XAFS Study on Nb-Mesostructured Materials Prepared from Layered-Perovskite Type Potassium Niobate and Alkyltrimethylammonium Chloride

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Nb-mesostructured materials were prepared using layered-perovskite type potassium niobate and hexadecyltrimethylammonium chloride, and were structurally characterized by X-ray diffraction and extended X-ray absorption fine structure analysis. The short-distance ordered structure around niobium of these mesostructured materials was found to form mainly linkages of edge-shared NbO_6 octahedra. Furthermore, it was found that the local structure of niobium depends on the pH of the reacted solution.

Introduction

Mesoporous materials have attracted much attention for application in catalysts and absorbents, because they have uniform nano-scale pores and high specific area. Functionalization of the pore wall by introduction of transition metal and modification of organic groups in the pore-wall lattice and/or the surface were investigated. Mesoporous materials containing niobium in the pore wall have been reported with regard to catalytic activity for oxidation and hydrodesulfurization [1,2]. Niobium compound is well known to be useful as a solid acid catalyst and precious metal support. [3,4]. Recently, we reported that Nb–mesostructured material and Nb–containing mesoporous silica could be prepared from using layered-perovskite type potassium niobate (K_2NbO_3F) and alkyltrimethylammonium chloride (C_nTMACl) [5,6]. However, the local structure of these mesostructured materials had not been clarified. The local structure is especially important when the material is utilized as a catalyst. In this study, we report preparation of Nb–mesostructured materials from K_2NbO_3F and structural characterization of the materials by X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS) analysis. The influence of the pH on the meso- and local-structure was also investigated.

Experimental

Nb–mesostructured materials were prepared from K_2NbO_3F and hexadecyltrimethylammonium chloride ($C_{16}TMACl$) as structure-directing agent (SDA), similarly to the previous procedure [5]. K_2NbO_3F was synthesized by a solid-state reaction from KF, K_2CO_3 and Nb_2O_5. The reacted solution was prepared to $K_2NbO_3F : C_{16}TMACl : H_2O = 1 : 1 : 4080$ (molar ratio), and the pH of this solution was adjusted to appropriate values (3.0, 5.0, 7.0, 9.0) by adding 1 $mol{\cdot}dm^{-1}$ HCl. The pH value of the reacted solution without HCl was about 10.5. Then, the solution was stirred with a magnetic stirrer at 323 K for 3 h. The resulting white precipitate was recovered by filtration and drying at 333 K overnight. $K_8Nb_6O_{19}$ was prepared from KOH and Nb_2O_5 by the previous procedure [7]. Identification of meso- and crystal-structure was performed by the powder X-ray diffraction method with CuKα radiation ($\lambda = 0.15418$ nm) using a diffractometer (Rigaku, RAD-PC). Nb K-edge EXAFS spectra were measured at BL-10B of the Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF), in Japan. The measurements were carried out in a transmission mode at room temperature. The EXAFS spectra were analyzed using REX 2000 (analysis program package from Rigaku). Fourier transform range was over $k = 30\text{-}130\ nm^{-1}$.

Results and Disscussion

Figure 1 shows a TEM image of mesostructured material prepared without HCl at pH 10.5. About 3 nm of layered periodicity was observed. The XRD pattern of the mesostructured material showed three peaks in the range $2\theta = 1\text{–}10°$, which were indexed to lamellar structure with $d_{100} = 3.1$ nm, whereas no apparent peak that clarified the local structure could be observed in high-angle region. This result showed that the mesostructured materials did not have long-distance ordered local structure. EXAFS is a powerful tool in the study of short-distance order in the local structure. Figure 2 shows k^3-weighted Fourier transforms of the EXAFS oscillations of prepared materials. K_2NbO_3F and $K_8Nb_6O_{19}$ were used as reference compounds of local structure of Nb-mesostructured materials. K_2NbO_3F with a K_2NiF_4-type structure consists of two-dimensional linkage by the corner-shared NbO_5F octahedra, and the Nb–(O)–Nb distance of corner-shared NbO_5F is reported to be 0.396 nm [8]. The $K_8Nb_6O_{19}$ with $[Nb_6O_{19}]^{8-}$ poly-ion has one corner-shared NbO_6 and four edge-shared NbO_6, and the Nb–(O)–Nb distance of edge-shared NbO_6 is reported to be 0.355 nm [9]. A peak was obtained around 0.36 nm in the EXAFS Fourier transform of K_2NbO_3F, whereas a peak around 0.30 nm was observed in that of the $K_8Nb_6O_{19}$ and the mesostructured material. Therefore, the local structure of the mesostructured material prepared with pH 10.5 resembled that of $K_8Nb_6O_{19}$, edge-shared linkage of NbO_6 units.

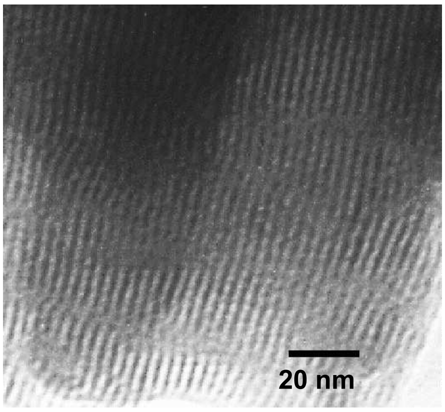

Figure 1 The mesostructured material prepared at pH 10.5.

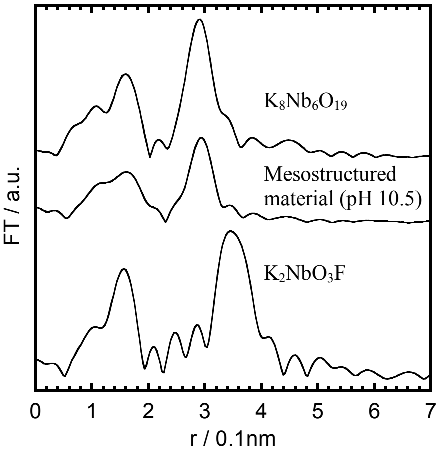

Figure 2 Fourier transforms of the EXAFS oscillations of prepared materials.

Secondly, mesostructured materials were prepared in solutions controlled to various pH values by adding HCl. Lamellar structure was obtained at pH 9.0, while 2d-hexagonal structure formed at pH 3.0–7.0. It is considered that 2d-hexagonal structured materials were obtained in the acidic condition because the amount of SDA in the mesostructured material decreased due to exchange between C_nTMA^+ and H^+. On the other hand, XRD peak could not be observed in high-angle. Therefore, these mesostructured materials were determined not to have the long-distance ordered local structure. In the Fourier transforms of the Nb K-edge EXAFS oscillations of mesostructured materials prepared under various pH conditions, the peak attributed to the Nb–(O)–Nb distance of edge-shared NbO_6 octahedra was observed. However, the intensity of this peak decreased with decreasing pH, indicating that the local structure approached amorphous. The EXAFS analysis clarified that the local structure of Nb could be controlled by controlling the pH of the reacted solution.

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References

[1] I. Nowak and M. Ziolek, *Micropor. Mesopor. Mater.*, **78**, 281 (2005).
[2] L. Cedeño, D. Hernandez, T. Klimova and J. Ramirez, *Appl. Catal. A,* **217**, 39 (2003).
[3] K. Tanabe, *Catal. Today*, **8**, 1 (1990).
[4] M. Shirai, K. Asakura and Y. Iwasawa, *J. Phys. Chem.*, **95**, 9999 (1991).
[5] M. Ogasawara, S. Kato, H. Tsukidate, T. Akaogi, Y. Moriya and S. Nakata, *Chem. Lett.*, **2004**, 1138.
[6] M. Ogasawara, S. Kato, H. Tsukidate, T. Akaogi, Y. Moriya and S. Nakata, *Chem. Lett.*, **2005**, 208.
[7] G.M. Walterman, *Japan Patent Application,* 59-207806.
[8] F. Galasso and W. Darby, *J. Phys. Chem.*, **66**, 1318 (1962).
[9] T. Ushikubo, Y. Koike, K. Wada, L. Xie, D. Wang and X. Guo, *Catal. Today*, **28**, 59 (1996).