XAFS Measurements of Rare-Earth *K*-Edges in CeO_2-Sm_2O_3 Binary System

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CeO_2 and Sm_2O_3 powders at a given ratio were mixed thoroughly by a ballmill. After the mixture powder shaped into a pellet, the pellet was heated in air at 1450°C. X-ray diffraction patterns of thus obtained CeO_2-Sm_2O_3 binary oxides shows that a single phase of C-type oxide formed below x = 0.2 (x = Ce/(Ce+Sm)) in atomic ratio) and a single phase of fluorite type oxide obtained above x = 0.6. C-type and fluorite type phases co-exist in a range between $0.3 \leqq x \leqq 0.5$.

Ce and Sm *K*-edge X-ray absorption spectra of the CeO_2-Sm_2O_3 binary oxides were measured at the beamline BL01B1 in a conventional transmission method at room temperature with Si (311) monochrometer and collecting mirror system. X-ray energy was calibrated by measuring Ce and Sm *K*-edge energies of CeO_2 and Sm_2O_3, respectively. In Fig. 1, k^3-weighed EXAFS function above the Ce *K*-edge of a CeO_2-Sm_2O_3 binary oxide (x=0.9) is shown, which demonstrates that the present measurements have provided EXAFS oscillation with good S/N ratios even in a wide k region. The interatomic distances, $R_{Ce\text{-}O}$ and $R_{Sm\text{-}O}$, of Ce-O and Sm-O in fluorite type region were evaluated by least-square fitting using theoretical data calculated from FEFF 7 code. In Fig. 2, $R_{Ce\text{-}O}$ (open circle) and $R_{Sm\text{-}O}$ (open square), are plotted against x. Both $R_{Ce\text{-}O}$ and $R_{Sm\text{-}O}$ increase with x though the average interatomic distance (cross) calculated from XRD data, which well agrees with a linear combination (open triangle) of $R_{Ce\text{-}O}$ and $R_{Sm\text{-}O}$ against x, decreases with x.

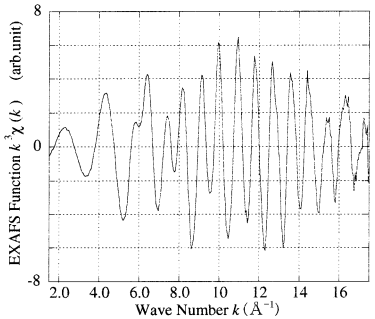

Fig. 1 Ce *K*-edge EXAFS function of CeO_2-Sm_2O_3 binary oxide (x = 0.90).

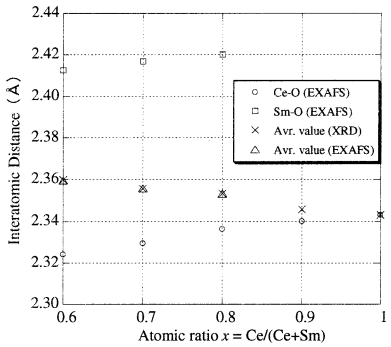

Fig.2 Variations of interatomic distances between rare earth and oxygen atoms in CeO_2-Sm_2O_3 binary oxides as a function of composition.

Analysis of the structure of Co-Mo/NaY sulfide catalysts under reaction conditions by means of XAFS

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1. Introduction

Currently, Co-Mo sulfide catalysts are used for ultra-deep-hydrodesufurization (HDS) treatment. But the reaction mechanism of HDS on the Co-Mo catalysts is not well-known. Clarifying the reaction mechanism is necessary to develop new catalysts. It is helpful to investigate HDSe reaction using organo-selen compounds because dynamic behavior of Se at active sites can be estimated by the mesurement of the amount of incorporated Se. Furthermore Se K-edge XAFS for the Se-exchanged catalysts can be used to investigate the local structure of incorporated Se atoms. In this study, we studied the behaivor of Se on Mo sulfide catalysts after HDSe reaction by mean of XAFS.

2. Experimental

MoS_x/NaY catalysts were prepared by a CVD method using $Mo(CO)_6$. MoS_2/Al_2O_3 catalysts were prepared by impregnation. The sample was sulfided at 673 K. The HDSe reaction of selenophene was performed using a closed circulation system at 623 K. Se and Se K-edge EXAFS spectra for catalysts after HDSe reaction were measured at BL01B1 in a transmission mode. The synchrotron radiation was monochromatized by a Si(311) monochromator

3. Results and Discussion

Fig.1 shows Fourier transform for k^3-weighted EXAFS oscillation of Se K-edge EXAFS of standard compounds and Mo sulfide catalysts after HDSe reaction. A sharp peak around 2.3 Å is assgined to Se-Mo bonding. The position of the peak is not shifted by HDSe reaction time. On the othe hand, the intensity of the peak is increased with reaction time for MoS_x/NaY catalytsts, although the intensity of the peak is invariant with reaction time for MoS_2/Al_2O_3 catalytsts. Taking into account the formation of highly dispersed Mo sulfide clusters in MoS_x/NaY, these results indicate that Se atoms move from on-top sites to bridged site during HDSe reaction in MoS_x/NaY.

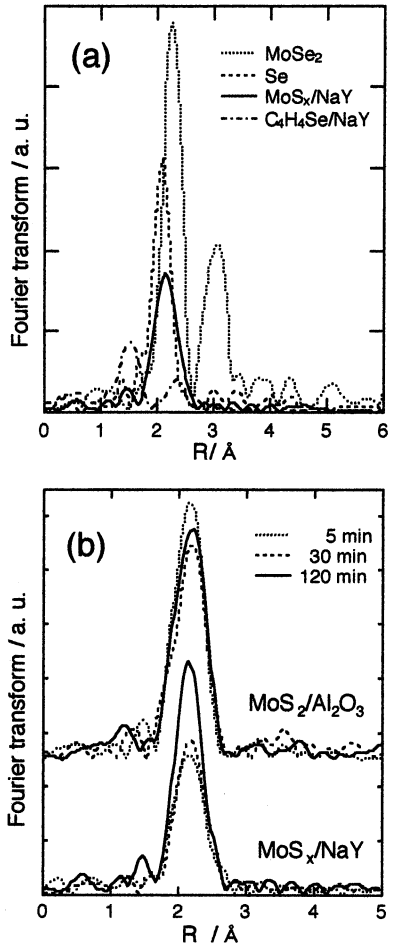

Fig. 1 Fourier transformations of Se K-edge EXAFS oscillation functions; (a): standard compounds, (b):Mo sulfide catalysts after HDSe reaction.