Chemistry

Characterization of Lanthanide-incorporated FSM-16 Type Mesoporous Silica

Keita IKEUE*, Takayuki TANAKA, Nao MIYOSHI, Masato MACHIDA
Department of Nano Science and Technology, Graduate School of Science and Technology
Kumamoto University, 2-39-1 Kurokami, Kumamoto, 860-8555 Japan.

Introduction

Metal-incorporated mesoporous silicas are attracting attention because of their possible acid and base characteristics. The synthesis of metal-incorporated mesoporous silica is facile in the MCM-41 systems because the formation of framework for MCM-41 proceeds on the basis of sol-gel process. By contrast, the metal-incorporated FSM-16 would rather be difficult to prepare because the synthesis uses polysilicate layer as a building parts of porous frameworks. Here we propose a novel and convenient method for metal incorporation into FSM-16 by applying intercalation of metallic ions in the sheet folding process of kanemite.

In the present study, we have synthesized the FSM-16 containing lanthanide, Ln= La, Ce and Pr. The local structure of Ln species was investigated by a XAFS.

Experimental

According to the procedure reported by Inagaki et al [1], FSM-16 was prepared form layered kanemite by intercalation of cetyltrimethylammonium bromide (CTAB) and subsequent folding of silicate sheets. Ln-incorporated FSM-16 (abbreviated as Ln-FSM-16) was synthesized by a modified sheet folding process of kanemite-CTAB system. The detail procedure was described in our previous paper [2].
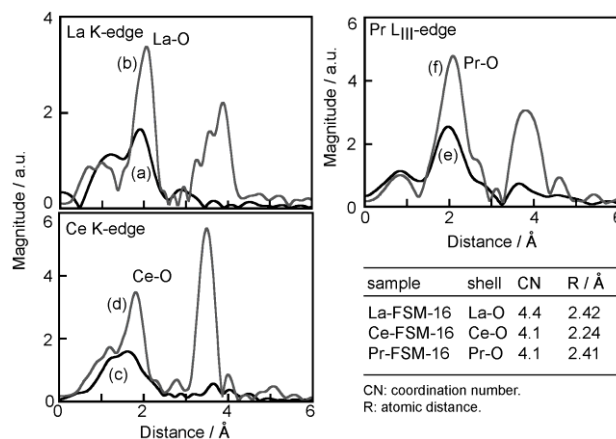
The X-ray absorption fine structure (XAFS) of La K-edge, Ce K-edge and Pr L_{III}-edge was recorded on NW10A and BL-7C at PF-AR and PF of KEK. Spectral recording was performed in a transmission mode. The XAFS data were processed by a REX 2000 program (Rigaku). The EXAFS oscilation was extracted by fitting a cubic spline function through the post-edge region. The k^3-weighted EXAFS oscillation in the 3.0-15 $Å^{-1}$ regions was Fourirer–tansformed.

Results and Discussion

XRD patterns of Ln-FSM-16 after calcination at 500 °C indicated peaks indexed as (100), (110) and (200) reflections in the range of $2\theta=2-5°$, which are corresponding to the well-ordered hexagonal mesoporous structure. In the range of $2\theta\geq10°$, the diffraction peaks due to crystalline Ln oxide compounds were not observed.

The structural information on Ln species was not obtained from XRD data because of amorphous nature of each silicate sheets. Therefore, the local structure of Ln species in the Ln-FSM-16 was next investigated by a XAFS.

Figure 1shows the Fourier transforms of La K-edge, Ce K-edge and Pr L_{III}-edge EXAFS for Ln-FSM-16 with corresponding Ln_2O_3 as references. For all of Ln-FSM-16 samples, a peak due to nearest Ln-O atomic distance at around 1.5-2.0 Å was observed. The peak corresponding to a second coordination shell observed for typical Ln-based bulk oxides, such as La_2O_3, CeO_2 and Pr_2O_3, was scarcely revealed at around 3.0-4.0 Å This result suggested that the formation of aggregated species was prevented. The detailed structural parameters for the nearest Ln-O shell were estimated by the curve-fitting analysis of EXAFS. The coordination number for Ln-O shell of Ln-FSM-16 was nearly 4, compared to 7 (La and Pr) or 8 (Ce) of bulk oxide, which is estimated form the crystallographic data of La_2O_3, CeO_2 and Pr_2O_3. Moreover, the atomic distance of Ln-O for Ln-FSM-16 was 0.050-0.10 Å shorter than that for bulk oxide. It is considered that the decrease in coordination number and atomic distance resulted form incorporation of Ln ions into distorted tetrahedral SiO_4 sites.

sample	shell	CN	R / Å
La-FSM-16	La-O	4.4	2.42
Ce-FSM-16	Ce-O	4.1	2.24
Pr-FSM-16	Pr-O	4.1	2.41

CN: coordination number.
R: atomic distance.

Fig.1 Fourier transforms k^3-weighted EXAFS of (a) La-FSM-16, (b) La_2O_3, (c) Ce-FSM-16, (d) CeO_2, (e) Pr-FSM-16, (f) Pr_2O_3. Ln-FSM-16 was calcined at 500 °C. Table shows the structural parameter for Ln-FSM-16 obtained from the EXAFS data.

References

[1] S. Inagaki et al., Bull. Chem. Soc. Jpn., 69, 1449 (1996).
[2] K.Ikeue et al., Solid State Sci., in press

*ikeue@chem.kumamoto-u.ac.jp