

XAFS study of spinel zinc titanium oxynitride as a photocatalyst with visible light activity

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Introduction

Zinc and titanium oxynitride ($Zn_xTiO_yN_z$) is a photocatalyst that has suitable bandgap position for water splitting reaction under visible light irradiation ($\lambda < 540$ nm)[1]. It is important to clarify crystal structure of a photocatalyst because it influences its photocatalytic performance significantly. However, crystal structure of $Zn_xTiO_yN_z$ is yet to be clarified.

Recently, Berthebaud et al. pointed out that, on the basis of X-ray powder diffraction, crystal structure of $Zn_xTiO_yN_z$ corresponded to that of a cation deficient spinel structure[2]. In the present study, XAFS measurements were carried out to discuss the local structure around Zn and Ti in $Zn_xTiO_yN_z$.

Experiments

$Zn_xTiO_yN_z$ was prepared by the previously reported method[1, 3]. Briefly, an oxide precursor was prepared by the polymerized complex method. The oxide precursor was then nitrided at 1023K for 0–8 h under 100 mL min^{-1} NH_3 flow to yield $Zn_xTiO_yN_z$ powder. XAFS of the Zn-K edge and Ti-K edge were measured in the BL9A beamline. Appropriate amount of the $Zn_xTiO_yN_z$ was mixed with 30 mg of BN powder and pressed into a disk 10 mm in diameter. Using the disks, XAFS were recorded in transmission mode at ring energy of 2.5 GeV and stored current from 450 to 280 mA.

Results and Discussion

Figure 1 shows the Fourier transforms of k^3 -weighted EXAFS spectra of the Zn-K and Ti-K edges for $Zn_xTiO_yN_z$ obtained by nitridation over various durations. Radial structure functions for Zn_2TiO_4 are also indicated for comparison. Three characteristic peaks were observed at 1.6, 2.6, and 3.1 Å in the radial structure function of Zn-K edge for Zn_2TiO_4 . By comparison with a crystal structure data of Zn_2TiO_4 [4], these peaks were attributed to Zn-O, $Zn_{octa}-M_{octa}$, and Zn-X bonds of the $Zn_xTiO_yN_z$ spinel structure, where M = Zn or Ti, X = Zn, Ti or O, and octa refers to octahedral sites of a spinel structure, respectively.

The peak at 2.6 Å, which was characteristic of octahedrally coordinated Zn species, became smaller than that at 3.1 Å with the progress of nitridation although it was prominent at the beginning of nitridation. Navrotsky et al. found in thermodynamic studies of spinels that Zn species located at octahedral sites were less stable than those located at tetrahedral sites[5]. Considering the

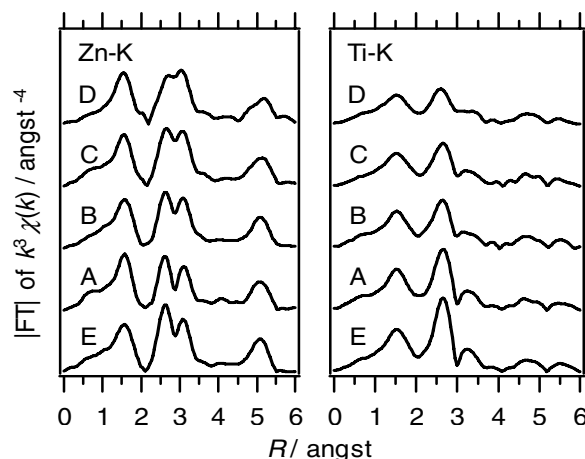


Figure 1. Fourier transforms of k^3 -weighted Zn-K and Ti-K edge EXAFS spectra for $Zn_xTiO_yN_z$ nitrided for (A) 0 h, (B) 2 h, (C) 4 h, (D) 8 h. Data for Zn_2TiO_4 (E) is shown for reference.

instability of six-coordinated Zn species, it is reasonable to suggest that Zn species at the octahedral sites of $Zn_xTiO_yN_z$ spinel volatilized in preference to those at the tetrahedral sites.

In the radial structure function of the Ti-K edge for Zn_2TiO_4 , three peaks were observed at 1.6, 2.6, and 3.2 Å, although the peak at 3.2 Å was almost absent unlike the radial structure function of Zn-K edge. Based on comparison with the crystallographic structural data[4], these peaks were attributed to Ti-O, $Ti_{octa}-M_{octa}$, and Ti-X bonds, respectively. The indistinct peak for the Ti-X bonds is probably because the Ti species are not located at tetrahedral sites in the Zn_2TiO_4 spinel structure and thus contribution to the peak is limited. Confirmation that the Ti species essentially exist at the octahedral site of the spinel structure is shown by the fact that, over the nitridation, the radial structure function of Ti-K edge for $Zn_xTiO_yN_z$ did not show characteristic changes in the peak positions.

References

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