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X-ray absorption fine structure analysis on the intermediate species of hydrothermal synthesis of decanoic acid-modified CeO_2 nanocrystals

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1 Introduction

Metal oxide nanocrystals have various applications including fillers in hybrid materials and inks for 3D printing. In these applications, the dispersibility of nanocrystals in matrix is important and we develop a synthetic method of surface-modified metal oxide nanocrystals[1,2] with improved affinity toward matrix. The developed methods use hydrothermal reaction of metal ion in the presence of organic molecules. By using this method, we have produced metal oxide nanocrystals whose surface is bound with organic molecules. However, the mechanism how the nanocrystals are formed has not been clarified. In this study, we analyzed the intermediate species of the synthetic reaction of surface-modified metal oxide nanocrystals by X-ray absorption fine structure (XAFS) measurements.

2 Experiment

Aqueous solution of $Ce(NO_3)_3$ was heated at 400°C in the presence of decanoic acid using a batch-type reactor to produce surface-modified CeO_2 nanocrystals. In order to analyze the intermediate species for this reaction, the same reactant was heated at 160~200°C and the reaction was quenched by immersing the reactor in a water bath. The liquid products were separated into the organic phase and the water phase. The XAFS spectra were measured to evaluate the chemical status of Ce atoms.

3 Results and Discussion

Firstly, we evaluated the concentration of Ce ions in the organic and water phases of the products using inductively coupled plasma measurements. The results showed that the concentration of Ce ion in the water phase is negligible and the Ce ions that existed in the water phase in the reactant were transferred to the organic phase during reaction. Figure 1 shows the X-ray absorption near edge structure (XANES) spectra of the intermediate species in the organic phases. Comparing with reference spectra, we notice that the intermediate speices were Ce^{3+} state instead of Ce^{4+}. Within the temperature range between 160 and 200°C, the XANES spectra of the intermediate proructs were almost the same, indicating that CeO_2 nanocrystals were produced at higher temperature. As a reference sample, we also measured cerium stearate where three stearic acid molecules bound with one Ce^{3+} ion. The XAFS spectrum of cerium stearate was similar to the intermediate species,

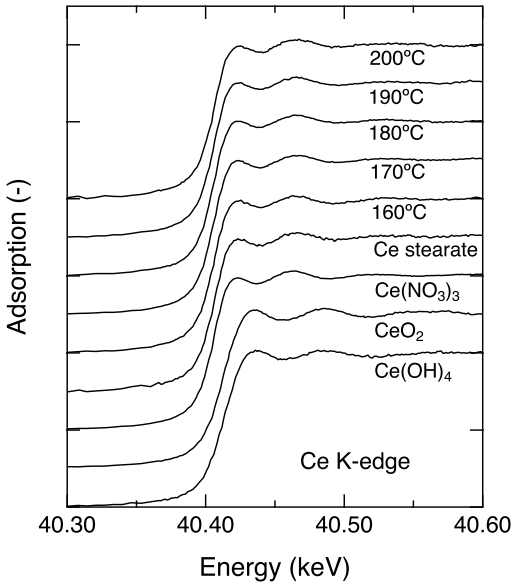

Figure 1 XANES spectra of the intermediate species during the synthesis of decanoic acid modified CeO_2 nanocrystals.

indicating that the intermediate species had a structure where three decanoic acid molecules bind with Ce^{3+} ion as shown in Fig. 2.

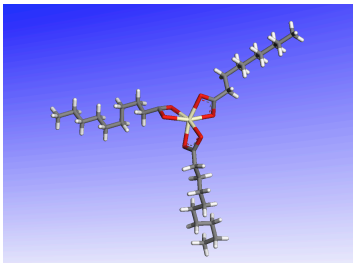

Figure 2 Suggested structure of intermediate species.

References

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