

Synthesis of Mesostructured Materials from K_2NbO_3F as Starting Material

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We synthesized mesostructured materials using layered perovskite K_2NbO_3F and C_nTMACl ($n = 12, 14, 16, 18$) as starting materials. In the case of $n = 16$, lamellar phase at pH 9, 10.5 was obtained, while 2D-hexagonal phase at pH 3–7 was observed. This result indicates that the mesophase structure depends on the pH of the reacted solution. The d_{100} of mesostructured materials increased with increasing length of the alkyl chain. This indicates that the periodicity of the mesostructure can be controlled by selection of the surfactant.

Mesoporous materials have attracted attention from the scientific and applicational points of view because they have ordered pores of uniform size and highly specific surface area. Regarding mesoporous silica, for example, numerous studies on the partial substitution of Si with transition metal,^{1,2} modification of pore surfaces with organic groups,^{3,4} pore size control,^{5,6} have been reported. Mesoporous materials consisting of transition metal oxides are promising for catalytic and electronic applications.^{7,8}

FSM-16 and KSW-2 were synthesized using a layered silicate, kanemite,^{9,10} as starting material. KSW-2 has a unique square shape pore, which is difficult to form from homogeneous solution. This suggests that it is possible to synthesize mesoporous materials with unique pore shape using a layered compound as a starting material. Except for the synthesis of FSM-16 and KSW-2 from kanemite, few studies on synthesis using a layered compound have been reported. K_2NbO_3F is known as a layered perovskite-type compound having high reactivity. It is reported that this compound changes to perovskite $KNbO_3$ when stirred in distilled water.¹¹ In the study reported here, we used layered perovskite K_2NbO_3F to synthesize mesostructured materials as porous material precursors.

Layered perovskite K_2NbO_3F was synthesized by an ordinary solid state reaction. KF , K_2CO_3 , and Nb_2O_5 were weighed in the molar ratio $KF/K_2CO_3/Nb_2O_5 = 4:1:1$ and mixed in ethanol using a mortar and pestle. The mixture was heated at 1083 K for 6 h in air. After the reaction, excess potassium fluoride was removed by washing the product with distilled water. The product was examined by the powder X-ray diffraction (XRD) method using a diffractometer (Rigaku RAD-PC $Cu K\alpha$).

The surfactant used as the structure directing agent (SDA) in the synthesis was alkyltrimethylammonium chloride (C_nTMACl , $n = 12, 14, 16, 18$). 0.3 g of powder K_2NbO_3F was dispersed to 80 cm^3 of distilled water and immediately added 12.6 cm^3 of 0.1 mol/ dm^3 C_nTMACl aqueous solution. The suspension was stirred with a magnetic stirrer at 323 K for 3 h and the pH was adjusted to appropriate values (1, 3, 5, 7, 9) by adding 1 mol/ dm^3 HCl. The resulting white precipitate was recovered by filtration and dried. Structural characterization of the products was performed using XRD and transmission electron microscopy (TEM, JEOL JEM-2010 200 kV).

Figure 1 shows XRD patterns of products synthesized from K_2NbO_3F and $C_{16}TMA$ at various pH. The products synthesized at pH 10.5 and 9 show three peaks in the range $2\theta = 1-10^\circ$, which were indexed to lamellar phase. In the case of products synthesized at pH 7, 5, and 3, the diffraction peaks were indexed on 2D-hexagonal phase. The d_{100} values were 3.3 nm at pH 10.5 and 4.1 nm at pH 7, indicating formation of mesostructure. No apparent peaks were observed in the range $2\theta = 1-2^\circ$ for the product synthesized at pH 1. This indicates that no ordered mesostructure phase was formed. The lamellar phase complexes were transformed to 2d-hexagonal phase by stirring in the water adjusted to pH 3–7 at room temperature. These results suggest that the mesostructure of the products depended on pH condition. Such a transformation has been confirmed in other mesostructured materials. In the case of MCM-41,¹² lamellar phase from synthesize at pH 13 was transformed to 2D-hexagonal by acidification at pH 10.7.

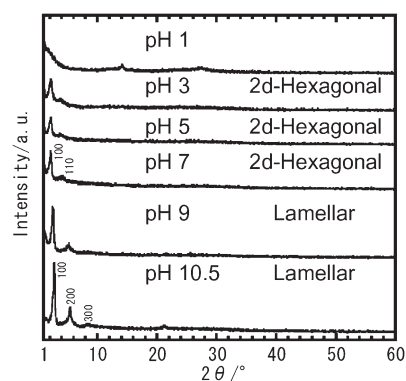


Figure 1. XRD patterns of products synthesized at various pH. (323 K, 3 h).

Figure 2 shows XRD patterns of the products synthesized from K_2NbO_3F and alkyltrimethylammonium chloride (C_nTMACl) at pH 10.5. The XRD peaks were indexed on 2d-hexagonal phase for $n = 12$ and lamellar phase for $n = 18$. For $n = 14$, 2D-hexagonal and lamellar phases coexisted in the product. Thus, it was found that the length of the alkyl chain affects the mesostructure of the product. This result is attributable to the relationship between the length of the alkyl chain and the curvature of surfactant assembly. For the same head-group surfactant, the curvature increases with decreasing length of the alkyl chain. Therefore, for $n = 12$, 2-D-hexagonal phase-containing rod-shape liquid crystal with large curvature and for $n = 16$ and 18, lamellar phase-containing plane-shape liquid crystal were formed. A TEM image of $K_2NbO_3F/C_{12}TMA$ complex synthesized at pH 10.5 is shown in Figure 3. A typical honeycomb like arrangement of meso ordered channels was observed.

Figure 4 shows XRD patterns of the products synthesized

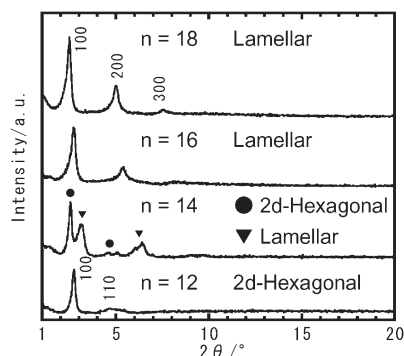


Figure 2. XRD patterns of the products using various surfactants. (323 K, 3 h, pH 10.5).

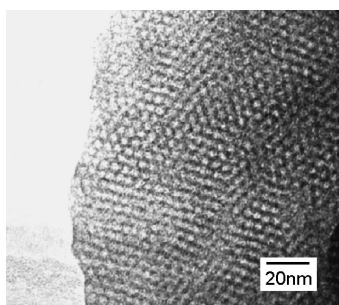


Figure 3. TEM image of the $K_2NbO_3F/C_{12}TMA$ complex.

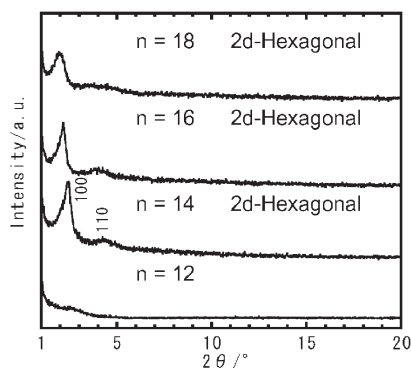


Figure 4. XRD patterns of the products using various surfactants. (323 K, 3 h, pH 7).

from K_2NbO_3F and C_nTMACl at pH 7. The XRD peaks were indexed on single phase of 2-D-hexagonal phase for $n = 14-18$, but the peaks for $n = 12$ were very weak, indicating collapse of the mesostructure phase. The relationship between the d_{100} of the obtained products, 2-D-hexagonal and lamellar mesophases, and number of carbon atoms in the alkyl chain of the surfactant is shown in Figure 5. The d_{100} of the products increased about 0.2 nm per carbon in the alkyl chain. This indicates that the periodicity of the mesostructure can be controlled by selection of the surfactant as in the case of FSM-16⁵ and MCM-41.⁶

The 2-D-hexagonal $K_2NbO_3F/C_{16}TMA$ complex from synthesis at pH 7 was calcined at 603 K for 3 h in order to remove SDA. The XRD peaks in the range of $2\theta = 1-10^\circ$ disappeared.

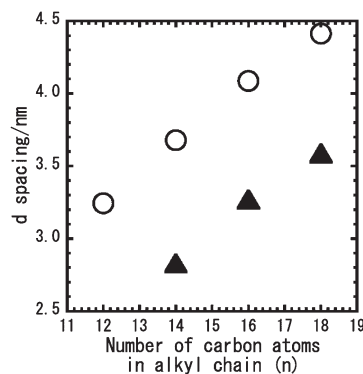


Figure 5. Relationship between d_{100} of the products and number of carbon atoms in alkyl chain (n). \circ 2-D-hexagonal, \blacktriangle lamellar.

This indicates that the mesostructure was collapsed by the calcination.

In conclusion, we synthesized mesostructure materials from layered perovskite K_2NbO_3F and C_nTMACl ($n = 12, 14, 16, 18$) as SDA. Lamellar and 2-D-hexagonal mesophases were obtained by adjusting the pH condition of the reacted solution and selection of the surfactant. Although improvement in thermal stability is required in order to obtain a mesoporous material, layered perovskite type compounds can be expected to offer a new route to synthesis of mesoporous materials.

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