

# Effect of Milling on the Formation of Nanocrystalline χ-Al<sub>2</sub>O<sub>3</sub> from Gibbsite

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Gibbsite (FG) with mean particle diameter ( $d_{50} = 13 \mu m$ ) was milled in an attrition mill for 12 and 24 h using alumina balls as grinding media and calcined at different temperatures in the range of 350°-600°C. The properties of the alumina obtained were determined by X-ray diffraction, N<sub>2</sub> physisorption, thermogravimetric/differential thermal analyses, and transmission electron microscopy. Without milling, the alumina obtained normally contained the mixed phases between  $\gamma$ - and  $\chi$ -phase alumina. On the other hand, high purity of nanocrystalline  $\chi$ phase alumina (100 wt%) can be produced by calcination of the 24-h milled FG at 600°C. The isothermal kinetics measurements revealed that the rate constant (k) for phase transformation increased as the particle size of gibbsite decreased and the calculated activation energy for transformation from FG to alumina decreased from 20.6 to 14.7 and 6.8 kJ/mol after milling for 12 and 24 h, respectively. The physical properties of nanocrystalline y-alumina obtained by the calcination of milled FG were comparable to those produced by the solvothermal method. The present results offer a simple way to prepare a large amount of pure  $\chi$ -phase alumina for particular industrial applications.

#### I. Introduction

A LUMINA (Al<sub>2</sub>O<sub>3</sub>) is one of the most common crystalline materials used as catalysts, catalyst supports, sorbent, coating, and ceramics.<sup>1–4</sup> Compared with the other oxides, alumina has high surface area, good catalytic activity, high mechanical resistance, good thermal stability, high strength, and toughness.<sup>5–7</sup> There are many methods to synthesize alumina such as solvothermal,<sup>5–7</sup> molten salt synthesis,<sup>8</sup> shock wave action,<sup>9</sup> sol–gel,<sup>10</sup> spray pyrolysis,<sup>11</sup> and thermal decomposition of aluminum hydroxide (boehmite and gibbsite).<sup>12,13</sup>

 $\chi$ -alumina is a crystallographic form of series of alumina, which is normally obtained by dehydration of gibbsite (<200 nm).<sup>14</sup> When it is fired,  $\chi$ -alumina will transform to  $\kappa$ alumina at a temperature in the range of 650°–750°C and consequently form  $\alpha$ -alumina at a temperature around 1000°C. The  $\chi$ -phase alumina has been used as catalysts and catalyst supports and interesting results were obtained.<sup>15–17</sup> For examples, CO hydrogenation activities of Co/Al<sub>2</sub>O<sub>3</sub> catalysts increased when the catalysts were prepared on the mixed  $\gamma$ - and  $\chi$ -phase Al<sub>2</sub>O<sub>3</sub>.<sup>15</sup> Khom-in *et al.*<sup>16</sup> studied the solvothermal-derived nanocrystal-

Manuscript No. 27288. Received December 23, 2009; approved April 8, 2010. This work was financially supported by the Thailand Research Fund (TRF) and the Office of Higher Education Commission, Ministry of Education, Thailand. line pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\chi$ -Al<sub>2</sub>O<sub>3</sub>, and mixed-phase  $\gamma$ - and  $\chi$ -Al<sub>2</sub>O<sub>3</sub> in the dehydration reaction of methanol to dimethyl ether. Meephoka *et al.*<sup>17</sup> used both  $\gamma$ - and  $\chi$ -Al<sub>2</sub>O<sub>3</sub> as supports for the preparation of Pt/Al<sub>2</sub>O<sub>3</sub> for CO oxidation reaction. Most of the recent studies show that highly stable nanocrystalline  $\chi$ -Al<sub>2</sub>O<sub>3</sub> can be prepared by the solvothermal method using aluminum iso-propoxide as the precursor. Such a technique, however, is quite tedious and costly because it requires a high-pressure reactor, high temperature, and long reaction time.

Gibbsite  $(\alpha$ -Al(OH)<sub>3</sub>) is a cheap starting material widely used in the transformation of alumina because it can be dehydrated to various phases  $(\chi, \gamma, \theta, \kappa, \alpha)$ .<sup>18,19</sup> Figure 1 shows the diagram of phase transformation of alumina from gibbsite. The transformation route depended on temperature, heating environment, particle size of staring gibbsite, and heating rate.<sup>20</sup> Typically, for small particles (<1 µm), the phase transformation process occurs by route 1 and produces  $\chi$ -alumina.<sup>14</sup> In addition, the transformation of bayerite<sup>21</sup> and diaspore<sup>22</sup> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has been studied. It was indicated that  $\chi$ -alumina was not formed from these starting materials.

The formation of  $\chi$ -alumina from gibbsite has been observed in previous works. Jang *et al.*<sup>12</sup> studied the effect of grinding on the phase transformation of gibbsite (starting particle size 64.2 µm). The  $\chi$ -phase alumina was observed at 450°C for the sample grind for 5 h (particle size 9.7 µm) and completed at around 910°C. Bhattacharya *et al.*<sup>20</sup> investigated the thermal decomposition of fine gibbsite (1.5 µm) and the formation of  $\chi$ alumina appeared at 500°C and its crystal remained until around 800°C. Mercury *et al.*<sup>23</sup> studied the decomposition of synthetic gibbsite by neutron thermodiffractometry and found that  $\chi$ -alumina was formed at the temperature above 500°C. The grinding method is an effective method for the reduction of particle size due to its simplicity, minimal environmental problems, convenient operation, and absence of wastes. Attrition mills are widely used in order to reduce particle size; moreover, they are ideally appropriate for the industrial process due to their high efficiency and availability in large scale.<sup>24</sup>

In the present study, the effect of milling on the phase transformation behavior of gibbsite was extensively investigated. The properties of the alumina obtained were investigated using a laser diffraction-based size analyzer, X-ray diffraction (XRD), thermogravimetric/differential thermal analyses (TGA/DTA), N<sub>2</sub> physisorption, transmission electron microscopy (TEM), and isothermal kinetics measurement.

## **II. Experimental Procedure**

## (1) Sample Preparation

Gibbsite with  $d_{50} = 13.0$  m (Merck, Darmstadt, Germany) was used as a starting material. In order to reduce its particle size,

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Gibbsite 
$$\longrightarrow \chi$$
-Al<sub>2</sub>O<sub>3</sub>  $\longrightarrow \kappa$ - Al<sub>2</sub>O<sub>3</sub>  $\longrightarrow \alpha$ - Al<sub>2</sub>O<sub>3</sub> (route 1)

**Fig. 1.** Phase transformation of alumina from gibbsite to  $\alpha$ -alumina.

the starting material was milled in an attrition mill for 12 and 24 h using alumina balls as grinding media and water as milling fluid. Approximately 100 g of gibbsite and water 300 mL were first mixed in a plastic pot. Alumina balls were weighed before and after milling as well as filled to a half volume of the milling pot. Cooling water was fed continuously in the attrition mill in order to remove heat. Rotational speed of the mill was fixed at 500 rpm. The sample was collected every 2 h and dried at 105°C overnight in an oven to remove water. The dried sample was subsequently milled using a mortar to deagglomerate. The samples were calcined in a tube furnace in air (95 mL/min) by heating to a desired temperature at a rate of 10°C/min and was held at this temperature for 4 h. Then, the samples were cooled down to room temperature in N<sub>2</sub> flow (75 mL/min).

The products are designed as  $FG^{**h}^{***C}$  where the first two asterisks represent the milling time and the latter three asterisks represent the temperature of calcination. The abbreviation of FG is gibbsite (starting material).

## (2) Characterization

Particle size distribution was measured using a laser diffractionbased size analyzer (reflective index 1.57; Malvern Mastersizer, Worcester Shire, England). All the samples were measured on DI water as dispersant. Dispersion and deagglomeration of particles were ensured by ultrasonic treatment before measurement. XRD analysis was carried out using a Siemens D5000 diffractometer (Karlsruhe, Germany) with  $CuK\alpha$  radiation with Ni filter. The scans were recorded in the  $2\theta$  range of  $10^{\circ}$ – $80^{\circ}$  using a step size of  $0.04^{\circ}$ . The average crystallite size was estimated using the Scherrer equation. The surface areas of samples were measured by N<sub>2</sub> physisorption using a micromeritics chemisorb 2750 (Norcross, GA). TGA/DTA of the ground and unground samples were performed (SDT Analyzer Model Q600 from TA Instruments, New Castle, DE) at a heating rate of 10°C/min in flowing air (100 mL/min). The morphology of samples was investigated by TEM (JEOL JEM 2010, Tokyo, Japan), operating at 200 kV.

The fraction of  $\chi$ -Al<sub>2</sub>O<sub>3</sub> was determined by quantitative XRD analysis, using CaF<sub>2</sub> (Merck, Germany) as an internal standard. A 0.2000±0.0001 g of sample was placed in a porcelain dish. One tenth of the sample weight of CaF<sub>2</sub> was weighed and mixed with the sample for 5 min. The analysis was calculated by the ratio of the integrated intensities of the 43° (CuK $\alpha$  2 $\theta$ ) of  $\chi$ -Al<sub>2</sub>O<sub>3</sub> and integrated intensities of the 28.1° (CuK $\alpha$  2 $\theta$ ) of CaF<sub>2</sub>. Their ratios were compared against a standard calibration curve of  $\chi$ -Al<sub>2</sub>O<sub>3</sub>/CaF<sub>2</sub>. The calibration curve was determined using a mixture of  $\chi$ -alumina and the same amount of CaF<sub>2</sub>, spanning the range of 20–90 wt%  $\chi$ -alumina.

#### (3) Isothermal Kinetic Measurements

The samples were heated at three different temperatures in the range of  $450^{\circ}$ – $600^{\circ}$ C with different holding times. The activation energy for the transformation of gibbsite to  $\chi$ -Al<sub>2</sub>O<sub>3</sub> was estimated by isothermal experiments according to the Arrhenius method.<sup>25</sup> First of all, the value of the rate constant (*k*) was calculated by the Johnsom–Mehl–Avrami equation (Eq. (1)).<sup>25</sup>

$$x(t) = 1 - \exp[-(kt)^{n}]$$
(1)

where x is the phase fraction of  $\chi$ -Al<sub>2</sub>O<sub>3</sub> at time (*t*) and *n* is the reaction exponent. For analyzing Eq. (1), it can be rewritten in the form of the following Eq. (2).

$$\ln(-\ln(1-x)) = n\ln k + n\ln t$$
 (2)

The value of k and n can be calculated from the slope and interception of a linear plot of  $\ln t$  and  $\ln(-\ln(1-x))$ . After the value of k is obtained, the activation energy ( $E_a$ ) can be estimated by the Arrhenius equation (Eq. (3)).

$$\ln k = \ln A - \frac{E_{\rm a}}{RT} \tag{3}$$

where A is a constant, R is the gas constant (8.314  $J \cdot (K \cdot mol)^{-1}$ ), and T is the working temperature. The value of  $E_a$  can be calculated from the slope of a linear plot of ln k and l/T.

#### III. Results and Discussion

# (1) Particle Size Distribution

The size distributions of gibbsite agglomerates and particles before and after milling are shown in Fig. 2. The median particle size  $(d_{50})$  decreased from 13 to 3 µm and 0.6 µm after milling for 12 and 24 h, respectively. Moreover, the unimodal pore size distribution in the starting gibbsite changed to bimodal distribution after milling for 24 h. During milling, the evolution of the distribution of gibbsite is lower, and the mean size decreased.<sup>24</sup> Regarding the starting specific surface area of  $25 \text{ m}^2/\text{g}$  and microscopic evidence (shown in Fig. 9), the 13 µm is referred to the agglomerate size of the raw powder, whereas the particle size in the as-delivered state was ca. 2-3 µm. It is noted that particle size distribution of the samples did not come from alumina balls because the weight loss of balls was determined to be <1% (initial weight 761.9 g and after milling 759.9 g). Milling run of the alumina balls for 24 h in pure water without gibbsite was carried out in order to determine the typical mean particle size of the wear debris (possible  $\alpha$  seeds and abrasives coming from the grinding media). The result is also shown in Fig. 2 and the typical mean particle size was determined to be 24 m.

#### (2) XRD and TGA/DTA Results

Figures 3 and 4 show the results from the TGA and DTA plots, of the gibbsite powder after milling for various times. Two weight processes were detected corresponding to two endothermic and one exothermic process. The decrease in mass at around  $150^{\circ}$ -600°C, accompanied by the endothermic peaks in DTA signal, is attributed to the dehydration of gibbsite to form



**Fig. 2.** The particle size distribution of unmilled and milled gibbsite at various milling times.



**Fig. 3.** The thermogravimetric curves of unmilled and milled gibbsite at various milling times.

alumina. The endothermic peak was shifted toward the lower temperature with an increasing milling time, indicating an acceleration of the dehydration of gibbsite by the milling process.<sup>21</sup> The overall weight losses of all the samples were approximately around 35%, which were in good agreement with the calculated value of 34.6% for the dehydration reaction

$$2\mathrm{Al}(\mathrm{OH})_3 \to \mathrm{Al}_2\mathrm{O}_3 + 3\mathrm{H}_2\mathrm{O} \tag{4}$$

The dehydration of FG0h (Fig. 4(a)) in first endothermic step (236°C) was due to loss of water in the sample. The second endothermic peak (306°C) is corresponding to a weight loss of 22.5%, XRD measurements of FG0h treated at 400°C also show a peak at  $2\theta = 14.4^{\circ}$  (Fig. 6(d)). It points out that boehmite formed at this range of temperature. In addition, the endothermic peak at around 526°C indicated that boehmite transforms to alumina. Figure 6(b) shows that diffraction peaks of mixed phases of alumina were observed at 500°C. However, this endothermic peak disappeared when milling time increased, indicating that the milling conditions affected the transformation sequence of gibbsite.<sup>12</sup>

XRD data were undertaken to study the transformation phases from gibbsite at various temperatures. The XRD patterns of FG0h, FG12h, and FG24h are shown in Fig. 5. The intensities of XRD peaks decreased and became wider as the milling time increased. It is due to decreasing of the crystallinity and particle size of gibbsite. Figures 6–8 shows the XRD pat-



**Fig. 4.** The differential thermal analyses curves of unmilled and milled gibbsite at various milling times.



**Fig. 5.** The X-ray diffraction patterns of unmilled and milled gibbsite at various milling times; (a) FG0h, (b) FG12h, and (c) FG24h.

terns of calcined FG0h, FG12h, and FG24h at various temperatures. For the calcined FG12h, the mixture between boehmite and  $\chi$ -phases was found at 400°C and the  $\chi$ -phase was observed at a higher calcination temperature. In the case of prolonged milling (FG24h), the transformation of gibbsite to  $\chi$ -alumina was completed at 350°C. This implies that the small particle sizes are effective for reduction in the transformation temperature of gibbsite to  $\chi$ -alumina.<sup>26</sup>

When particle size of gibbsite is small, the dominant peak  $(2\theta = 14.4^{\circ})$  of boehmite would be reduced (Figs. 6(d) and 7(d)). As a result,  $\gamma$ -alumina occurred from the small particle size of gibbsite. It has been known that the dehydration sequence of gibbsite in air is affected by its particle size. In small gibbsite particles ( $<10 \,\mu$ m), boehmite is rarely formed, but in the case of larger particles (>100  $\mu$ m), boehmite is formed because the water formed by the decomposition of the gibbsite cannot rapidly escape from the larger particles.<sup>2,12,20,27</sup> Consequently, transformation of gibbsite occurred through route 1 (Fig. 1). However, the boehmite phase may be observed from the small particle size of gibbsite, if the gibbsite particle is a crystal.<sup>20</sup> Bhattacharya *et al.*<sup>20</sup> found that crystal gibbsite (0.25  $\mu$ m) can produce boehmite at 400°C. Nevertheless, Jang *et al.*<sup>12</sup> used ground gibbsite losing the crystalline structure, and boehmite was not observed at low temperature. When FG0h was heated, boehmite was observed at 400°C and  $\chi$ -alumina was formed at 450°C. However,  $\chi$ -alumina was not the only phase of alumina that occurred



**Fig. 6.** The X-ray diffraction patterns of FG0h calcined at various temperatures, b, boehmite; x,  $\chi$ -Al<sub>2</sub>O<sub>3</sub>; o,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (a) 600°C, (b) 500°C, (c) 450°C, and (d) 400°C.



**Fig.7.** The X-ray diffraction patterns of FG12h calcined at various temperatures, b, boehmite; x,  $\chi$ -Al<sub>2</sub>O<sub>3</sub> (a) 600°C, (b) 500°C, (c) 450°C, and (d) 400°C.

at this temperature; the peak of  $\gamma$ -alumina was also observed. For the micrometer sizes, both transition routes (Fig. 1) may possibly occur, which depends on the heat treatment conditions.<sup>28</sup> The decomposition of boehmite would occur at 300°C at atmospheric pressure. The typical temperature reported for the decomposition of boehmite to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is 450°C.<sup>29</sup>

In the past,  $\alpha$ -seeding has been shown to influence phase development and transformation kinetics of alumina.<sup>26,30</sup> It may be possible that the  $\gamma$  peaks in Figs. 6–8 could have been enhanced by such a seeding effect. However, in the present study, the contamination from abrasives appeared to have very little impact on the reduction of transformation temperature of gibbsite to  $\chi$ -alumina due to the very small amount presented. The amounts of wear debris obtained by milling the alumina balls in water for 24 h with and without gibbsite were only 2 and 3 wt% of the gibbsite weight, respectively. According to the literature, the effect of  $\alpha$ -seeding was dependent not only on the size of the seeds but also on the amount of the seeds presented. For examples, Kano et al.<sup>26</sup> showed that the presence of 50 wt%  $\alpha$ alumina seeding reduced the transformation temperature of gibbsite to α-alumina by 120°C (from 1030° to 910°C), while for 5 wt% α-alumina seeding, the transformation temperature decreased only about 30°C. Similarly, Xie et al.<sup>30</sup> reported that Al(OH)<sub>3</sub> can be transformed to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at a relatively lower temperature (1100°C) with the help of seeds by wet grinding of



**Fig. 8.** The X-ray diffraction patterns of FG24h calcined at various temperatures, b, boehmite; x,  $\chi$ -Al<sub>2</sub>O<sub>3</sub> (a) 600°C, (b) 500°C, (c) 400°C, (d) 350°C, and (e) 300°C.

Table I. The BET Surface Area and Alumina Phase of Unmilled and Milled Samples after Calcination at  $600^{\circ}C$ 

Samples	Phase	Surface area (m <sup>2</sup> /g)
FG0h FG0h600C FG12h600C FG24h600C	γ and χ χ χ	25.1 101.8 110.5 122.6

high-purity Al<sub>2</sub>O<sub>3</sub> balls when the seed concentration was increased to >10 wt%. Moreover, the average particle size of the abrasives in this study was much larger than those reported in the literature for reduction in the transformation temperature of gibbsite powder (i.e., 24  $\mu$ m (this work) as compared with 0.6  $\mu$ m in Xie *et al.*<sup>30</sup>).

## (3) BET Surface Area

Based on BET surface analyses of calcined samples summarized in Table I, the FG0h had significantly smaller surface area. After calcinations, the structure of gibbsite was destroyed, resulting in a drastic increase in surface area of the calcined samples. With the same calcination temperature, FG24h600C had the highest surface area of 122.6 m<sup>2</sup>/g. The increase in the surface area of treated samples is due to the decrease in particle size. These results are in good agreement with that of Ogata *et al.*,<sup>19</sup> who used gibbsite as the starting material and found that the specific surface area increased when the calcination temperature increased.

Table II summarizes the crystallite size  $(d_{XRD})$  and the fraction of  $\chi$ -phase of the calcined samples. It can be seen that the increase in calcination temperature resulted in a larger crystallite size. Meanwhile, the fraction of  $\chi$ -alumina increased with the increasing calcination temperature. These results indicated that high-purity  $\chi$ -alumina can form at the higher temperature. Du et al.<sup>21</sup> also reported that the fraction of  $\alpha$ -phase in  $\alpha$ -alumina synthesized from bayerite would increase with increasing calcination temperature. Macêdo et al.<sup>25</sup> found that the high fraction of  $\alpha$ -alumina can be produced from  $\gamma$ -alumina when the calcination temperature increased from 750° to 900°C. At low temperature (450°C), the fraction of  $\chi$ -alumina rapidly increased from 0.58 to 0.89. It is implied that mechanical activation affected the formation of  $\chi$ -alumina. Under isothermal condition, the fraction of  $\chi$ -alumina increased when the particle size decreased. It is confirmed that the small particle size of gibbsite can produce high purity of  $\chi$ -alumina. In comparison with pure  $\chi$ -alumina prepared by the solvothermal method as reported previously by our group (crystallite size 6 nm and BET surface area 168 m<sup>2</sup>/g),<sup>17</sup> the physical properties of  $\chi$ -alumina obtained by the calcination of FG24h were comparable to those of the solvothermally derived ones.

## (4) Kinetics Measurements

Table III summarizes the transformation rate constants (k) of unmilled and milled gibbsite, which was calcined at different

Table II. The Particle Size  $(d_{XRD})$  of the Samples after Calcination and the Fraction of  $\chi$ -Phase

Samples	<i>T</i> (°C)	$d_{\rm XRD} \left( {\rm nm} \right)^{\dagger}$	Fraction of $\chi$ -phase <sup>‡</sup>
FG0h	450	3.8	0.58
	500	4.1	0.72
	600	4.4	0.88
FG12h	450	3.7	0.68
	500	3.8	0.94
	600	4.2	0.95
FG24h	450	3.3	0.90
	500	3.7	0.99
	600	3.8	1

<sup>†</sup>Calculated by the Scherrer equation. <sup>‡</sup>Calculated by quantitative XRD.

 
 Table III.
 Rate Constant (k) for Milled and Unmilled Gibbsite at Different Temperature

Milling time (h)	$k  (\min^{-1})$
$T = 600^{\circ} \text{C}$	
0	0.0142
12	0.0178
24	0.0359
$T = 500^{\circ} \text{C}$	
0	0.0110
12	0.0153
24	0.0248
$T = 450^{\circ}\mathrm{C}$	
0	0.0033
12	0.0054
24	0.0188

temperatures. For any constant temperature, *k* increased with the increasing milling time. At a low temperature, the milling can increase *k* more significantly. For example, at 450°C activation of the sample, milling for 24 h increased the reaction rate constant 5.7 times (compared with the sample for 0 h), but at 600°C it increased only 2.5 times. Panchula and Ying<sup>31</sup> synthesizing  $\alpha$ -alumina from milled and unmilled  $\gamma$ -alumina reported that *k* increased with the increase in calcination temperature and milling time from 30 to 120 min.

Table IV. Activation Energy of Milled and Unmilled Gibbsite

FG0h         20.6           FG12h         14.7           FG24h         6.8	Sample	$E_{\rm a}$ (kJ/mol)
	FG0h FG12h FG24h	20.6 14.7 6.8

Table IV shows the activation energy for phase transformation of unmilled and milled gibbsite to  $\chi$ -alumina. The activation energy decreased from 20.6 to 14.7 and 6.8 kJ/mol after milling for 12 and 24 h, respectively. This result indicated that the activation energy decreased with the decreasing particle size of the starting gibbsite. In general, reducing the particle size would lead to an increasing surface energy of the particle, thereby resulting in the decreasing of activation energy for phase transformation and transformation temperature as shown in the DTA profile.<sup>28</sup> The XRD patterns also confirmed that the transformation temperature of gibbsite to  $\chi$ -alumina reduced from 450° to 350°C after milling for 24 h. It may be attributed to the fact that gibbsite grows to the critical size of phase transformation and then transform to  $\chi$ -alumina at a lower temperature.<sup>28,31</sup> Moreover, the milling of gibbsite for 12 and 24 h can be up to 28% and 67% of the activation energy compared with that of the unmilled gibbsite. Several researchers observed the kinetics of transition alumina. Macêdo *et al.*<sup>25</sup> studied the ki-



Fig. 9. The transmission electron micrographs of FG0h (a, b), FG12h (c), and FG24h (d).



Fig. 10. The transmission electron micrographs of FG0h400C (a), FG0h600C (b), FG12h400C (c), FG12h600C (d), and FG24h600C (e).

netics of  $\gamma$ - to  $\alpha$ -alumina. They found that the activation energy of this phase transformation was  $201 \pm 4$  kJ/mol. Chang *et al.*<sup>28</sup> studied the size effect of  $\chi$ -alumina to  $\alpha$ -alumina. The activation energy reduced from 506 to 321 kJ/mol when  $d_{50}$  of  $\chi$ -alumina decreased from 155 to 40, respectively. Yang *et al.*<sup>32</sup> presented the formation during  $\theta$ -Al<sub>2</sub>O<sub>3</sub> to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> transformation. They

used three kinds of  $\theta$ -powder (as-received, homogenized, homogenized, and additionally unaxial-pressed compact) as the starting material. The activation energy was 299, 189, and 148 kJ/mol, respectively. Candela and Perlmutter<sup>33</sup> studied the kinetics of boehmite formation by the thermal decomposition of gibbsite under water vapor pressure from 100 to 3200 Pa. The

activation energy was  $142\pm10$  kJ/mol. In the present work, the value of activation energy was lower than those reported in the above-mentioned works due to the lower transformation temperature.

#### (5) TEM Observation

The effect of grinding on the morphology of gibbsite and  $\chi$ -Al<sub>2</sub>O<sub>3</sub> were studied by TEM observation. Figure 9 shows the TEM micrographs of unmilled (a and b) and milled (c and d) gibbsite powder. The unmilled fine gibbsite clearly consisted of pseudohexagonal plates, while irregular and flaky particles were observed for milled samples. It revealed that the milling effectively changed the morphology of gibbsite and reduced particle size. Figures 10(a) and (b) show the TEM micrographs of FG0h400C and FG0h600C, respectively. Figure 10(a) shows that the structure is a strip. It was due to the formation of boehmite. However, this structure disappeared when gibbsite was milled for 12 h and calcined at the same temperature (Fig. 10(c)). It was probably due to the decreasing of boehmite phase in calcined samples. Figures 10(b), (d), and (e) exhibited the TEM micrographs of FG0h600C, FG12h600C, and FG24h600C, respectively. Figures 10(d) and (e) indicated that the dispersed  $\chi$ -alumina with narrow size distribution was obtained from milled gibbsite, whereas the larger particle of mixed phase  $(\chi, \gamma)$  was obtained from unmilled one (Fig. 10(b)). Besides, the morphology of samples is similar to that of gibbsite treated by mechanical milling.

## IV. Conclusions

High-purity nanocrystalline  $\chi$ -alumina can be produced from milled gibbsite (FG12h and FG24h). The transformation temperature of gibbsite to  $\chi$ -alumina decreased from 450° to 350°C when the milling time of gibbsite was increased from 12 to 24 h, respectively. For the unmilled gibbsite (FG0h), the mixed  $\chi$  and  $\gamma$ -phase Al<sub>2</sub>O<sub>3</sub> were formed at 450°C. The fraction of  $\chi$ -alumina increased with the increase in the milling time and calcination temperature. The activation energy for phase transformation of gibbsite to  $\chi$ -Al<sub>2</sub>O<sub>3</sub> also decreased with the reducing particle size of the starting gibbsite.

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