Research Article
Effects of Different Raw Materials in the Synthesis of Boehmite and $\gamma$- and $\alpha$-Alumina

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1. Introduction

Alumina polymorphs are mainly prepared by thermal decomposition of precursors, which are generally produced by precipitation of aluminum oxyhydroxides from solution of reagent grade aluminum salts. Depending on the synthesis conditions, different alumina polymorphs are obtained, which differ in chemical composition and crystal structure [1]. Boehmite, $\gamma$-AlOOH, is one of the most popular precursors of alumina, and its transformation into $\alpha$-Al$_2$O$_3$ involves a complex sequence of transitional alumina polymorphs, which, among others, depends strongly on the chemical synthesis routes, the degree of crystallinity of the precursor, the presence of impurities, the alkalinity, and so forth [2–8]. Natural boehmite occurs in the orthorhombic crystal structure while synthetic boehmite is amorphous or nanocrystalline depending on the experimental conditions [9]. Synthetic boehmite is frequently developed in order to produce pure electronic grade Al$_2$O$_3$ ceramics and components. Boehmite transforms into stable $\alpha$-Al$_2$O$_3$ via the sequence AlOOH $\rightarrow$ $\gamma$ $\rightarrow$ $\delta$ $\rightarrow$ $\theta$ $\rightarrow$ $\alpha$-Al$_2$O$_3$ [5, 9].

Recently, nanostructured alumina polymorphs were obtained by the present authors, from an aluminum solid waste [10, 11]. This fine powdered solid waste can be described as a complex and heterogeneous blend of several components, among others: metallic aluminum, aluminum nitride, corundum, spinel, quartz, calcite, and iron oxide, along with other minor oxides and salts [12]. The process consisted of the formation of the precursor, $\gamma$-AlOOH, by a precipitation method, in which NaOH solution was used as the alkalizing agent [13]. The thermal treatment at different temperatures of the so-obtained boehmite led to the formation of different polymorphs of Al$_2$O$_3$, by means of topotactic reactions.

The present work describes the application of the above procedure to the synthesis of two polymorphs of alumina: the metastable $\gamma$-Al$_2$O$_3$ and the stable $\alpha$-Al$_2$O$_3$, from different raw materials. Thus, the aim was to evaluate their effect on the physical and chemical characteristics of boehmite and $\gamma$-
and α-alumina. Two raw materials were used as aluminum source: the pure reagent AlCl$_3$·6H$_2$O and the aluminum waste previously mentioned. Also two different alkalinizing agents were tested, NaOH and n-butylamine, in order to evaluate the effect of using strong or weak alkaline solutions.

## 2. Experimental

### 2.1. Reagent and Synthesis.

The boehmite produced in this study was based on the process described by Gonzalo-Delgado et al. (2011) [14]. Two aluminum raw materials were used, namely, an aluminum waste from the scrap milling process in the tertiary aluminum industry [12] and a reagent grade AlCl$_3$·6H$_2$O (Panreac). The waste consisted principally of 31.2% Al metal, 20.0% Al$_2$O$_3$ (corundum), 15.0% MgAl$_2$O$_4$ (spinel), 8.4% AlN, 8.0% SiO$_2$ (quartz), 8.2% CaCO$_3$ (calcite), 1.8% Fe$_2$O$_3$ (hematite), 1.5% TiO$_2$, 1.5% chloride (Na/K), 0.7% Al$_2$S$_3$, and other minor metal oxides. The starting solution of Al$^{3+}$ from the aluminum waste was prepared by dissolving AlCl$_3$·6H$_2$O in distilled water. A solution of similar concentration was prepared by dissolving AlCl$_3$·6H$_2$O in distilled water. The initial pH values of the aluminum solutions ranged between 3.89 and 3.98. Aliquots of 400 mL of the corresponding Al$^{3+}$ solutions were subjected to an alkalinizing process by dropwise addition of two different alkalizing agents up to pH 8: a 1 M solution of NaOH (Panreac, reagent grade) or a 1 M solution of n-butylamine (Aldrich, >99%). In all the cases, a colloidal suspension started to appear at low pH values. The massive precipitation took place at different pH values (5.7–6.3) depending on both the starting Al$^{3+}$ solution and the alkalinizing agent. Thus, when n-butylamine was used the precipitation occurred to a lower pH value than for NaOH. At these values of pH the instantaneous precipitation of the aluminum hydroxide occurs, according to the following general equation.

$$\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \quad (1)$$

As the pH value increases the evolution of inter/intraparticle aggregates of the aluminum hydroxide takes place and aluminum oxyhydroxide is formed.

$$\text{Al(OH)}_3 + \text{OH}^- \rightarrow \text{AlOOH} + 2\text{H}_2\text{O} \quad (2)$$

Figure 1 shows the pH curves for the four samples; the massive precipitation is marked as a grey zone. Images of the formation stage of the colloidal suspension and the massive precipitation stage are also included. Alkalinization was stopped to pH 8, because this is the value in which boehmite is formed. Values higher than 8 favor the formation of bayerite, α-Al(OH)$_3$, and nordstrandite, Al(OH)$_3$ [15, 16]. As observed in this figure, the amount of alkalinizing agent used in the precipitation process is higher when the aluminum source is the waste, due to the presence of other elements such as iron. The suspensions were kept stirring for 24 h for aging. Then the solid was filtered (Figure 2), washed three times with distilled water and once with ethanol, dried at 60°C for 48 h, and crushed in a mortar to get a fine powder. From hereinafter, AlNa and AlB correspond to alumina precursors obtained using AlCl$_3$·6H$_2$O as the source of aluminum and NaOH and n-butylamine as the alkalinizing agent, respectively, and AWNa and AWB correspond to alumina precursors obtained using the aluminum waste as the source of aluminum and NaOH and n-butylamine as the alkalinizing agent, respectively.

The so-obtained alumina precursors were subjected to calcinations under air atmosphere to 600°C and 1400°C, into a muffle furnace (Thermoconcept HT0417) for 7 h and a heating rate of 10°C min$^{-1}$, in order to get γ- and α-Al$_2$O$_3$. The products obtained at 600°C are named as γ-AlNa, γ-AlB, γ-AWNa, and γ-AWB and those obtained at 1400°C as α-AlNa, α-AlB, α-AWNa, and α-AWB, in relation to the nomenclature used for the corresponding precursor.

### 2.2. Techniques.

Samples were characterised as follows. Powder X-ray diffraction (XRD) was carried out using a
3. Results and Discussion

The XRD patterns of the alumina precursors obtained from alkalization of Al\(^{3+}\) solutions are shown in Figure 3. All of them exhibit the characteristic XRD profile of boehmite, γ-AlOOH, according to the reference file JCPDS 01-088-2112 (2θ value for the hkl index 120 = 28.13°). Nevertheless, several differences are observed. The samples obtained from waste exhibit lower crystallinity than those obtained from pure reagent. The four hkl indexes, 020, 120, 031, and 051, are well defined for samples AlNa and AlB, but the first one is scarcely observed in samples AWNa and AWB. The absence of 020 reflection is generally observed for boehmites with very low crystallite size, such as those obtained by “sol-gel” methods [17]. The hkl index, 120, of boehmite appears centered at a higher 2θ value for samples obtained from waste (~28.2°) than for samples obtained from pure aluminum chloride (27.3–27.5°). This reflection was used to determine the crystallite size by the Scherrer equation [18]. The results are shown in Table 1. All samples present crystallite size smaller than 3 nm; this indicates that all the boehmites are nanocrystalline. Similar crystallite sizes are reported by Bokhimi et al. [17] for boehmites obtained at low temperature from AlCl\(_3\)-6H\(_2\)O and NH\(_4\)OH as the alkalizing agent. Thus, it might be assumed that, for the formation of boehmite in our experimental conditions, the source of Al\(^{3+}\) produces a higher influence on the position of XRD reflections, the reticular space, and the crystallinity than the alkalizing agent.

The TG/DTA curves of the samples are shown in Figure 4. The profile of TG curves is quiet similar for all cases. It can be observed that the total dehydration/dehydroxylation takes place in consecutive stages with bad defined inflexions. The total mass loss (from room temperature to 1300°C) varied according to the starting Al\(^{3+}\) solution and the alkalizing agent. Thus, for samples obtained from AlCl\(_3\) the mass loss (32.1% for AlNa and 35.8% for AlB) is smaller than for samples obtained from waste (39.1% for AWNa and 40.9% for AWB), indicating that the boehmite (AlOOH-nH\(_2\)O) obtained from waste retains higher amount of water. The value of n calculated from total mass loss was 0.84, 1.08, 1.32, and 1.46 for AlNa, AlB, AWNa, and AWB, respectively. For the same aluminum starting solution the water content is higher when n-butylamine is used as alkalizing agent. The water content in boehmite is strongly dependent on the experimental synthesis conditions [2]. From 600 to 1300°C, the metastable alumina polymorphs evolve towards the stable polymorph, and mass losses should not be observed. Nevertheless, mass losses ranging between 1 and 2% are observed in TG curves. It is attributable to certain amount of remnant hydroxyl groups according to Tsukada et al. [19] which is favored by both the waste and n-butylamine. Thus, this mass loss is higher for samples from waste and also higher from samples from n-butylamine (AlNa, 1.05%; AlB, 1.47%; AWNa, 1.51%; and AWB, 1.86%).

The results of the thermal analyses are collected in Table 2. From the profile of the DTA curves it can be observed that not only the dehydration/dehydroxylation processes but also the transformation of the metastable alumina phase into the stable polymorph is highly affected by the alumina precursor. Thus, this last process is attained at very much higher temperature for samples obtained from the waste (1280 and 1293°C) than for samples obtained from the reagent grade Al\(^{3+}\) solution (1024 and 1103°C) and it can be attributable to the presence of impurities in the waste, which stabilize the metastable alumina phase [10].

XRD patterns of the phases obtained at 600°C for 7 h are shown in Figure 5. All the patterns are quiet similar and consist of diffuse profiles with very significant background and only a very broad peak, which can be indexed as the hkl index 400 of the γ-alumina according to the reference file JCPDS 00-029-0063 (2θ diffraction angle for the hkl index 400 = 45.83°). The diffraction angles, reticular spaces, and crystallite

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**Table 1: Diffraction angle, reticular space, and crystallite size of boehmites.**

| hkl   | 2θ (°) | d (Å) | Cryst. size (nm) |
|-------|--------|-------|-----------------|
| 120   | 27.54  | 3.2362| 2.40            |
| 120   | 27.33  | 3.2601| 2.34            |
| 020   | 28.81  | 3.0967| 1.82            |
| 020   | 28.86  | 3.0911| 2.67            |
Table 2: Thermal analyses results.

| Sample | T (°C)   | Δm_p (wt, %) | Δm_t (wt, %) | T_peak (°C) | DTA | E (µV·min/mg) |
|--------|----------|--------------|--------------|-------------|-----|---------------|
| AlNa   | 25–283   | 18.3         | 32.1         | 128         | Endo| 7.9           |
|        | 283–475  | 11.1         |              | 377         | Endo| 0.9           |
|        | 475–1300 | 2.7          |              | 1024        | Exo | 0.6           |
| AlB    | 25–349   | 11.9         | 35.8         | 118         | Endo| 12.8          |
|        | 349–479  | 7.2          |              | 402         | Endo| 0.6           |
|        | 479–1300 | 3.8          |              | 1103        | Exo | 0.8           |
| AWB    | 25–168   | 12.8         | 40.9         | 125         | Endo| 20.8          |
|        | 168–343  | 16.8         |              | 230         | Endo| 1.1           |
|        | 343–523  | 7.9          |              | 441         | Endo| 0.4           |
|        | 523–1300 | 3.4          |              | 883         | Exo | n.d.          |
|        |          |              |              | 1293        | Exo | n.d.          |
| AWNa   | 25–348   | 16.6         | 39.1         | 133         | Endo| 15.8          |
|        | 348–556  | 5.5          |              | 811         | Exo | 0.8           |
|        | 556–1300 | 1.9          |              | 873         | Exo | n.d.          |

n.d.: not determined.

Figure 4: TG and DTA curves of the boehmites obtained AlCl₃·6H₂O (AlNa, with NaOH, and AlB, with n-butylamine) and aluminum waste (AWNa, with NaOH, and AWB, with n-butylamine).
size are collected in Table 3. This peak is shifted to a lower angle when NaOH solution was used as the alkalizing agent. Because the transformation of boehmite into $\gamma$-$\text{Al}_2\text{O}_3$ is pseudomorphic at this temperature [10, 17], these transitional alumina polymorphs will have a crystallite size highly dependent on the precursor crystal dimensions, and thus, nanocrystalline gamma alumina polymorphs were obtained with crystalsize below 4 nm.

XRD patterns of samples obtained at 1300°C for 7 h are shown in Figure 6. All the patterns are quiet similar and consist of well-defined and very narrow peaks, which are characteristic of well-cristallized samples with large crystallite size. Patterns fit well with that of $\alpha$-$\text{Al}_2\text{O}_3$ of the reference file JCPDS 01-075-1862. The position of the XRD reflections is quiet similar for the four samples, but the effect of butylamine in peaks intensity is noticeable. In this way the samples obtained using this alkalizing agent are more crystalline than those using NaOH. The diffraction angles, reticular spaces, and crystallite size are collected in Table 4.

Table 3: Diffraction angle, reticular space, and crystallite size of the hkl index 400.

| hkl 400 | $2\theta$ (°) | $d$ (Å) | Cryst. size (nm) |
|---------|---------------|---------|------------------|
| AlNa    | 45.62         | 1.9870  | 3.84             |
| AlB     | 45.80         | 1.9796  | 3.89             |
| AWNa    | 45.43         | 1.9894  | 2.89             |
| AWB     | 45.84         | 1.9779  | 3.87             |

Table 4: Diffraction angle, reticular space, and crystallite size of the hkl index 210.

| hkl 210 | $2\theta$ (°) | $d$ (Å) | Cryst. size (nm) |
|---------|---------------|---------|------------------|
| AlNa    | 25.52         | 3.4880  | 69.25            |
| AlB     | 25.52         | 3.4871  | 76.74            |
| AWNa    | 25.51         | 3.4891  | 75.38            |
| AWB     | 25.52         | 3.4877  | 75.38            |

The $\gamma$-$\text{Al}_2\text{O}_3$ is generally described as a defect spinel structure with aluminum cations distributed over octahedral and tetrahedral sites, while $\alpha$-$\text{Al}_2\text{O}_3$ has a trigonal structure in which every aluminum atom is coordinated octahedrally. During the transformation of gamma to alpha alumina, the aluminum and oxygen atoms arrange and the gaps between the chains and the crystal defects are reduced and accordingly the crystal dimension enlarges.

Concerning the BET specific surface area of boehmites, when the waste was used as aluminum source, the value is higher (119.5 m$^2$ g$^{-1}$ for AWNa and 116.6 m$^2$ g$^{-1}$ for AWB) than for samples obtained from reagent grade aluminum solution (66.9 m$^2$ g$^{-1}$ for AlNa and 66.8 m$^2$ g$^{-1}$ for AlB). Nevertheless, these values are in general low in comparison to those reported in the literature for nanocrystalline boehmite [14, 20]. This can be attributable to the very low temperature of outgassing (50°C) used prior to adsorption measurements, which was not high enough to remove or absorb water and/or other species generated during the synthesis process. Guzmán-Castillo et al. [7] reported that pseudoboehmites exhibit higher values of specific area than boehmites. In our case samples obtained from waste exhibit higher specific area and according to the XRD profiles (Figure 3) they may be considered as pseudoboehmites.

The values of specific surface area (BET) for boehmites and $\gamma$-alumina are collected in Table 5. The specific surface area of $\gamma$-alumina is higher when n-butylamine is used as the alkalizing agent.
4. Conclusions

The characteristics of boehmite are highly dependent on the Al source and the alkalizing agent used in the process of synthesis. The samples with smaller crystallite size are obtained using the waste as aluminium source. Thus, the source of Al$^{3+}$ produces a higher influence on the position of XRD reflections, the reticular space, and the crystallinity than the alkalizing agent. The value of $n$ in the stoichiometry of boehmite $\gamma$-AlOOH$\cdot n$H$_2$O is very dependent on both the aluminium source and the alkalizing agent. It is higher for samples obtained from the aluminium waste and for the same aluminium starting solution when n-butylamine is used as the alkalizing agent.

The dehydration/dehydroxylation process of boehmite to form $\gamma$-Al$_2$O$_3$ is highly affected by the raw materials and also the process of transformation of the metastable alumina into the stable polymorph, corundum. This last process is attained at very much higher temperature for samples obtained from the waste than for samples obtained from reagent grade Al$^{3+}$ solution, and it can be attributable to the presence of impurities in the waste, which stabilize the metastable alumina.

Boehmites with highest specific surface area are obtained from waste. The use of n-butylamine as the alkalizing agent favors the formation of $\gamma$-Al$_2$O$_3$ with the highest $S_{BET}$.

In the case of $\alpha$-Al$_2$O$_3$, the samples obtained using n-butylamine as the alkalizing agent are more crystalline than those using NaOH, but any effects are not observed for the different aluminium source.

Competing Interests

The authors declare that they have no competing interests.

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