

# Preparation of $\alpha$ -alumina nanoparticles with various shapes via hydrothermal phase transformation under supercritical water conditions

Y Hakuta<sup>1</sup>, N Nagai<sup>2</sup>, Y-H Suzuki<sup>2</sup>, T Kodaira<sup>1</sup>, K K. Bando<sup>1</sup>, H Takashima<sup>1</sup> and F Mizukami<sup>1,2</sup>

<sup>1</sup>National Institute of Advanced Industrial Science and Technology (AIST), Ibaraki, 305-8565 Japan

<sup>2</sup>Kawaken Fine Chemicals Co., Ltd., Tokyo, 103-0012 Japan

E-mail: y-hakuta@aist.go.jp

**Abstract.** Alumina ( $\text{Al}_2\text{O}_3$ ) fine particles are widely used as industrial materials including fillers for metal or plastics, paints, polisher, cosmetics and electric substrates, due to its high hardness, chemical stability, and high thermal conductivity. The performance of those industrial products is closely related to the particle size or shape of the alumina particles used, and thus a new synthetic method to control size, shape, and crystal structure of the aluminum oxide is desired for the improvement of the performance. Hydrothermal phase transformation using various aluminum compounds such as oxide, hydroxide, and salt as a starting material, is known as one of the synthetic methods for producing alumina fine particles; however, the influence about the size and shape of the starting aluminum compounds has been little mentioned, although they strongly affect the size and shape of the final products. In this study, we investigated the influence of the shape, size and crystal structure of the starting aluminum compounds on those of the products, and newly succeeded in the production of rod-like  $\alpha$ - $\text{Al}_2\text{O}_3$  nanoparticles from fibrous boehmite nanoparticles using hydrothermal phase transformation under supercritical water conditions.

## 1. Introduction

Alumina ( $\text{Al}_2\text{O}_3$ ) fine particles are widely used as industrial materials including fillers for metal or plastics, paints, polisher, cosmetics and electric substrates, due to its high hardness, chemical stability, and high thermal conductivity. The performance of those industrial products is closely related to the particle size or shape of the used alumina particles, and thus a new synthetic method to control size, shape, and crystal structure of the aluminum oxide is desired for improvement of the performance.

Several methods for producing  $\alpha$ - $\text{Al}_2\text{O}_3$  fine particles such as solid-state reaction with fine  $\alpha$ - $\text{Al}_2\text{O}_3$  seeding additives [1], calcination of aluminum derivatives made by sol-gel [2] and with molten salt method [3] have been reported so far. Hydrothermal phase transformation under supercritical condition, where the critical temperature and pressure of water is 374°C and 22.1 MPa, respectively, [4][5] using various aluminum compounds such as oxide, hydroxide, and salt as a starting material, is known as one of the synthetic methods for producing alumina fine particles; however, how the size and shape of the starting aluminum compounds affect those of the product alumina has been little mentioned, although they strongly affect the size and shape of the final product. In this study, we investigated the influence of the shape, size and crystal structure of the starting aluminum compounds



on those of the product, and newly succeeded in the production of rod-like  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles from fibrous boehmite nanoparticles.

## 2. Experimental

### 2.1. Materials

Six kinds of the starting materials used in this study are listed in the Table 1. These starting sols were prepared by sol-gel method using aluminum isopropoxide [6].

**Table 1.** Starting materials and their properties

Name	Chemical formula,	Crystal structure	Morphology	Size <sup>a</sup> / nm
Fib	AlO(OH)	Pseudo-boehmite	Fibrous	W: 10, L: 1,400
Pil	AlO(OH)	Pseudo-boehmite	Pillar	W: 10, L: 200,
Plt	AlO(OH)	Boehmite	Plate	L: 300
Amr	Al(OH) <sub>3</sub>	Amorphous	Spherical	D: 10
Gib	Al(OH) <sub>3</sub>	Gibbsite	Hexagonal plate	L: 200
Bay	Al(OH) <sub>3</sub>	Bayarite	Spherical	D: 10 – 20

<sup>a</sup>“W”, “D” and “L” mean width, diameter, and length of the particle, respectively.

### 2.2. Procedure

Experiments were conducted using a batch-type reactor made from stainless steel with 10 cm<sup>3</sup> in volume. The starting sols prepared with distilled water were put into the reactor, and then the reactor was set in the electric furnace or molten salt bath kept at a given temperature. At an appropriate time interval, the reactor was taken out from the furnace (or the bath) and then immersed into a water bath for cooling. The product was recovered by evaporation to dryness under atmosphere. The treatment temperature was in the ranges of 400 to 500 °C and the pressure was 15 to 40 MPa. The time was 15 min to 8 h.

### 2.3. Analyses

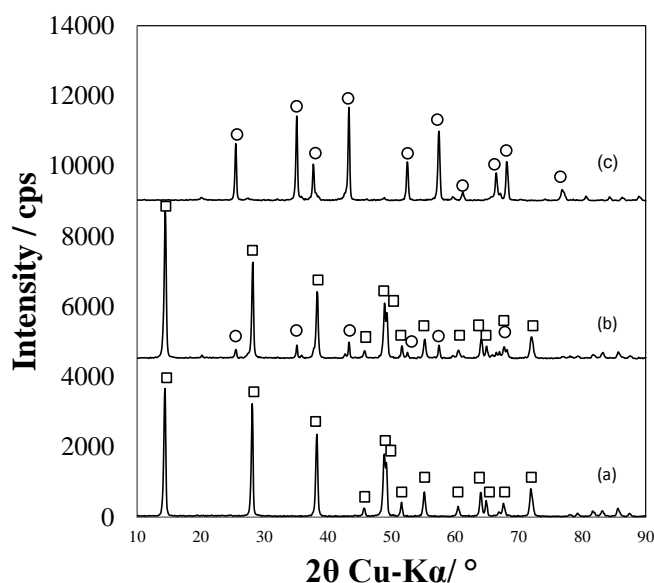
Crystal structure of the products was characterized by powder X-ray diffraction (XRD) on a mini Flex II, RIGAKU. The size and morphologies of the products were evaluated by transmission electron microscopy (TEM) observation on a TECNAI G-20 (FEI Company) at 200 kV and scanning electron microscope equipped with energy dispersion X-ray spectrometry (SEM-EDX: Hitachi.: model S-800).

## 3. Results and discussion

### 3.1. Effect of reaction temperature and pressure

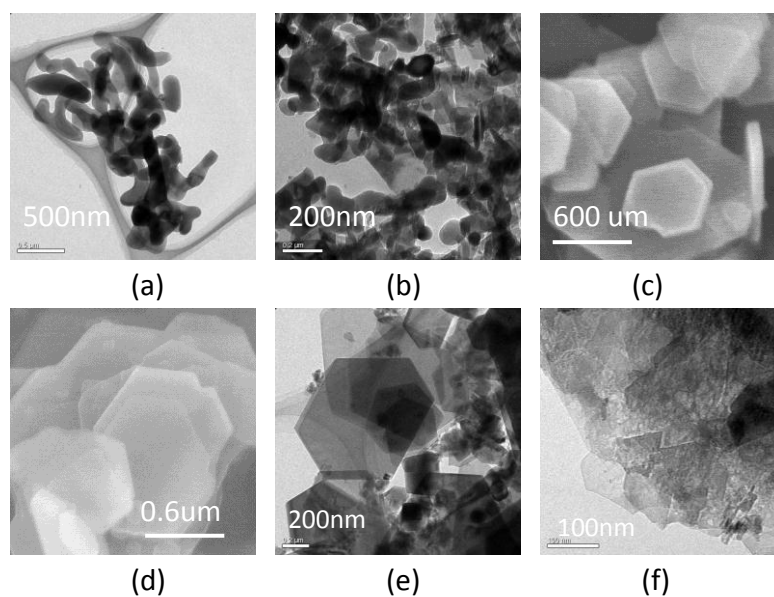
We conducted experiments varying reaction time from 15 min to 5 h besides temperature, pressure and starting sols. From the results, we confirmed that the hydrothermal phase transformation finished in 5 h. So, we discuss the results of 5 h reaction time in this paper.

We examined the effect of the reaction temperature on the crystal structure using fibrous AlO(OH) sols, “Fib”. Reaction pressure and time were fixed at 30 MPa and for 5 h, respectively. Figure 1 shows XRD profiles of the particles obtained. As shown in figure 1, at 400 °C, the product remained crystalline AlO(OH). At 450 °C, the product was a mixture of AlO(OH) and a few  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. At 500 °C,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was obtained as a single phase.



**Figure 1.** XRD profiles of (1) the products obtained at various reaction temperatures of (a) 400, (b) 450 and (c) 500 °C at 30 MPa and for 5 h.

Symbols mean open square: boehmite, open circle:  $\alpha$ -alumina.



**Figure 2.** TEM and SEM images of the products from various starting sols of (a) Fib, (b) Pil, (c) Plt, (d) Amr, (e) Gib and (f) Bay. Reaction temperature and pressure was 500 °C and 30 MPa, respectively.

### 3.2. Effect of shape of the starting sols

Next, we have evaluated the effect of the shape of the starting  $\text{AlO}(\text{OH})$  sols on the crystal structure. When the starting materials were pillar-like  $\text{AlO}(\text{OH})$  sols, “Pil” and plate like  $\text{AlO}(\text{OH})$  sols, “Plt”, the products were a mixture of metastable Tohdite ( $5\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) and  $\alpha\text{-Al}_2\text{O}_3$ , and Tohdite only, respectively, even at 500 °C. Figure 2 shows TEM images of the products. From the TEM observations, the  $\alpha\text{-Al}_2\text{O}_3$  obtained from “Fib” was rod-like particles with ca. 100 nm in diameter and 200 – 300 nm in length (figure 2(a)). Furthermore, large plate like Tohdite particles were obtained

from “Pil” and “Plt” as shown in figure 2 (b) and (c). According to literatures [4,5], as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles which have been obtained so far under similarsupercritical hydrothermal conditions are plate-like or cubic in shape and relatively large in size, rod-like  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> fine particles are new. Although a detailed mechanism is unknown, it is considered that the reason why we could obtain fine and rod-like  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles different from the literatures is derived from the high reactivity of the starting fibrous AlO(OH) sols.

### 3.3. Effect of crystal structure

We also examined the effects of the crystal structure of the starting sols. Experimental results were summarized in Table 2. Amorphous Al(OH)<sub>3</sub> (Amr) and gibbsite(Gib) transformed to plate-like metastable Tohdite particles with 1  $\mu$ m in diameter as shown in figure 2 (d) and (e). While, bayerite(Bay) transformed to plate-like  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> fine particles with ca.100 nm in diameter as shown in figure 2 (f). It is concluded that under hydrothermal and supercritical water conditions, the shape and crystal structure of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> fine particles can be controlled by selecting the starting compound of alumina.

**Table2.**Summary of results obtained with supercritical water treatment at 500 °C, 30MPa and for 5 h.

Starting sols	Product		
	Crystal structure	Morphology	Size <sup>a</sup> / nm
Fib	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	Rod	D: 50, L:200
Pil	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> (Tohdite)	Rod, (Hexagonal plate)	D: 50, L: 100,
Plt	Tohdite	Hexagonal plate	L: 1 ,000-2,000
Amr	Tohdite	Hexagonal plate	L: 1 ,000-2,000
Gib	Tohdite	Hexagonal plate	L: 1 ,000-2,000
Bay	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	Plate	L: 40

<sup>a</sup>” D” and “L” mean diameter, and length of the particle, respectively.

## 4. Conclusion

A novel method for synthesizing the shape controlled  $\alpha$ -alumina fine particle using phase transformation under supercritical water conditions was developed. Here, we investigated the influence of shape, size, and crystal structure of the starting aluminum oxides on those of the products under the hydrothermal phase transformation. As the results, rod-like  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles were obtained from the fibrous AlO(OH) sols under the supercritical water conditions (500 °C, 30 MPa). On the other hand, metastable Tohdite particles were obtained from plate-like AlO(OH) and Al(OH)<sub>3</sub> sols. It is concluded that under hydrothermal and supercritical water conditions, the shape and crystal structure of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> fine particles can be controlled by selecting the starting aluminum oxides.

## References

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