. (a) ion exchanged and (b) calcined.

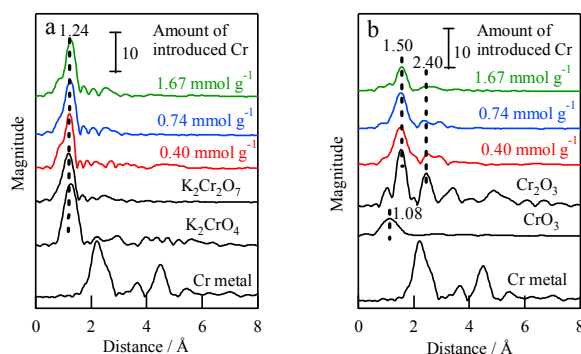


Figure 2: Fourier transforms of *k*<sup>3</sup>-weighted EXAFS spectra of Cr-TS. (a) ion exchanged and (b) calcined.

### References

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