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Differences in crystal growth behaviors of boehmite particles with octanoic acid and sodium octanoate under supercritical hydrothermal conditions

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ABSTRACT

Crystal growth behaviors of boehmite particles with octanoic acid and sodium octanoate under supercritical hydrothermal condition were investigated. It was confirmed that adding carboxylic acid is effective in synthesizing hexagonal plate particles with high aspect ratios, while rhombic plate particles were obtained with nitric acid at similar pH condition. To investigate the modification under basic condition, sodium octanoate was used as the additive instead of octanoic acid. The increase in concentration of octanoic acid brought about high aspect ratio boehmite particles, while adding sodium octanoate resulted in low aspect ratio boehmite. Since the particles synthesized at more acidic condition were densely covered by octanoic acid, it is considered that the surface modification by octanoic acid was facilitated at such acidic condition. These results indicate that pH in the reaction field is one of the important factors to obtain the carboxylic acid modified boehmite particles with high aspect ratios, as well as other factors such as the carboxylic acid concentration and treatment time.

1. Introduction

Demands for high-performance materials are becoming greater. Adding nano- to micro- sized fillers to organic polymers is one of the promising approaches to improve the performance of such organic materials. Affinity to organics and morphology of fillers are important factors to achieve the optimum properties of the polymer composites [1]. Poor affinity of particles to polymers causes aggregation of the particles and contact failure between the particles and polymers, which leads to poor performance of the composites [2]. Morphology of filler particles influences the performance of polymer composites [1]; in general, plate-like particles are effective in adding shielding performance, for example, for electromagnetic interference [3], while high aspect ratio particles efficiently increase thermal conductivity [4,5] of the polymer composites.

Our group has attempted to improve affinity of boehmite to organics and control of boehmite morphology; boehmite is a filler particle which can be used to enhance thermal conductivity [6] and mechanical strength of polymers [7]. We have recently found that the affinity of boehmite to organics can be improved by treating boehmite particles with long-chain carboxylic acids under supercritical hydrothermal condition, and in addition, the morphology of boehmite can be changed from rhombic plate to hexagonal plate with high aspect ratios, when boehmite powders with low crystallinity were used as a starting material [8]. It has been concluded that carboxylic acids act as a capping agent in the process of anisotropic crystal growth of boehmite through the dissolution-recrystallization mechanism. It was suggested that carboxylic acids with carbon numbers lower than 10 led to the surface-modified particles at denser coverages, and in such condition high aspect ratio particles were obtained. Moreover, the aspect ratio of obtained boehmite increased with increasing concentration of carboxylic acid added in the hydrothermal treatment. He et al. have suggested that zeta-potential of boehmite increases positively with decreasing pH [9]. Raising acidity in the reaction field enhances adsorption of carboxylic acid on the surface of boehmite particles, so controlling pH in the reaction field can be expected to greatly change the molpholgy of boehmite by tuning the zeta-potential of particles.

In this study, we investigated the crystal growth behaviors of boehmite with octanoic acid under supercritical hydrothermal condition. We chose octanoic acid as the modifier because octanoic acid was effective in raising aspect ratios of boehmite particles in the previous study [8]. To examine the effect of pH at basic condition, sodium octanoate was used as the additive instead of octanoic acid. The effects of treating time and concentrations of octanoic acid

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and sodium octanoate on the crystal growth behaviors were also reported.

2. Experimental

Experimental apparatus and procedure are similar to the previous study [8]. As a staring material, a boehmite powder (Pural SCF, Sasol Ltd.) was used (the TEM image of raw material is shown in Fig. S1 in Supplementary data). Octanoic acid, decanoic acid, nitric acid, sodium octanoate and sodium hydroxide were purchased from Wako Chemicals. In the experiments with octanoic acid, decanoic acid and sodium ocanoate, particles were recovered in the same procedure as the previous study [8]. In the typical experimental procedure, the reaction temperature was fixed at 400 °C and the treating time was at 10 min. The treating time was varied in some experiments between 5 min to 30 min. In the experiments with nitric acid and sodium hydroxide, particles were collected with a 5.0 mL water. An 8 mL of ethanol was added to the product composite solution which consisted of water, additives (nitric acid or sodium hydroxide) and particle products. By centrifugation and decantation, the product particles were recovered. Then, the product particles were again washed with an additional 8 mL ethanol, and collected by centrifugation and decantation. The obtained particles were dried in air for one day at room temperature, and then dried in an oven at 60 °C for one day. The dried particles were milled using agate mortal, and used for the following analyses.

Morphology of the products was investigated using a transmission electron microscopy (TEM, TecnaiG2 30, FEI Co.). The amount of octanoic acid on the particle surface was evaluated by the weight loss measured by a thermogravimetric analysis (TGA, TG-DTA2000, Bruker Corp.). The condition and procedure of TEM and TG-DTA analyses are the same as described in the previous study [8]. To determine the mean lengths of particles, more than 50 particles were inspected for all the experiments except for the case with 0.1 mol/L octanoic acid, where not less than 30 particles were examined. The numbers of particles counted to determine the mean lengths and the standard errors from the TEM size distributions are shown in Table S1 in Supplementary data.

Values of pH in the reaction fields were estimated in the same method as the previous study [10]. A dissociation constant of nitric acid in supercritical hydrothermal condition was obtained from the literature [11]. We used a dissociation constant of heptanoic acid in supercritical hydrothermal condition [12] as that of octanoic acid. Note that the dissociation constants of hexanoic and heptanoic acids are almost the same at ambient temperature.

3. Results and discussion

3.1. Effect of acids on morphology of boehmite

In the previous study, we used carboxylic acids of C6 to C18 as additives, and confirmed that the high aspect ratio hexagonal plate particles can be produced in the 10 min treatments under supercirical hydrothermal condition [8]. To check the effect of another type of acids, the experiment using nitric acid was conducted. The TEM image of the particles obtained from the experiment is given in Fig. 1, together with the TEM images of the products treated without any additives and with octanoic and decanoic acids in the

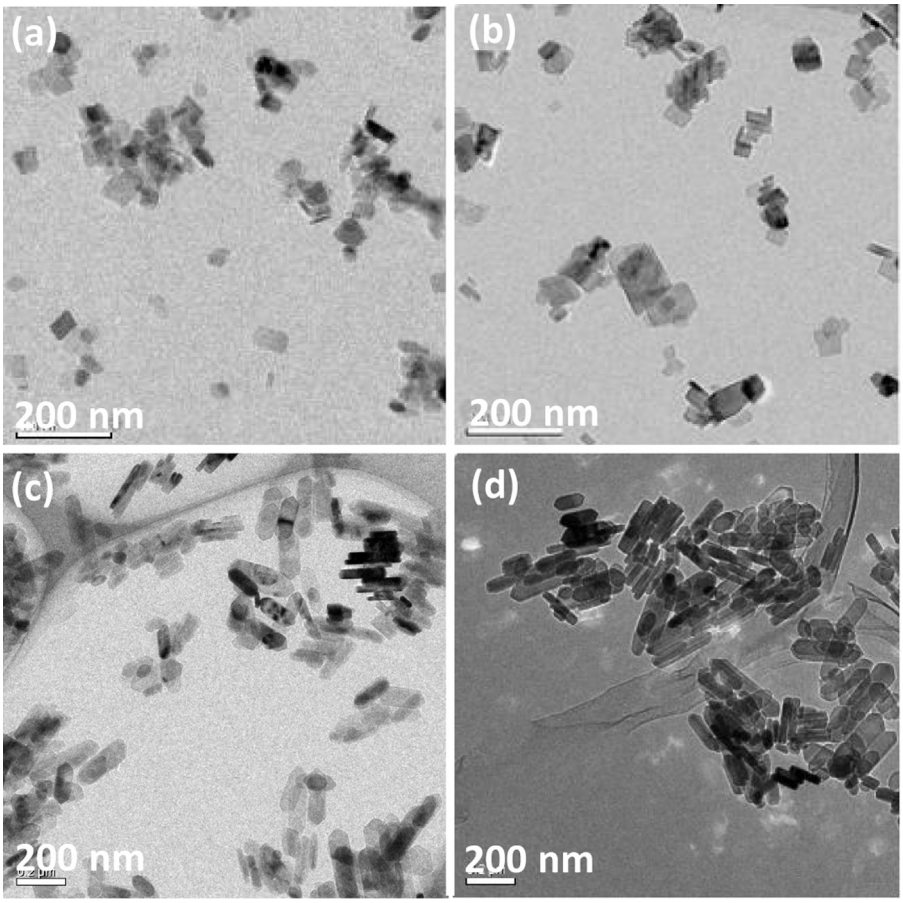

Fig. 1. Comparison of TEM images of products treated with and without additives ((a) no additives, (b) nitric acid (0.001 mol/L), (c) octanoic acid (3.2 mol/L) and (d) decanoic acid (3.2 mol/L)) for 10 min at 400 °C.