



## Original Research Paper

# The impact of nanocrystallite size and shape on phase transformation: Application to the boehmite/alumina transformation

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## ARTICLE INFO

## Article history:

Received 11 March 2016

Accepted 13 June 2016

Available online 28 June 2016

## Keywords:

Phase transformation

Boehmite

Alumina

Nanoparticles

Thermal process

## ABSTRACT

The thermal activation of oxyhydroxides is a key industrial process in preparing oxide materials. When dealing with nanoparticles, the phase transition properties are drastically modified. By preparing size- and shape-controlled boehmite nanoparticles, we demonstrate that the transformation temperature into  $\gamma$ -alumina is significantly altered. Rhombus crystallites were obtained from boehmite precipitated at basic pH, whereas crystallites precipitated at pH 4.5 were hexagonal. For the same crystallite size (ca. 4.5 nm), the transition temperature of the hexagonal crystallites was 315 °C whereas that of the rhombus ones was only 270 °C. A thermodynamic model was developed to rationalize these observations: the transition temperature results from a compromise between the crystallite size and the ratio of the lateral and basal surfaces. Consequently, the as-determined kinetic data could be a powerful tool for developing new efficient calcination processes and optimizing alumina properties.

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## 1. Introduction

Many oxide materials used in industrial applications derive from their hydrated forms, hydroxide or oxyhydroxide that are available either as ore or synthetic materials. These hydrated forms require thermal treatment to obtain the activated phases needed for industrial applications [1]. This phase transformation is also a necessary step for several oxides such as the anatase/rutile TiO<sub>2</sub> transition [2]. For several nanosized materials, the crystallite size, shape and surface properties have proven to be critical parameters governing these solid-solid transitions (kaolinite/metakaolinite [3], anatase/rutile [2] or cubic/monoclinic yttria [4]). In textbooks, reported transition temperatures correspond to bulk phases and are adequate for large-size crystallites. On contrary, at the nanoscale, the surface energies are no more negligible compared to bulk energies and it can be expected that the surface energy contribution (and thus the crystallite size and shape) modify the transition temperature: this phenomena have been recently theoretically investigated for the goethite/hematite transition [5]. Another example of the crucial role of surface energy can be found for the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> transition [6]: at 800 K, the transition alumina is thermodynamically stable compared to the high-temperature

alumina phase, if its surface area is greater than 75 m<sup>2</sup>/g. Nevertheless, no experimental studies have yet demonstrated the effects of crystallite morphology (i.e. taking into account both size and shape) on phase transition temperatures.

To achieve this goal, we focus on the boehmite/ $\gamma$ -alumina ( $\gamma$ -AlOOH/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) transformation. Alumina is among the most widely used oxide materials. The  $\gamma$ -alumina is of particular interest due to its importance in the preparation of controlled porosity catalysts with enhanced textural, surface and mechanical properties [1,7,8]. This oxide is typically obtained by calcinating aluminum oxyhydroxides (Al<sub>2</sub>O<sub>3</sub>·xH<sub>2</sub>O), among which boehmite ( $\gamma$ -AlOOH) is the most important precursor material. Boehmite is easily obtained via aqueous precipitation or the sol-gel route [8,9]. To improve the catalyst support properties, the boehmite crystallite size, shape, sample porosity, and surface area are optimized through the preparation conditions. Numerous advanced methods have been developed to prepare boehmite particles with various shapes and to recover after activation the final material with the desired surface properties [10,11]. During the final calcination step,  $\gamma$ -AlOOH is converted into the desired alumina phase. Because the oxygen sublattice of the boehmite becomes cubic after the departure of the bulk water molecules [12], its decomposition into the transition alumina involves only short-range rearrangements of the atoms in the crystal structure, without significant alterations of the crystallite shape. This type of transformation is referred to

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as topotactic [13] and requires little energy. Consequently, precise control over the calcination process can maintain the boehmite textural properties designed during the synthesis step. As reported in the literature [14,15], this transformation spreads over a wide temperature range from 380 to 650 °C. The transformation temperature and thermal stability reportedly depend on the boehmite crystallite size [16]. Several works [14,16,17] have indicated that the boehmite transformation temperature into  $\gamma$ -alumina increases with increasing boehmite platelet thickness. Bokhimi et al. [14] correlated the transformation temperature to the crystallite thickness and reported a transformation temperature ranging between 380 and 530 °C for crystallites having thicknesses of 1.1 nm and 26.3 nm, respectively. These experimental results are explained by the bulk d(OH–O) bending distance between the AlOOH sheets, which decreases for large crystallites. As this distance decreases, its energy increases causing an increase in the transition temperature. More recently, it has been shown [18] that platelet- and rod-shaped boehmite nanoparticles lead to different phase transformation sequences between 600 and 1100 °C: for the same calcination temperature, the surface and catalytic properties depend on the initial boehmite morphology. Moreover, the thermal stability of  $\gamma$ -alumina is strongly correlated with the particles morphology, inherited from the boehmite one: for instance, it has been suggested that the presence of penta-coordinated Al<sup>3+</sup> sites, only formed on the (100) surface [19], is detrimental to  $\gamma$ -alumina stability [20]. Finally, the surface energy of the different exposed surface, depending on the operating conditions such as temperature [15,19] and water pressure [21,22] is a key parameter in nanoparticles phase transition.

In the present paper, we prepared a set of boehmite samples of varying size and shape. Kinetic simulations of the non-isothermal thermogravimetric analyses (TGA) of these samples allowed to isolate the reaction of interest, the boehmite transformation into alumina (as follows) and its starting temperature ( $T_i$ ) to be precisely determined:



Strong variations of the starting temperature are found according to crystallite morphology. To rationalize these observations, these temperatures were calculated by developing a model based on the thermodynamic data found in the literature that considers the surface energy contribution to the phase transition temperature.

## 2. Experimental section

### 2.1. Sample preparation

The initial starting material was synthesized in an aqueous medium by precipitating aluminum nitrate ( $\text{Al}(\text{NO}_3)_3$ , 0.1 mol L<sup>-1</sup>) with sodium hydroxide (NaOH, 1 mol L<sup>-1</sup>) at room temperature and aging the precipitate at 100 °C for one week as reported by Jolivet et al. [23] The final pH was 4.5. The suspension was then washed via centrifugation and dried overnight at 80 °C. This boehmite synthesized under acid conditions was denoted starting material A.

The second starting material, denoted N (neutral condition), was obtained using the same method but with a final pH of 6.5, leading to a different crystallite shape.

The third starting material was an industrially precipitated boehmite provided by a catalyst manufacturer (Axens SA, Rueil-Malmaison, France) that was obtained at a basic pH of approximately 9 by neutralizing an aqueous solution of aluminum sulfate with a sodium aluminate solution as reported by Morgado et al. [24] This boehmite synthesized under basic conditions was denoted starting material B.

The final starting material was synthesized via the hydrolysis of an aluminum alkoxide. A large excess ( $\text{H}_2\text{O}/\text{Al} \approx 100$ ) of hot (85 °C) distilled water was rapidly poured into aluminum tri sec butoxide,  $\text{Al}(\text{OC}_4\text{H}_9)_3$  under stirring and maintained for 15 min. The obtained sol was dried at 80 °C, then ground to yield a boehmite referenced as SG.

To modify the crystallite size, hydrothermal treatment of the A, N, B and SG starting materials was applied over times ranging from 3 to 55 h at either 150 or 180 °C under stirring. The suspension concentrations were approximately 100 g L<sup>-1</sup>, with no adjustment of the pH. The resulting suspensions were dried in an oven at 80 °C for 24 h. The samples were identified according to the following notation: X (X = starting material, A, N, B or SG) – Y (hydrothermal treatment period in h) – Z (hydrothermal treatment temperature in °C). For example, B-6-180 indicates a hydrothermal treatment of the B sample for 6 h at 180 °C. The as-obtained samples (13) were then characterized in terms of phase purity and crystallite size and shape.

### 2.2. Sample characterization

The crystal phase was investigated by Powder X-Ray Diffraction (PXRD). Data were collected on a PANalytical X'Pert Pro  $\theta$ - $\theta$  diffractometer in Bragg–Brentano geometry, using filtered Cu K $\alpha$  radiation and a graphite secondary-beam monochromator. Diffraction intensities were measured at room temperature by scanning from 2° to 72° with a step size of 0.05° ( $2\theta$ ).

TEM observations were performed on a JEOL2100F-FEG (Field Emission Gun) microscope. A small amount of powder was dispersed in water using an ultrasound bath. Then a droplet was deposited on a carbon-coated grid and allowed to dry.

The nitrogen adsorption-desorption isotherms were collected at 77 K using an adsorption analyser Micromeritics ASAP 2420. Before analysis the samples were outgassed in vacuum for 6 h at 110 °C. Specific surface area (SSA) was determined, from adsorption isotherm, by the BET method. The relative error associated with adsorption-desorption analyses was estimated to be 5% for the SSA.

Thermogravimetric analyses (TGA) were performed with a Mettler Toledo thermo balance using ca. 16 mg of powder. These experiments were done under 25 mL min<sup>-1</sup> air gas flow. Water concentration in the air flow was less than 20 ppm.

## 3. Results and discussion

### 3.1. Crystallite size and shape of the materials

The set of boehmite particles with controlled morphologies was prepared as explained in the Experimental Section. Briefly, three samples have been prepared by aqueous precipitation in acidic (A), neutral (N) and basic (B) media and one by sol-gel (SG) method. For these starting materials, hydrothermal treatments have been performed. The recovered samples are labeled with the following notation: X (X = starting material) – Y (hydrothermal treatment period in h) – Z (hydrothermal treatment temperature in °C). For example, B-6-180 indicates a hydrothermal treatment of the B sample for 6 h at 180 °C.

The crystalline phase was investigated via PXRD with boehmite as the only crystalline phase detected in the samples (see the Supporting Information Figs. ESI 1, 2, and 3). The main features of the boehmite samples are summarized in Table 1 for the starting materials and in Table 2 for the materials after hydrothermal treatment.

Regarding the shape, the boehmite crystallites are often considered to exhibit two main surface types [25]: the basal (010) surface resulting from the splitting of hydrogen bonds between the

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