Synthesis of Mesostructured Materials Using Nb-containing Layered Perovskites and Cationic Surfactants

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Mesostructured composites of layered perovskites and cationic surfactants were synthesized. Layered perovskite HCa_2Nb_3O_10 and alkyltrimethylammonium (C_TMA) or alkylpyridinium (C_Py) surfactants formed lamellar-type composites. The interlayer spacings of the composites increased with increasing carbon number of alkyl group in the surfactants. The spacings were also affected by the Nb:surfactant ratio in the reacting solutions. From comparison between size of molecule and interlayer spacing, it is suggested that two types of composites formed, which contain C_16Py^+ ions with mono- or bilayer arrangements.

Key Words: Layered perovskite, Mesostructured composite, Cationic surfactant

1 INTRODUCTION

Nb-containing layered perovskites have attracted attention from the scientific and applicational points of view because they exhibit photocatalytic activity, ion conductivity and intercalating behavior of organic molecules. Some Nb-containing layered perovskite-type compounds have been synthesized and investigated regarding their intercalation reaction with alcohols and alkylamines [1,2]. Recently, we reported the synthesis of mesostructured composites using single-layered perovskite, KLaNb_2O_7 and cationic surfactants as structure directing agents (SDA) [3]. In this case, 2-D-hexagonal- and lamellar-type mesostructured composites were obtained by adjusting pH of reacting solution. In the case of mesoporous materials synthesized from homogeneous solutions such as mesoporous silica, MCM-41, the mesostructure of the materials mainly depends on synthetic conditions and SDA[4]. While KSW-2 which is synthesized using a layered silicate, kanemite as starting material has a unique square shape pore, which is difficult to form from homogeneous solution[5]. This suggests that structure of layered compounds as starting materials is an important factor for controlling the mesostructure of the resultant composites.

In this study, we synthesized mesostructured composites using multi-layered perovskites, KLaNb_2O_7 and KCaNb_2O_10 shown in Figure 1 as the starting materials and investigated the structure of the composites.

2 EXPERIMENTAL

2.1 Synthesis of layered perovskites and their protonate forms

Layered perovskites KLaNb_2O_7 and KLaNb_2O_7 were synthesized by an ordinary solid state reaction. KCO_3, La_2O_3, CaCO_3, and Nb_2O_5 were weighed in the appropriate molar ratio and mixed in ethanol using a mortar and pestle. KLaNb_2O_7 was obtained by heating at 1373 K for 24 h in air and KLaNb_2O_7 was obtained by heating at 1523 K for 18 h in air. The products were examined by the powder X-ray diffraction (XRD) method using a diffractometer (Rigaku RAD-PC, CuKα radiation). The protonated compounds, HLaNb_2O_7 and HCaNb_2O_10, were prepared by ion exchange in 6 mol/dm^3 HNO_3 aqueous solution at 333 K for 24 h and in 6 mol/dm^3 HCl aqueous solution at 333 K for 16 h, respectively.
2.2 Synthesis of layered perovskite-cationic surfactant composites

The surfactants used as the SDA in this study were alkyltrimethylammonium chloride (C.TMACl, n = 12, 14, 16, 18) and alkylpyridinium chloride (C.PyCl, n = 12, 16), where n is the number of carbon atoms in alkyl chain. 0.3 g of HLaNb2O7 or HCa2Nb3O10 powders were dispersed into distilled water (100 cm³ for HLaNb2O7 or 110 cm³ for HCa2Nb3O10) and then 0.1 mol/dm³ C.TMACl or C.PyCl aqueous solution was added. Nb:SDA ratios in the suspensions were 1:1 - 12:1. The suspension was stirred with a magnetic stirrer at 343 K for 3 h. The resulting white precipitate was recovered by filtration and dried. Structural characterization of the products was performed using XRD. Thermogravimetry and differential thermal analysis (TG-DTA) of the composites were performed from room temperature to 1000°C (Rigaku TG8120, heating rate: 10 K/min).

3 RESULT AND DISCUSSION

Figure 2(a) and (b) shows XRD patterns for HLaNb2O7-C.TMA and HCa2Nb3O10-C.TMA composites. In the case of n = 14-18 for HLaNb2O7 and n = 12-18 for HCa2Nb3O10, the (001) peaks of the composites observed at angles lower than those of the protonate forms, HLaNb2O7 or HCa2Nb3O10. These peaks shifted to lower angle with increasing number of carbon atoms in alkyl chain. These results indicate formation of lamellar type composites and expansion of interlayer space due to intercalation of the surfactants. Figure 3 shows relationship between the number of carbon atoms and the d-spacings of (001) plane, d001, for HLaNb2O7-C.TMA and HCa2Nb3O10-C.TMA composites containing the same surfactant was about 0.4 nm. As shown Figure 1, HLaNb2O7 and HCa2Nb3O10 consist of double and triple NbO6 octahedra sheets, respectively. This difference in d001 is corresponding to a thickness of a single NbO6 octahedra sheet. In addition, the d001 increased linearly with increasing number of carbon atoms, n for both composites and the slopes were nearly equal to each other. These results indicate that arrangements of C.TMA ions in the interlayer are same for these composites. On the other hand, the XRD pattern of HLaNb2O7-C.TMA composite was different from that of lamellar or 2-D-hexagonal type mesostructured materials, suggesting a formation of an unidentified type composite.

Figure 4 shows the XRD patterns of HCa2Nb3O10-C.Py composites synthesized at various Nb:C.PyCl ratios. It was found that two types of lamellar phases formed for 3:1 and 12:1. The product for 6:1 was a mixture of these lamellar phases. While the XRD patterns of the products for Nb:C.PyCl = 12:1, 6:1 and 3:1 in the reacting suspensions showed that lamellar-type HCa2Nb3O10-C.Py composites formed in single phases, respectively. Relationship between d001 values of the HCa2Nb3O10-
C-Py composites and number of carbon atoms of the surfactants is shown in Figure 5. The \(d_{001}\) data of HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_x\)TMA composites are also shown for comparison. The \(d_{001}\) of HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_{12}\)Py and HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_{16}\)Py (12:1) composites are close to the straight line drawn for the HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_x\)TMA composites. This result suggests that C\(_x\)Py\(^+\) ions were incorporated into HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_{12}\)Py and HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_{16}\)Py (12:1) with an arrangement similar to the interlayer of HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_x\)TMA composites. On the other hand, HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_{16}\)Py (3:1) composite has larger \(d_{001}\) than HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_{12}\)Py (12:1) composites in spite of containing the same surfactant. The difference in \(d_{001}\) implies that the composites for Nb:C\(_x\)PyCl=3:1 and 12:1 incorporate C\(_x\)Py ions in a different arrangement in the interlayer. Figure 6 shows TG curves of HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_x\)Py composites. Weight losses were observed around 300, 400 and 600°C, which are attributed to combustion and/or decomposition of the surfactant. Total weight loss for the 3:1 composite is larger than that for the 12:1 composite, indicating that the amount of the C\(_x\)Py\(^+\) ion incorporated in the 3:1 composite is larger than that in the 12:1 composite. From this result, it is suggested that the amount of C\(_x\)Py ion in the composites affects the arrangement of the surfactant.

Structure models of HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_x\)Py composites for Nb: C\(_x\)PyCl =3:1 and 12:1 are shown in Figure 7. The thickness of the [Ca\(_2\)Nb\(_3\)O\(_{10}\)] layer is estimated to be 1.2 nm from the structure of

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**Figure 4** XRD patterns of HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_x\)Py composites synthesized at various Nb:C\(_x\)PyCl ratios

**Figure 5** Relationship between \(d_{001}\) values of the HCa\(_2\)Nb\(_3\)O\(_{10}\)-surfactant composites and number of carbon atoms of the surfactants. □ C\(_{12}\)Py, ● C\(_{16}\)Py

**Figure 6** TG curves of HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_x\)Py composites

**Figure 7** Structure models of HCa\(_2\)Nb\(_3\)O\(_{10}\)-C\(_x\)Py composites for Nb: C\(_x\)PyCl = (a) 12:1 and (b) 3:1
KCa,NbO₉ and the length of a CaPy⁺ ion is 2.4 nm. Taking into account of these dimensions and dₓₒ of the composite for Nb: CaPyCl = 3:1, the interlayer spacing of the composite is estimated to be 3.2 nm, which is larger than the length of a CaPy⁺ ion. This suggests that the organic species in the interlayer would be form a bilayer arrangement with tilting. In the case of Nb:CaPyCl = 12:1, the interlayer spacing is estimated to be 2.1 nm, which is smaller than the length of a CaPy⁺ ion, suggesting that the organic species in the interlayer form a monolayer arrangement with tilting.

4 CONCLUSIONS

In the present study, we synthesized the composites consisting of multi-layered perovskite and cationic surfactants. The lamellar-type composites formed for the combinations of HLaNb₂O₆- or HCa₂-Nb₂O₆-C,TMA and HCa₂-Nb₂O₆-C.Py. The interlayer spacings of the composites were affected by the size of the surfactant and Nb:surfactant ratio in the reacting suspensions. From the results of XRD analysis for the composites, structural models of the HCa₂-Nb₂O₆-C.Py composites were proposed. From the comparison between size of the molecule and the interlayer spacing, it is suggested that two types of composites formed, which contain CaPy⁺ ions with mono- or bilayer arrangements. The arrangement would be controlled by the amounts of surfactants in the interlayer.

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