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Original Research Paper

Bottom-up synthesis of aluminophosphate nanosheets by hydrothermal process

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ABSTRACT

Hydrothermal treatment of aqueous mixtures of boehmite (AlOOH), phosphoric acid, and tetramethylammonium hydroxide provided two types of layered aluminophosphates having tetramethylammonium ion (TMA^+) as an interlayer cation, despite the fact that TMA^+ ion acts as a structure-directing agent of microporous $AlPO_4$ materials and less likely leads to a lamellar structure. The layered aluminophosphates were formed in amorphous gels, so that they were obtained as precipitates. Upon dispersing the precipitates to water under agitation, the layered aluminophosphates were transferred to the aqueous phase, resulting in transparent aqueous sols. Because they had bulky interlayer cation TMA^+, it is likely that in the sols, layered aluminophosphates were exfoliated, providing aluminophosphate nanosheets. Moreover, their characterization results suggest that the layered compound formed at 170 °C consisted of aluminophosphate layers with kanemite-like structure. Furthermore, the prolonged hydrothermal treatment at 170 °C led to the formation of microporous ATT-type $AlPO_4$ crystals. Under the synthesis condition employed in this study, layered aluminophosphates were formed at early stage, and then structurally converted to microporous $AlPO_4$ crystals.

1. Introduction

Metalate nanosheets are two-dimensional materials. There is some possibility that novel chemical and physical properties emerge due to their highly anisotropic shapes. Upon exfoliating layered metalates consisting of negatively charged metalate slabs and interlayer cations, the metalate slabs are obtained as metalate nanosheets. Conventionally, metalate nanosheets have been prepared by the ion exchange of interlayer cations for bulky tetraalkylammonium ions, which causes the swelling and exfoliation of the layered metalates in aqueous solution [1–3]. The resulting metalate nanosheets have so large lateral size that their aqueous sols have interesting properties such as liquid crystalline properties [4,5]. Unlike the conventional method, we have synthesized metalate nanosheets by bottom-up process, which utilizes the acid-base reactions between metallic acid and tetraalkylammonium hydroxide in aqueous solutions [6–10], although the lateral size of the resulting nanosheets is not so large.

The applications of metalate nanosheet thin films have been studied extensively [11–16]. Thin films of metalate nanosheets are fabricated by Layer-by-Layer method and Langmuir-Blodgett method. Bottom-up synthesis of metalate nanosheets has some possibility that continuous monolayer thin films of metalate nanosheets are fabricated by depositing nanosheets directly on chemically modified substrate surface. However, the bottom-up syntheses, which we have studied, were conducted in basic aqueous solutions. Since basic solutions cause corrosion and dissolution of many types of substrates, bottom-up synthesis of metalate nanosheets in acidic or neutral aqueous solutions is desirable for thin film fabrication. Moreover, we previously reported the bottom-up synthesis of titanate nanoflakes in ionic liquid solvents [17]. However, the synthesis conditions providing titanate nanoflakes were limited, because OH^- ion reacted with ionic liquid molecules. Also for the investigation of the influence of ionic liquid solvent on morphology of metalate nanosheets obtained by bottom-up process, synthesis in acidic or neutral solvents is preferable.

It is known that layered aluminophosphates and aluminum phosphates with different crystal structures are hydrothermally synthesized in acidic or neutral solutions [18–24]. So, we envisaged that layered aluminophosphates or aluminophosphate nanosheets would be synthesized in acidic or neutral solutions by bottom-up process. However, there were some problems.

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Although tetraalkylammonium ions such as TMA^+ ion are used for our bottom-up process of metalate nanosheets, they have ability to act as a structure-directing agent of crystalline microporous aluminum phosphates $AlPO_4$. Furthermore, although the metalate nanosheets that we have synthesized by bottom-up process included only one type of cation, aluminophosphate nanosheets include two types of cations, i.e. Al^{3+} and P^{5+}, so that the formation reactions would be more complex. So, the objective of this study is to examine if aluminophosphate nanosheets are synthesized in acidic or neutral aqueous solutions by bottom-up process.

2. Experimental procedure

2.1. Synthesis

Typical synthesis was conducted, as follows: 30 mmol of boehmite (AlOOH; CATAPAL C1, Sasol Chemicals) was dispersed in 18.6 mL of distilled water. 85% phosphoric acid (30 mmol of H_3PO_4) was added to the suspension. The suspension was stirred for 1 day. Then, 25% tetramethylammonium hydroxide ($N(CH_3)_4OH$; TMAOH) solution (30 mmol of TMAOH) was added to the suspension. The suspension was further stirred for 1 day. The resulting mixture was used as a reaction gel, was about 35 g in weight, had a molar ratio of 1 AlOOH:1 H_3PO_4:1 TMAOH:50 H_2O, and was 7.5 in pH. The reaction gel was hydrothermally treated for 1–14 days at 80–170 °C, resulting in the formation of gel-like precipitates. The precipitates were collected by certification at 9000 rpm for 15 min.

The precipitates were washed, as follows: they were dispersed in 200 mL of distilled water, were stirred for 1 day, and then were collected by centrifugation. The supernatant and washed precipitates were characterized. This washing process was repeated four times.

2.2. Characterization

X-ray diffraction (XRD) measurements were performed on a Rigaku Ultima IV diffractometer with a monochromatic CuKα irradiation. XRD patterns were recorded at a scan rate of 2° min^{-1} in the 2θ range of 2–70°. Powders or thin films prepared from aqueous suspensions of precipitates or aqueous colloids were used as a sample. The thin film samples were prepared by evaporating the suspensions or colloids on a glass substrate under the ambient condition.

Transmission electron microscopy (TEM) images were captured using a JEOL JEM-2100 model at an accelerating voltage of 200 kV. The samples were prepared by evaporating a drop of aqueous suspension of samples on a Cu grid supported with a Formvar thin film. Hydrophilic treatment was conducted for the Cu grid before use.

Wavelength-dispersive type X-ray fluorescence analysis (WD-XRF) was conducted on a Bruker-AXS S8 TIGER-MA model for estimating Al/P molar ratio in the precipitates before and after washing. The chemical composition was evaluated by digital scan screening analysis using a fundamental parameter software. Measurement were made for the powdery sample placed on a polypropylene film, which is the bottom of a sample holder.

3. Results and discussion

3.1. Synthesis of aluminophosphate nanosheets

The aqueous mixtures of AlOOH, H_3PO_4 and TMAOH were hydrothermally treated for 1 day at different temperatures. XRD measurements were conducted for the thin films prepared from aqueous suspensions of the precipitates. Some peaks appeared at low diffraction angles (Fig. 1). Before the hydrothermal treatment, only peaks assigned to pseudo-boehmite was observed. Upon hydrothermally treating at 80–170 °C, peaks with *d*-spacing of 1.42 and 0.71 nm appeared. For the sample prepared at 170 °C, peaks with *d*-spacing of 2.36, 1.16, and 0.77 nm were also observed. Their *d*-spacings had a relation of 1:1/2:1/3, indicating high orientation of formed crystals. Because the peaks attributed to high orientation were observed at low diffraction angles, it is inferred that two types of layered aluminophosphates were formed at 80 and 170 °C. Hereafter, the compounds with a basal spacing of 1.42 and 2.36 nm are called "layered aluminophosphate A" and "layered aluminophosphate B," respectively. Moreover, the basal spacings of the layered aluminophosphates were as large as 1.42 and 2.36 nm, suggesting the presence of tetramethylammonium (TMA^+) ion in the interlayer.

Next, the aqueous mixtures of AlOOH, H_3PO_4 and TMAOH were hydrothermally treated at 170 °C for different periods. The formed precipitates were collected by centrifugation, and then evaporated under the ambient condition. For the resulting powders, XRD measurements were made (Fig. 2). When the hydrothermal period was shorter than 7 days, the formed crystalline phases were only layered aluminophosphates. The hydrothermal treatment for further longer periods decreased the amount of the layered aluminophosphates and provided the formation of $AlPO_4$-12-TAMU (ATT-type $AlPO_4$), which is one of microporous aluminophosphates synthesized using TMA^+ as a structure-directing agent [25]. After 14 days of hydrothermal treatment, the sample contained only $AlPO_4$-12-TAMU. Since tetraalkylammonium ion acts as a structure-directing agent of zeolites, hydrothermal treatment of aqueous mixtures of AlOOH, H_3PO_4 and tetraalkylammonium ion ordinarily leads to the formation of microporous $AlPO_4$ crystals. However, these results suggest that under the synthesis condition employed in this study, layered aluminophosphates were formed at early stage, and then structurally converted to microporous $AlPO_4$.

When layered materials with a bulky interlayer cation such as TMA^+ are dispersed in water, the swelling and exfoliation of the layered materials occur, resulting in the formation of nanosheets. However, in this study, such layered materials were obtained as

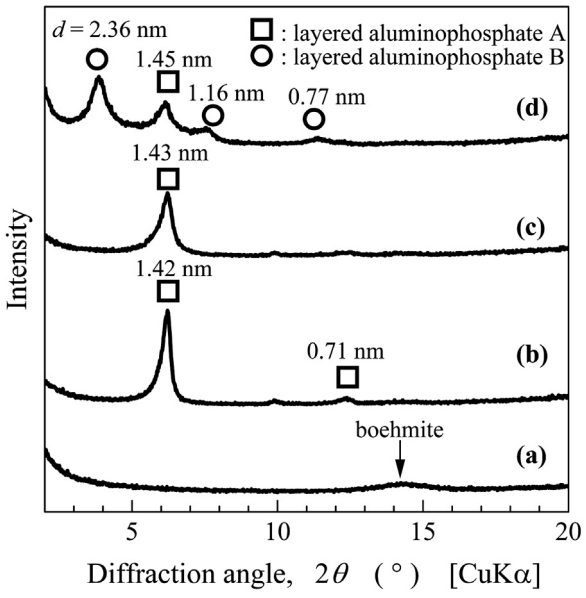

Fig. 1. XRD patterns of the thin films fabricated from the precipitates (a) before hydrothermal synthesis and after hydrothermal synthesis at (b) 80 °C, (c) 120 °C and (d) 170 °C for 1 day.

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