

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

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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 ($S_{\text{BET}} > 400 \text{ m}^2 \text{ g}^{-1}$) 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^{-1} . 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 K_2CrO_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^{-1} 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 K_2CrO_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 Cr_2O_3 . The band at 5993 eV reappeared after calcination at 673 K. The Cr-TS sample with Cr amount of 1.55 mmol g^{-1} also showed same behavior of chromium during calcination, while Cr-TS with Cr of 0.56 mmol g^{-1} did not show. The former sample had S_{BET} of 413 $\text{m}^2 \text{ g}^{-1}$ and the latter one had 3 $\text{m}^2 \text{ g}^{-1}$ 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^{-1} ($S_{\text{BET}}=441 \text{ m}^2 \text{ g}^{-1}$).

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 CrO_3 species with the disorder of the CrO_4 tetrahedron. The broadening was

probably due to the formation of Cr_2O_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 Cr_2O_3 , though the band at 2.52 Å due to Cr-Cr bond of Cr_2O_3 in octahedral geometry was significantly small. This indicated that the small Cr_2O_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 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 CrO_3 and then reduced to Cr_2O_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.

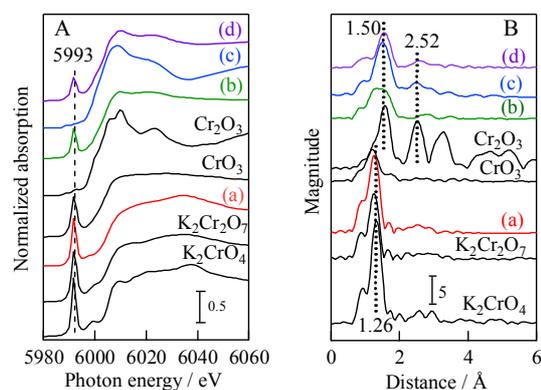


Figure 1: XANES spectra (A) and Fourier transforms of k^3 -weighted EXAFS spectra (B) of Cr-TS with Cr amount of 1.88 mmol g^{-1} after (a) ion exchange, (b) calcination at 473 K for 0 h, (c) 573 K 0 h, and (d) 673 K 2 h.

References

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