Boehmite Nanometric With High Surface Area Synthesized from a Microwaves Hydrothermal Method


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ABSTRACT

Nanocrystalline boehmite (γ-AlOOH) is a cost-effective material for the production of γ-Al₂O₃ finding many industrial applications as catalyst or catalyst support, membranes and adsorbents. This paper reports the synthesis of Boehmite (γ-AlO(OH)) nanoparticles by a hydrothermal microwave method (MH). The precursor solution was placed in a sealed teflon autoclave and placed in adapted microwave. Finally, the reaction system was heat treated at 180°C by 180 minutes. The sample in powder form were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and adsorption of nitrogen (BET and BJH methods). The diffraction lines of XRD revealed the presence of a family composed of alumina, the boehmite. In morphologic analysis of boehmite sample was possible observe the formation of particles agglomerates with irregular morphology composed by nanosized particles. The surface area value of the boehmite sample synthesized was about 226 m²·g⁻¹.

Keywords: microwaves, hydrothermal, boehmite, high surface area

1 INTRODUCTION

Boehmite is a monohidroxi aluminium oxide (γ-AlO(OH)). Micropcrystalline boehmites has found important applications in the preparation of catalysts, coatings on various substrates, membranes, etc. Moreover, various forms of alumina are developed by thermal treatment of boehmite. Because these applications, many researchers focused on the relation between the synthesis of boehmite and its chemical and physical properties [1]. Nanocrystalline boehmite (γ-AlO(OH)) is a cost-effective material for the production of γ-Al₂O₃ finding many industrial applications as catalyst or catalyst support, membranes and adsorbents [2].

Boehmites have been produced by different methods like a conventional-hydrothermal (CH) [1,3], a quick, simple route was established by direct reaction between activated aluminum and hot water [4], precipitation method [2], spray pyrolysis [5] and hydrothermal hot-press method [6]. The conventional hydrothermal method is often used due to its simplicity, allowing the control of grain size, morphology and degree of crystallinity by easy changes in the experimental procedure. A variation of this method, microwave hydrothermal synthesis (MH), has been shown to be superior to conventional method at least in three aspects, i.e., the MH process leads to very rapid heating to temperature of treatment, extremely rapid kinetics of crystallization by one-to-two orders of magnitude compared to (CH) process and new phases [7]. The ability of microwaves to couple energy directly to the material is the primary advantage of microwave processing as compared to conventional techniques. The volumetric heating ability of microwaves allows for more rapid, uniform heating, decreased processing time, and often enhanced material properties. The application of microwave heating to the manufacturing of ceramic and polymeric materials has the potential to improve the quality and reduce manufacturing costs [8]. Because of these advantages of using microwave energy, various ceramic powders were obtained by hydrothermal microwave method using low temperature and short time, i.e., recently, Moura et al [9] synthesized CuO plates at 130°C for 30 minutes without any surfactant or templates. Kejson et al [10] reported the formation and the growth of urchin-nanostructures by the addition of polyethylene glycol (PEG). The work temperature was 120°C for 1 hour. The surface area of CuO was 170,5m²·g⁻¹ the obtained powder is a promising candidate for potential application in nanocatalysis. Herein, we reported a simple method for the synthesis of Boehmite (γ-AlO(OH)) nanoparticles in the aqueous solution of Al(NO₃)₃·9H₂O and NH₃·H₂O by the hydrothermal microwaves method.

2 EXPERIMENTAL

2.1 Synthesis of the Boehmite (γ-AlO(OH)) in nanoparticles

In synthesis methodology of the boehmite was employing the precursor 2.5x10⁻² mol of Al(NO₃)₃·9H₂O (99% purity) and NH₃·H₂O. Initially the aluminum nitrate salt was dissolved in 100mL under constant stirring at room temperature by 10 minutes. In the solution was added 27mL of NH₃·H₂O. In following 23mL of deionized water was added and finally the obtained solution was submitted a constant stirring at room temperature again by 15 minutes. The final precursor solution presented pH = 11. The final
solution has been transferred for into a sealed teflon autoclave and placed in a adapted domestic microwave (2.45GHz, maximum power 800 Watts). The reaction system has been treated at 180°C by 3 hours, with a heating rate 20°C/minute. The autogenous pressure in the sealed autoclave was stabilized at 12 bar. The autoclave oven was cooled to room temperature naturally. The resulting white precipitated was collected, washed with deionized water several times until pH = 7, and thus, the final sample in powder form were dried in an oven at 120°C by 24 hours.

2.2 Characterizations

The obtained sample in powder form was characterized by means X-ray diffraction (XRD) technique using a SHIMADZU equipment (XRD 6000 model), with Cu-Kα radiation (λ = 1.5418 Å) in the range from 5 to 85° with 0.02°/min. The crystallite size of the Boehmite (γ-AlO(OH)) was calculated using the Scherrer equation (1) [11]:

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]  

(1)

Where \( \lambda \) is the wavelength of X-ray, \( \theta \) is the Bragg angle and \( \beta \) is the pure full width of the diffraction line of maximum intensity.

The morphology of the particles agglomerated of the synthesized sample by means MH method was observed using a Field-Emission Scanning Electronic Microscopy (FEG-SEM Philips XL30).

The textural properties of sample such as surface area, pore size and pore volume were determined by adsorption-desorption of nitrogen technique. This analysis has been performed in apparatus (ASAP 2000 - Micrometrics). Prior to measurements samples were degassed at 500°C for 5 hours and 10⁻³torr. The Surface Area value, \( S_{\text{BET}} \), was calculated by means BET method [12].

From the data of surface area was determined the average particle size used the following equation (2) [13].

\[
D_{\text{BET}} = \frac{6}{D_t S_{\text{BET}}}
\]  

(2)

Where \( D_{\text{BET}} \) is an equivalent spherical diameter (nm), \( D_t \) is theoretical density (g.cm⁻³) and \( S_{\text{BET}} \) is a surface area (m².g⁻¹).

3 RESULTS AND DISCUSSIONS

Figure 1 shows the XRD pattern of the synthesized sample by means hydrothermal microwave method at 180°C by 180 minutes.

In an attempt to obtain the zinc aluminate spinel, Chen et al. [14] obtained the phase boehmite and little amount of ZnO by conventional hydrothermal method at 185°C/1200 minutes. In another research Mazloumi et al. [3] prepared rosette-like boehmite nanostructures via an elementary hydrothermal process at 200°C by 24h (1440 minutes) under autogenous pressure control. In this work, was possible to obtain boehmite at 180°C in only 180 minutes of reaction time; is short time when compared with these authors [1,3,15]. The accelerates kinetics used by microwave hydrothermal method can be the explication for this case [7]. Músic et al. [15] obtained boehmite at a temperature of 160°C, from a time of 5h (300 minutes), before this time they detected the presence of alpha alumina and bayerite over the obtained structure. Li et al. [6] synthesized boehmite by means hot-press method at 180°C during 180 minutes at 80MPa (800 bar). In this work the maximum pressure observed was 12 bar.

The crystallite size calculated by equation (1) was 8.09 nm. This result is close to the crystallite size obtained by an conventional hydrothermal process at 200°C for 24 hours (8.0 nm) [3]. Músic et al. [15] obtained boehmite by conventional hydrothermal process at 160°C with reaction time of 10h, pH = 11.72 and crystallite size in (020) direction was 12.8 nm. This crystallite size is bigger when paralleled with values obtained this work due at reaction time is longer, which can lead to particle growth.

Figure 2 and 3 shows micrographs obtained by SEM for boehmite sample (γ-AlO(OH)) composed by nanoparticles. The micrographs presented in Figure 2 and 3 shows imagens with amplification of 100.000X e 150.000X, respectively.
Figure 2: Image of SEM for boehmite sample (γ-AlO(OH)) composed by nanoparticles synthesized by means MH. Amplification of 100.000X.

Figure 3: Image of SEM for boehmite sample (γ-AlO(OH)) composed by nanoparticles synthesized by means MH. Amplification of 150.000X.

It is possible observe in the micrographs obtained by SEM, evident characteristic of particles with nano size of the boehmite sample in powder form obtained by hydrothermal method. Also it is possible observe agglomerated nanoparticles which lead to porous structure formation. These agglomerated are easily dispersions, possibly interconnected by means Van Der Walls forces. According to the micrographs it is possible to observe that the nanoparticles of the sample synthesized form spherical agglomerates. Thus, it can be stated that the unitary nanoparticles have a strong tendency to a state of agglomeration (nanoparticle size – 8.09nm). Micrograph of a boehmite sample obtained in work of Mazloumi et al. [3] shows the rosette-like nanostructures form, and micrograph of SEM of boehmite sample of the work of Mahmood et al. [4] nanofibers form, that’s an evidence the influence of the method of preparation of the boehmite as well of the type of precursors used over the final morphological characteristics of the powder obtained.

Table 1 shows values for surface area, particle size, crystallite size and ratio of particle size and crystallite size ($D_{\text{BET}}/D_{\text{Drx}}$) of boehmite sample obtained by MH.

<table>
<thead>
<tr>
<th>Surface area ($m^2\cdot g^{-1}$)</th>
<th>Particle Size $D_{\text{BET}}$ (nm)</th>
<th>Crystallite Size $D_{\text{Drx}}$ (nm)</th>
<th>$D_{\text{BET}}/D_{\text{Drx}}$</th>
</tr>
</thead>
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<tr>
<td>226.30</td>
<td>8.636</td>
<td>8.09</td>
<td>1.07</td>
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Table 1: Values for surface area, particle size, crystallite size and ratio of the particle size and crystallite size ($D_{\text{BET}}/D_{\text{Drx}}$).

The nanoparticles of boehmite sample obtained in this work presents surface area value of 226.30$g/m^2$, this result is greater than the result presented by Mazloumi et al [3] which obtained rosette-like boehmite nanoparticles powders that shows 143.08 $m^2\cdot g^{-1}$ and lower than that Músic et al [1] γ-AlO(OH) nanofibers thats show surface area of 246 $m^2\cdot g^{-1}$. The smaller surface area value 143.08 $m^2\cdot g^{-1}$ [3] can be associated with long reaction time and higher temperature; these factors lead particles to grow [1]. In another work Cai et al. [16] synthesized γ-AlO(OH) hollow spheres by a hydrothermal precipitation reaction of potassium aluminum sulfate in the presence of urea in pure water. The autoclave was maintained at 180°C by 180 minutes, without microwaves exposition, and the BET surface area value was 93.6 $m^2\cdot g^{-1}$. This latest research reports the synthesis of a sample of boehmite using the same values of temperature time of reaction used in this work, but presents as result lower surface area value.

According to the relationship $D_{\text{BET}}/D_{\text{Drx}}$, it was found that the powder has a ratio close to unity (1.07), showing that the particles are nearly single crystal, also known as monocystal, ie, the particle size is equivalent to the size of crystallites.

The isotherm shown in Figure 4 can be classified as type IV according to IUPAC classification [17] that indicates that this powder can be classified as mesoporous material (average pore diameter between 2-50 nm) associated with the presence of micropores. The hysteresis loop presented in this isotherm, generally between 0.45 and 0.95 P/Po, is of type H3, this type of hysteresis reveals the presence of mesopores that in general are associated with aggregates non-rigid particles. This type of hysteresis reveals the presence of pores with the following morphology: in wedges form, cones and/or parallel cards [18].
Figure 4: Isotherm of adsorption-desorption of N$_2$ for boehmite sample synthesized by hydrothermal method assisted by microwave.

Table 2 shows the values for pore volume (Vp) and average pore diameter (Dp), determined by BJH method for boehmite sample synthesized by hydrothermal method assisted by microwave.

<table>
<thead>
<tr>
<th>Pore volume (cm$^3$.g$^{-1}$)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.438</td>
<td>6.68</td>
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</table>

Table 2: Values for pore volume (Vp) and average pore diameter (Dp) of the boehmite sample synthesized.

According to Flory [19], the adsorption of nitrogen can be applied to evaluate the porous materials whose pore size diameters between 2-50nm are classified as mesopores. Based on this information and referring to Table 2 it is possible note that boehmite sample obtained in this work has a characteristic of mesoporous material with pores very near the upper limit of the micropores (2nm).

4 CONCLUSION

The hydrothermal method assisted by microwave was effective for the synthesis of boehmite using reaction conditions far milder than the values of time found in the literature to obtain this same material. The boehmite sample synthesized in this work presented particles with nanometer dimensions and high surface area value, such values were following: 8.09 nm and 226m$^2$/g, respectively. The synthesis method used in this work demonstrates be a promising candidate to obtain of boehmite in short time (180 minutes) for application in nanocatalysis.