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ScienceDirect
Ceramics International 34 (2008) 1971–1974
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Synthesis of platelet-shaped boehmite and γ-alumina nanoparticles via an aqueous route

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Received 4 June 2007; received in revised form 18 June 2007; accepted 16 July 2007
Available online 19 August 2007

Abstract

Synthesis and characterization of γ-boehmite and γ-alumina nanoparticles with a platelet shape are described.

First an environmentally friendly hydrothermal synthesis method is applied to form nanostructured γ-boehmite, starting from the hydrolysis of aluminium alkoxide. Subsequently γ-alumina nanopowder is obtained after calcination of the γ-boehmite at 600 °C.

Transmission electron microscopy (TEM) reveals that the particle size of γ-AlOOH and γ-Al_2O_3 lies between 30 and 80 nm. Furthermore, the nanopowders have been characterized by photon correlation spectroscopy (PCS) and X-ray diffractometry (XRD).

Keywords: B. Electron microscopy; B. Platelets; γ-Al_2O_3; Hydrothermal synthesis

1. Introduction

Alumina is a low-cost material used in many domains like catalysis, electronics and thin-film coatings [1,2]. Transition aluminas include a series of metastable forms that exist in an extended temperature range, but all of them lead to α-alumina by calcining at high temperatures. Transition aluminas, and γ-alumina in particular, having a high specific surface area, are widely used as adsorbents, catalysts and catalyst supports [3–5]. Aluminium oxide–hydroxide, γ-AlOOH (boehmite) is used as the starting material for the preparation of γ-alumina. Consequently, its dehydration has been the subject of many previous studies [6,7]. Dehydration of γ-boehmite to form γ-alumina and the further transformations through the transition alumina series involve short-range rearrangements of atoms only in the crystal structure. The conversions are topotactic and require only a small energy. The temperatures at which they are observed are variable and depend on the crystallinity of the γ-boehmite precursor as well as on the thermal treatment conditions. Therefore, the characteristics of γ-alumina such as specific surface area and porosity are strongly affected by the morphology of the boehmite precursor [8].

Numerous methods for synthesis of γ-AlOOH nanopowder have been reported in literature, such as sol–gel synthesis [9], spray pyrolysis [10] and hydrothermal treatment [11].

Recent works report on the hydrothermal synthesis of γ-boehmite nanoplatelets [12–15]; however, these methods either make use of alcohol as the reaction medium or use neutralizing agents such as ammonia and precipitating agents such as urea.

The objective of the work reported herein, is to synthesize γ-AlOOH and γ-Al_2O_3 nanoparticles with well-defined and regular platelet shape by means of a hydrothermal treatment without any additives.

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0272-8842/$34.00
doi:10.1016/j.ceramint.2007.07.022

2. Experimental

2.1. Sample preparation

The γ-AlOOH platelets are synthesized by adding the aluminium precursor such as aluminium isopropoxide (0.5 M Al) (AIP) ($Al(OC_3H_7)_3$ 98+%, Aldrich), to 50 ml distilled water followed by vigorously stirring during 1 h at 80 °C. Subsequently, the mixture is poured into a 125-ml Teflon liner (75% filled), which fits into a stainless steel pressure vessel. The vessel is placed in an oven for 12, 24, 48 and 96 h at 200 °C and then allowed to cool down to room temperature. The suspension is filtered and washed with distilled water several times and subsequently dried in an oven at 60 °C in air. Finally, the γ-AlOOH is calcined in dry air at 600 °C (heating rate 10 °C/min) for 15 min yielding the γ-Al_2O_3 nanoplatelets.

2.2. Characterization

XRD measurements, performed on a Siemens D-5000 diffractometer with Cu $K\alpha_1$ radiation, are used to determine the crystalline phase. The morphology of the nanostructured γ-boehmite and γ-alumina material is investigated with a Philips CM12 transmission electron microscopy (TEM) using an accelerating voltage of 120 kV. For this analysis, the powder is dispersed in methanol, dropped onto a Formvar/carbon 200 Mesh Cu coated grid and dried at room temperature.

TGA experiments (Du Pont Instruments 951 Thermogravimetric analyzer) are performed on a ∼30 mg sample from room temperature to 900 °C in a flowing atmosphere (100 ml/min) of dry air at a heating rate of 10 °C/min.

Photon correlation spectroscopy (PCS) was used to measure the mean particle size and particle size distribution. The analysis of γ-AlOOH and γ-Al_2O_3 suspensions was performed on a ZetaPlus with BI-PALS option and BI-MAS particle sizing option (Brookhaven Instruments Corporation). The samples for PCS analysis were prepared in distilled water with no addition of dispersants; stable suspensions were obtained.

3. Results and discussion

The calcination temperature of 600 °C for the conversion of γ-AlOOH into γ-Al_2O_3 is derived from the TGA curve, as reported in Fig. 1.

The dehydration of the aluminium oxide–hydroxide appears to occur in three steps with a total weight loss of approximately 15% up to 600 °C, followed by a continuous mass loss of about 1% up to 900 °C. These kinds of curves have already been reported in literature [16]. The first two steps can be attributed to the desorption of physically adsorbed water, the third step to the conversion of γ-AlOOH into γ-Al_2O_3 and the weight loss at a temperature above 600 °C is associated with the elimination of residual hydroxyls.

Fig. 2 shows the X-ray diffraction patterns of the samples after (a) hydrothermal treatment and (b) further calcination at 600 °C for 15 min.

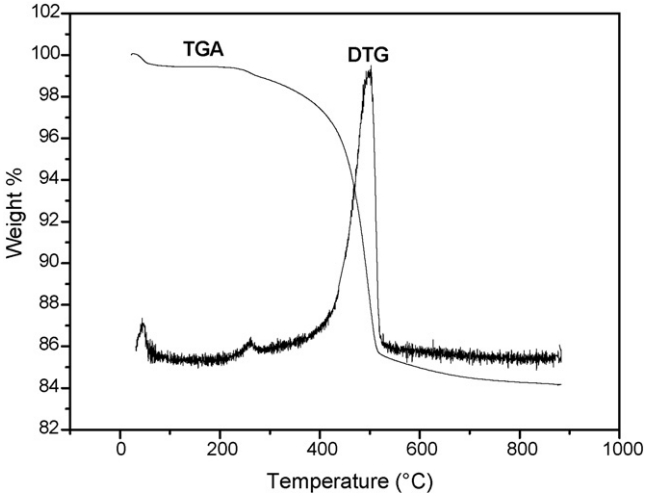

Fig. 1. TGA and DTG curves of the dehydration of boehmite (heating rate 10 °C/min).

As can be seen from Fig. 2a all of the diffraction peaks can be indexed to orthorhombic γ-AlOOH. The XRD pattern shown in Fig. 2b can be indexed to face-centered cubic γ-Al_2O_3.

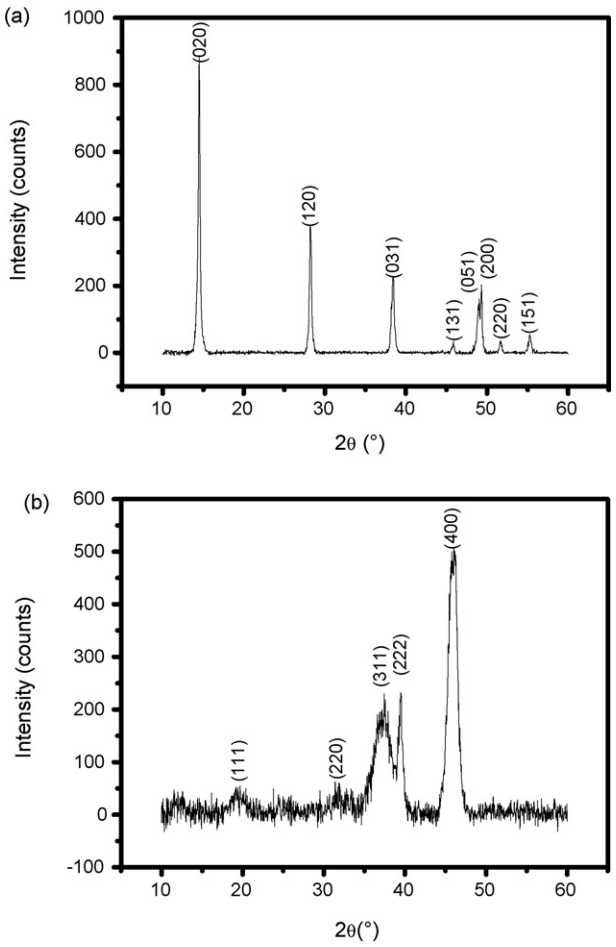

Fig. 2. XRD pattern of (a) the sample after hydrothermal treatment (γ-AlOOH JCPDS cards no. 21-1307); (b) the sample after calcination at 600 °C for 15 min (γ-Al_2O_3 JCPDS cards no. 29-0063).

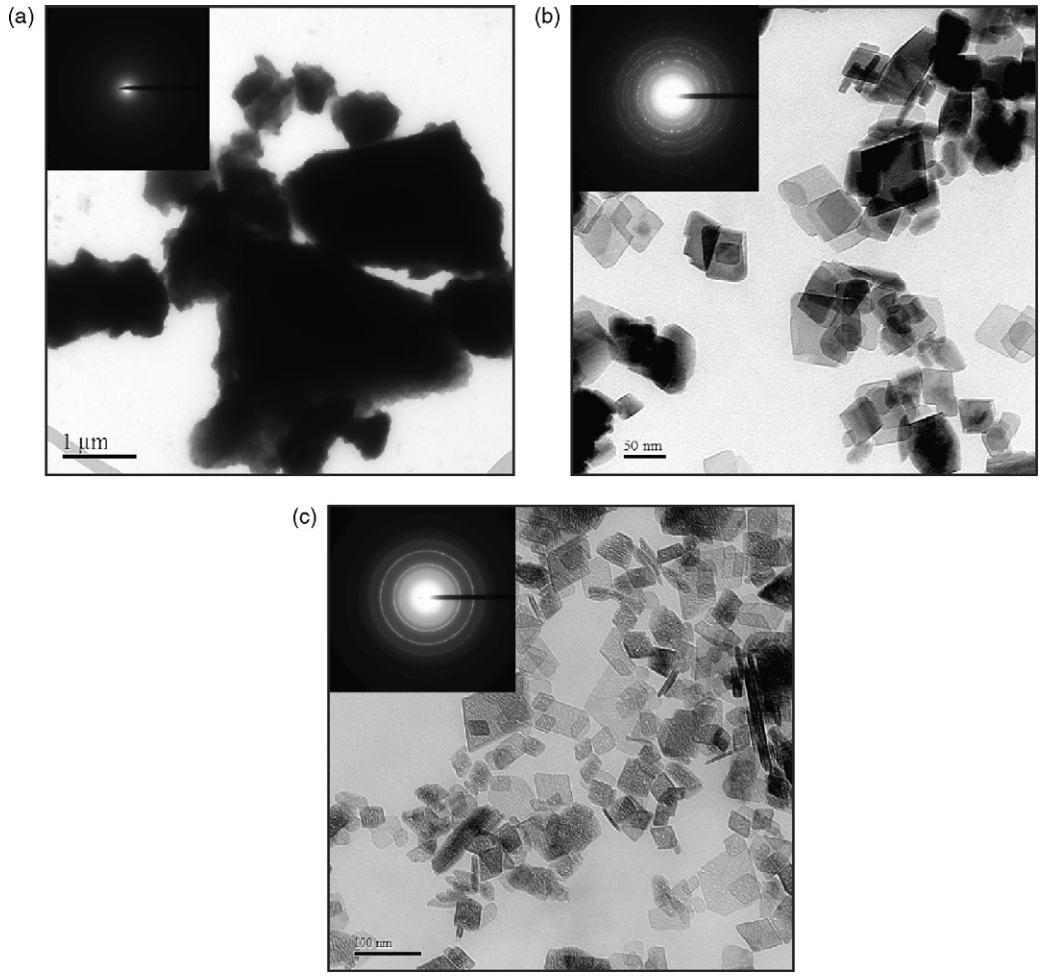

Fig. 3. TEM micrographs of (a) fresh γ-AlOOH sample without hydrothermal treatment; (b) γ-AlOOH sample obtained after hydrothermal treatment. Inset: electron diffraction pattern of γ-boehmite; (c) γ-Al_2O_3 powder calcined at 600 °C for 15 min. Inset: electron diffraction pattern of gamma-alumina.

According to the well-known Yoldas process [17,18], γ-boehmite can be obtained by introducing an aluminium alkoxide in an excess of distilled water under vigorous stirring at 80 °C. However, no platelets of γ-AlOOH are obtained according to this synthesis method. Indeed, the TEM micrograph of the fresh γ-AlOOH sample without hydrothermal treatment (Fig. 3a) did not show platelet particles; instead the particles are irregularly shaped.

On the contrary, after hydrothermal treatment at 200 °C during 24 h and without the use of any additives, platelets of

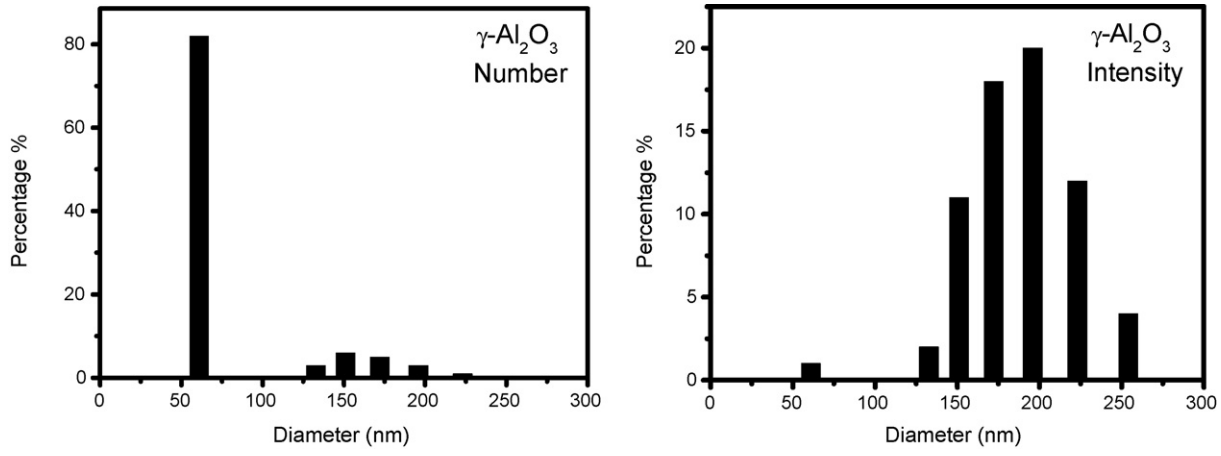

Fig. 4. Size distribution of an aqueous dispersion of γ-Al_2O_3 particles without the use of dispersant as determined by PCS.

γ-AlOOH are obtained. The morphology of the γ-AlOOH sample and the γ-Al_2O_3 nanopowder, yielded after calcination of γ-AlOOH, is analyzed by transmission electron microscopy images. TEM micrographs reveal that both the γ-AlOOH sample (Fig. 3b) and the γ-Al_2O_3 sample (Fig. 3c) consist of a similar platelet shape.

This is in accordance with the work of Lippens et al. [19], who showed that during the solid transformation of γ-AlOOH into γ-Al_2O_3 topotaxy occurs: each monocrystal of γ-AlOOH transforms into a small particle of γ-Al_2O_3, conserving its overall original shape.

The images clearly indicate that the γ-AlOOH and the γ-Al_2O_3 platelets have a particle size varying from 30 to 80 nm, based on length measurements of 40 nanoplatelets.

A variation of the hydrothermal reaction time from 12 to 96 h did not show a significant influence on the morphology and size of the γ-AlOOH nanopowder.

The particle size distribution of γ-Al_2O_3, measured by PCS, based on number and intensity is shown in Fig. 4.

Although it is known that the calculation of the mean particle diameter in PCS is based on a model in which the particles have a spherical shape (the powders in this study have a platelet shape with similar aspect ratio), this technique is used to have a notion about the sizes. According to PCS results (based on number), more than 80% of the γ-Al_2O_3 particles have a mean diameter of about 60–70 nm. Furthermore, these data are well reproducible and it can be concluded from the experiments that the γ-Al_2O_3 nanopowder has a low agglomeration degree.

4. Conclusions

In summary, an additive-free and entirely aqueous method is successfully applied for the synthesis of γ-boehmite and γ-alumina nanoparticles with a well-defined and regular platelet shape. First nanocrystalline γ-AlOOH platelets were prepared under hydrothermal conditions, after hydrolysis of aluminium isopropoxide. Finally, γ-Al_2O_3 platelets were obtained after thermal treatment at 600 °C. This approach offers a new route to synthesize γ-AlOOH and γ-Al_2O_3 nanopowders with diameter ranging from 30 to 80 nm and with low agglomeration degree.

Acknowledgment

M.K. Van Bael is a postdoctoral fellow of the Fund for Scientific Research of Flanders (FWO Vlaanderen).

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