

In situ EXAFS study on the formation of smectite-type clays containing cobalt cations in lattice

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Smectite-type clays containing cobalt cations in octahedral sheets (MST (Co)) were prepared by a hydrothermal treatment of a water slurry of silicon-cobalt hydrous oxide prepared from water glass and cobalt chloride. The formation of silicate fragments having smectite-type structure was studied by EXAFS.

Keyword: Smectite; Clay; Porous-materials.

1. Introduction

Smectite-type materials have layered structures in which each layer is composed of one octahedral sheet sandwiched by two tetrahedral sheets. The octahedral sheets contain divalent or trivalent cations which are surrounded by six oxygen atoms in octahedral structure and the tetrahedral sheets contain Si⁴⁺ ions which are surrounded by four oxygen atoms in tetrahedral structure. We reported that smectite-type clays containing several divalent cations in octahedral sheets (MST(M), M: cation) was prepared by hydrothermal treatment of a water slurry of silicon-cation hydrous oxide prepared from water glass and metal chloride (Arai, Guo, Shirai, Nishiyama & Torii, 1996; Shirai, Aoki, Torii & Arai, 1999.). MST(M) samples are porous materials and have high surface areas and pore volumes after calcination at 873 K. By changing pH values of the water slurry during a hydrothermal treatment, the pore structure can be controlled (Torii *et al.*, 1997). We proposed that small fragments having smectite structure exist as pillars between silicate layers in MST(Mg) (Shirai, Aoki, Miura *et al.*, 2000). In this paper we studied the structure of MST(Co) by EXAFS. The size and formation of silicate fragments having smectite-type structure from the water slurry of silicon-cobalt hydrous oxide are discussed.

2. Experimental

2.1. Sample Preparation.

A silicon-cobalt hydrous precipitate (Prec(Si-Co)) was obtained by adding an aqueous solution of cobalt chloride to an aqueous water glass (SiO₂ 29.04%, Na₂O 9.4 %, NIHON

KAGAKU KOGYO) solution controlled in pH with an aqueous solution of sodium hydroxide. The Si/Co ratio was fixed at 8/6. After filtration and washing the Prec(Si-Co) material with distilled water, a slurry was prepared from the Prec(Si-Co) materials and an aqueous solution of sodium hydroxide. Following a hydrothermal treatment (423-523 K), the slurry was filtrated, dried at 353 K and calcined at 873 K, and then the final product (MST(Co)) was obtained.

2.2. XAFS.

Data were collected at BL-7C and 10B at the Photon Factory of National Laboratory for High Energy Physics, Tsukuba. The storage ring was operated with an electron energy of 2.5 GeV. Data were recorded in the transmission mode in the region of the Co K edge (7709.5 eV) at room temperature. The transmission spectra were collected using ion chambers that were filled with nitrogen gas. EXAFS oscillation was extracted from the EXAFS raw data by using a cubic spline method and normalised with the edge height. The *k*³-weighted EXAFS spectra were Fourier transformed to R space.

3. Results and discussion

3.1. Pore structure and growth of silicate fragments in MST(Co).

Pore diameters evaluated from nitrogen-desorption isotherms with the BJH method of MST(Co) samples hydrothermally synthesized are shown in Fig. 1. Surface area (SA) and pore volume (PV) values are also shown. MST(Co) samples have high surface areas and pore volumes after calcination at 873 K. Both samples have micro- and mesopores, but the MST(Co) prepared at 423 K for 2 hours have more micropores than that at 523 K for 4 hours.

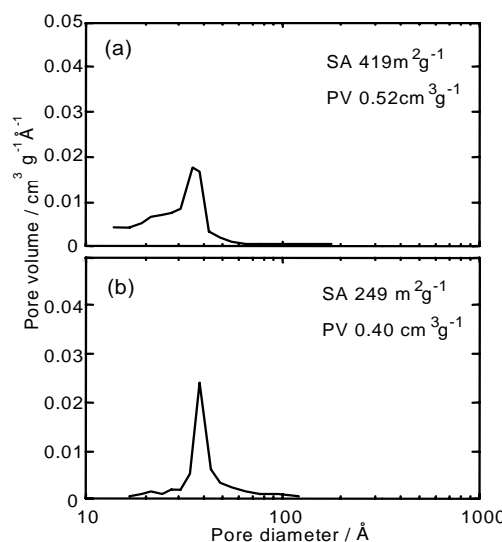


Figure 1

Pore size distributions of MST(Co) samples hydrothermally synthesized at 423K for 2 hours(a) and at 523K for 4 hours(b).

Fig. 2 shows Fourier transforms of Co K-edge EXAFS spectra of MST(Co) samples prepared. Both Fourier transforms showed two peaks at similar distances (phase uncorrected); the peaks between 0.1 and 0.2 nm are ascribed to Co-O bond and the peaks between 0.2 and 0.3 nm are ascribed to the Co-O-Co and Co-O-Si bonds. The radial distribution functions in Fig. 2 are similar to those of EXAFS Fourier transforms for smectite-type materials including nickel and zinc cations in octahedral sheets (Shirai, Aoki, Minato *et al.*, 2000). No other bonds derived from cobalt oxides were observed in the EXAFS Fourier transforms of the MST(Co) samples calcined at 873 K. The intensity of peak assigned to Co-O-Co and Co-O-Si bonds in the EXAFS Fourier transforms of MST(Co) prepared at 523 K is larger than that at 423 K. We did not calculate the coordination numbers of the Co-O-Co and Co-O-Si bonds.

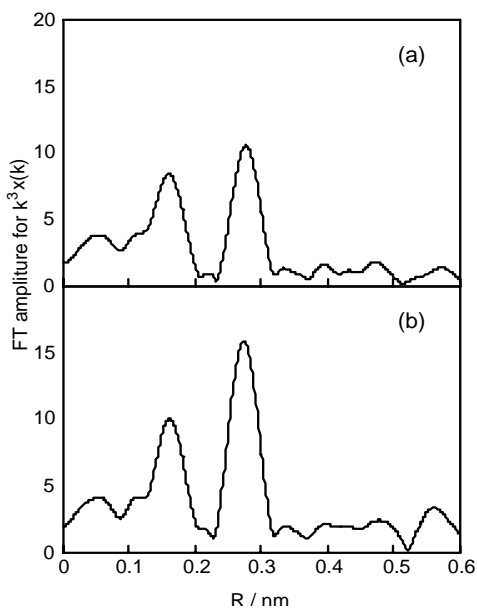


Figure 2 Fourier transforms for EXAFS oscillations Co K-edge EXAFS for MST(Co) samples hydrothermally synthesized at 423 K for 2 hours (a) and at 523 K for 4 hours (b) (phase shifts are not corrected).

EXAFS result indicate that MST(Co) samples have smectite structure and that the size of silicate fragments with smectite structure in MST(Co) samples prepared at 523 K is larger than that at 423 K. It is probable that the size of silicate fragments of MST(Co) samples prepared at higher temperatures is larger than those at lower temperatures. We have proposed that small silicate fragments having smectite structure were intercalated in smectite layers in MST(M) and that pores are formed between the layers (Shirai, Aoki, Miura *et al.*, 2000). Small fragments having smectite structure would become short pillars in MST(Co) and the distance between the pillars would become short. MST(Co)

samples prepared at low temperatures have small smectite fragments and more small pores (micropores) would be formed.

3.2. Smectite structure of the precipitate from water glass and cobalt chloride.

Fig. 3 shows Fourier transforms of Co K-edge EXAFS spectra of the Prec(Si-Co) materials. The EXAFS Fourier transforms of the Prec(Si-Co) materials dried at 353 K showed similar EXAFS Fourier forms to MST(Co).

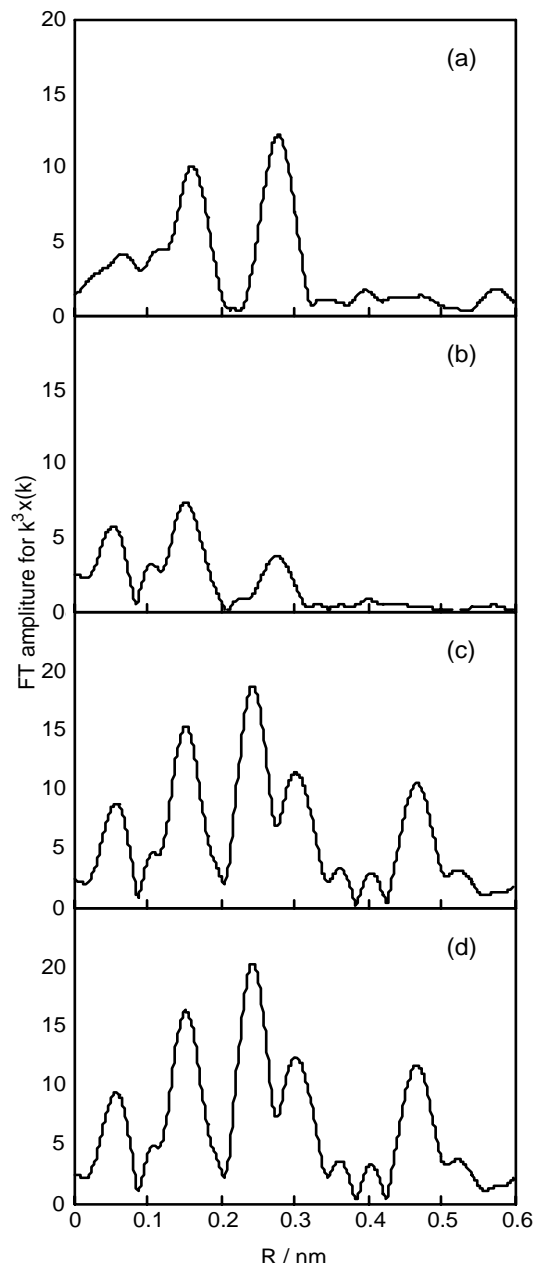


Figure 3 Fourier transforms for Co K-edge EXAFS oscillations of Prec(Si-Co) dried at 353 K (a), calcined at 873 K (b), the cobalt hydroxide precipitate calcined at 873 K (c), and cobalt oxide (d) (phase shifts are not corrected).

The peak intensity between 0.2 and 0.3 nm of EXAFS Fourier transform of the Prec(Si-Co) materials, which are ascribed to the Co-O-Co and Co-O-Si bonds, became weak after calcination at 873 K. However, no peak assigned to cobalt oxides were observed. A cobalt hydrous precipitate was obtained by adding an aqueous solution of cobalt chloride to an aqueous solution of sodium hydroxide. The EXAFS Fourier transform of the cobalt hydrous precipitate after calcination at 873 K resembles that of Co_3O_4 , indicating that the spinel structure of cobalt oxides was formed after calcination of the cobalt precipitate at 873 K. Fig. 3 indicates that cobalt atoms were well dispersed in the Prec(Si-Co) material, so that cobalt oxide particles were not formed after calcination of the Prec(Si-Co) material at 873 K.

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