THE ROLE OF THE ALUMINUM SOURCE ON THE PHYSICOCHEMICAL PROPERTIES OF γ-AlOOH NANOPARTICLES

Rafael Romero Toledo1,*, Luis M. Anaya Esparza2, J. Merced Martínez Rosales1

1Department of Chemical Engineering, University of Guanajuato, Noria Alta s/n. C.P. 36050, Guanajuato, Gto., México.
2University of Guadalajara, University Center of Los Altos, Av. Rafael Casillas Aceves No. 1200, C.P. 47620, Tepatitlán de Morelos, Jalisco, México
r.romerotoledo@ugto.mx

The effect on the physicochemical properties of aluminum salts on the synthesis of γ-AlOOH nanostructures has been investigated in detail using a hydrolysis-precipitation method. X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM), were used to characterize the synthesized samples. The specific surface area, pore size distribution and pore diameter of the different γ-AlOOH structures were discussed by the N2 adsorption-desorption analysis. According to the results of the nanostructure, characterization revealed that for synthesized γ-AlOOH nanostructures from AlCl3 and Al(NO3)3, obvious XRD peaks corresponding to the bayerite phase are found indicating an impure γ-AlOOH phase. Furthermore, the nitrogen adsorption-desorption analysis indicated that the obtained γ-AlOOH nanoparticles from Al2(SO4)3 of technical grade (95.0% of purity) and low cost, possess a high BET surface area of approximately 350 m2/g, compared to the obtained nanostructures from aluminum sources reactive grade, which was attributed to the presence of Mg (0.9 wt.%) in its nanostructure.

Keywords: nanofibers; pseudoboehmite; aluminum source; hydrolysis-precipitation

УЛОГА НА ПОТЕКЛОТО НА АЛУМИНИУМ КАКО ИЗВОР НА ФИЗИКОХЕМИСКИТЕ СВОЙСТВА НА НАНОЧЕСТИЧКИТЕ НА γ-АЛУМИННИЙ

Подробно е испитана улогата на физикохимските својства на алуминиумовите соли во синтезата на наноструктурите на γ-AlOOH со примена на методот хидролиза-преципитација. За карактеризација на синтетизираните примероци се користени рендгенска флуоресценција (XRF), Фуршетова трансформирана инфрацрвена спектроскопија (FTIR), рендгенска дифракција на пракш (XRD), скенирачка електроскопија на емисија на поле (FESEM) и трансмисионата електроскопија (TEM). Специфичната површина, распределбата на димензите на порите и пречникот на порите на разните структури на γ-AlOOH беа дисктуриран врз основа на анализата на атсорпција-десорпција на азот. Според резултатите на наноструктурата, карактеризацијата на оки дека за наноструктурите на γ-AlOOH, синтетизирани од AlCl3 и Al(NO3)3, се појавуваат очигледни XRD пикови што одговараат на бајерит-фаза, што укажува на нечиста γ-AlOOH-фаза. Исто така, анализата на атсорпција-десорпција на азот покажува дека наночестичките на γ-AlOOH добиени од технички (95.0% чистота) и евтин Al2(SO4)3 имаат висока BET површина од приближно 350 m2/g споредено со наноструктури од алуминиум со голема чистота, што се припишува на присутноста на Mg (0.9 wt.%) во наноструктурата.

Ключни зборови: нановлакна; псевдобохемит; извор на алуминиум; хидролиза-преципитација
1. INTRODUCTION

Aluminum oxyhydroxides (γ-AlOOH) are important industrial materials with important industrial applications [1]. They are the precursor of γ-Al₂O₃ [2] and other crystalline structures such as η-, δ-, θ-, κ-, χ- and α-alumina [3]. The γ-AlOOH is widely used as a catalytic support and catalyst [4, 5], adsorbent [6], ceramic, abrasive and filter [7]. In addition, it is a low-cost material which has received considerable attention during the past decades [4, 6]. In the area of catalysis, it exhibits catalytic activity in the process of methanol dehydration to dimethyl ether [8]. Furthermore, another study revealed that γ-AlOOH has a strong influence on the distribution of products for the hydrogenation of CO and shows excellent selectivity of acetaldehyde for the reaction of methanol and synthesis gas [9]. Bing et al. observed specific activity for the syngas conversion to ethanol [10] and it was recently found that the simple aluminum oxyhydroxide (γ-AlOOH), as a solid acid catalyst, gave an attractive performance for the 3-methyl-2-cyclopentenone generation from 2,5-hexanediol with high selectivity (> 71%) via hydrogenolysis and successive hydrolysis [11].

The γ-AlOOH has a layered structure with octahedral layers bonded together through hydrogen bonds [12], which contains a large number of available hydroxyl (OH) groups to connect with a variety of nanostructured materials [13]. Therefore, researchers have broadly addressed the development of new routes to prepare γ-AlOOH structures [12–15]. The hydrolysis-precipitation route is one of the promising, mild and attractive methods for the synthesis of high-quality γ-AlOOH nanostructures. However, the effectiveness of this synthesis route depends on the experimental conditions (temperature and processing time, initial pH and the aluminum source) [16]. To date, γ-boehmite has been synthesized with different morphologies (whisker, single-crystal nanobelts, nanorods, nanoflakes, nanofibers and flower-like among others) and synthesis routes, as well as different experimental conditions [15–18]. Nonetheless, it is important to indicate that the potential applications of this material depend on its size and shape control. On the other hand, the stability and textural properties of nanostructures are crucial and determinant for current applications. Some authors have emphasized that materials with high pore volume may improve the adsorption performance if it is used as an adsorbent or catalyst material, and the loading capacity if it is applied as a catalytic support. These properties improve the diffusion and transport of reagents and reactants [15, 19].

The basic or acidic, texture and stability properties of the nanostructures can be strongly influenced by the preparation route and conditions [20]. Different authors have shown that the properties of γ-boehmite, such as nanoparticle size, shape, and structure, depend on the synthetic conditions and the nature of the aluminum precursors and their degree of impurities [21]. Additionally, aluminum precursors with the presence of impurities may be used to obtain materials with interesting properties and applications. In our laboratory, we have reported that Al₂O₃ nanostructures synthesized using aluminum sulfate (technical grade with a purity of 95% by weight) exhibited better textural properties than those obtained with aluminum sulfate (analytical grade with a purity of 99.98% by wt.), due to improvement by the presence of small amounts of impurities, such as Mg (0.33 wt.%) [22].

Undoubtedly, the research and development of producing γ-AlOOH with various structures is beneficial for many branches of modern science and technology. However, reports concerning the synthesis of γ-AlOOH by a simple, environmentally favorable, and low-cost synthesis method with interesting textural properties are still limited. This work aimed to study the effect of the purity of the aluminum source (chloride, nitrate and two different aluminum sulphates) on the textural properties of γ-AlOOH nanoparticles via a hydrolysis-precipitation route. The chemical composition, structure, and morphology were investigated by the XRF, XRD, FTIR, N₂ adsorption–desorption, FESEM and TEM studies.

2. EXPERIMENTAL SECTION

2.1. Chemicals

The following chemicals were used: Al₂(SO₄)₃–18H₂O, AlCl₃–6H₂O, Al(NO₃)₃–9H₂O chemical reagents analytical grade were purchased from Sigma–Aldrich, México and aluminum sulfate Al₂(SO₄)₃–18H₂O (technical grade, 95.0% of purity) was purchased from Alfa-Omega Chemical S.A de C.V. México. Anhydrous ammonia gas (purity ≥ 99.98%) was purchased from Praxair; México, and distilled water was provided by the University of Guanajuato.

2.2. Pseudoboehmite synthesis

Initially, 100 g of each aluminum precursor was dissolved into distilled water and stored before the experiment. The Al₂(SO₄)₃–18H₂O (technical grade) was filtered using milli-pore filter paper for
removal of insoluble impurities. In order to study the effects of the different kinds of Al resources on the physico-chemical properties, the experiments were carried out similarly. First, 1000 ml of the aqueous solution was added to a solution of water and ammonia gas at a rate of 1000 ml/h using a peristaltic pump (Cole palmer instrument Co., USA), under rigorous mechanical agitation (400 rpm), at a temperature of 65 ± 1°C to reach a pH of 9 to 11 (depending on the aluminum precursor). After aging for 20 min at the same temperature, the obtained precipitate was filtered and washed three times, with cold and hot distilled water, to remove \( \text{SO}_4^{2-} \) completely (BaCl\(_2\) detection). The precipitate was dried in an oven at ~110 °C for 12 h.

The overall reactions leading to the formation of pseudoboehmite using different aluminum salts can be represented by Eqs. (1) – (3).

\[
\begin{align*}
\text{Al}_2(\text{SO}_4)_{3} + 6\text{NH}_3 + 6\text{H}_2\text{O} & \rightarrow 2\text{AlOOH} + 3(\text{NH}_3)\text{SO}_4 + 2\text{H}_2\text{O} \\
2\text{AlCl}_3 + 6\text{NH}_3 + 6\text{H}_2\text{O} & \rightarrow 2\text{AlOOH} + 6\text{NH}_4\text{Cl} + 2\text{H}_2\text{O} \\
\text{Al(NO}_3\text{)}_3 + 3\text{NH}_3 + 3\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_3 + 3\text{NH}_4\text{NO}_3 \\
\text{Al(OH)}_3 & \rightarrow \text{AlOOH} + \text{H}_2\text{O}
\end{align*}
\]

2.2. Characterization

The elemental chemical quantifications were determined by high-resolution wavelength dispersive-X-ray fluorescence spectra (XRF) were recorded by a NEX-CG RIGAKU spectrometer of cartesian geometry, equipped with a Pd anode X-ray tube. Fourier transform infrared (FTIR) spectra were obtained using an FT-IR Nicolet 470 spectrometer in the range 400–4000 cm\(^{-1}\) at room temperature. The X-ray powder diffraction (XRD) patterns were identified using a Siemens D-500 X-ray diffractometer, equipped with CuK\(\alpha\) radiation (\(\lambda = 1.54\ \text{Å}\)). Data were collected from 10 to 80° (20), with a scan rate of 0.03°/s. The microstructures were studied by transmission electron microscopy (TEM) using a Philips Tecnai F20 microscope operated at 200 kV, while the surface morphology of the samples were investigated with a field-emission scanning electron microscope (JEOL JSM 7600-F). Surface area, pore volume, and pore size distribution were determined by \( \text{N}_2 \) adsorption-desorption with a Micromeritics, ASAP 2010. The samples were degassed at 150 °C for 3 h, under vacuum. Nitrogen adsorption isotherms were measured at liquid \( \text{N}_2 \) temperature (77 K), and \( \text{N}_2 \) pressures ranging from \( 10^{-6} \) to 1.0 P/P\(_0\). The specific surface areas were calculated by means of the Brunauer–Emmett–Teller (BET) method and the pore size distribution was obtained according to the Barret–Joyner–Halenda (BJH) method.

3. RESULTS AND DISCUSSION

3.1. X-ray fluorescence (XRF)

The quantitative chemical analysis (XRF) results are presented in Table 1. As expected, the aluminum (Al) and oxygen (O) content dominate due to its nature. The \( \text{Al}_2(\text{SO}_4)_{3}\)-A and \( \text{Al}_2(\text{SO}_4)_{3}\)-B samples present a similar content of sulfur (S). The \( \text{AlCl}_3\)-C sample has a high chlorine (Cl) content, due to its nature. However, the \( \text{Al}_2(\text{SO}_4)_{3}\)-A exhibits the presence of magnesium (Mg), attributed to the impurity degree of the precursor, which has also been reported in previous works [16, 23].

<table>
<thead>
<tr>
<th>Samples</th>
<th>Concentration (%)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum source</td>
<td>Al</td>
</tr>
<tr>
<td>( \text{Al}_2(\text{SO}<em>4)</em>{3})-A</td>
<td>7.53</td>
</tr>
<tr>
<td>( \text{Al}_2(\text{SO}<em>4)</em>{3})-B</td>
<td>7.88</td>
</tr>
<tr>
<td>( \text{AlCl}_3)-C</td>
<td>5.47</td>
</tr>
<tr>
<td>( \text{Al}_2(\text{SO}<em>4)</em>{3})-D</td>
<td>6.3</td>
</tr>
<tr>
<td>Pseudoboehmite</td>
<td></td>
</tr>
<tr>
<td>( \gamma)-\text{AlOOH}-A</td>
<td>38.0</td>
</tr>
<tr>
<td>( \gamma)-\text{AlOOH}-B</td>
<td>38.1</td>
</tr>
<tr>
<td>( \gamma)-\text{AlOOH}-C</td>
<td>36.1</td>
</tr>
<tr>
<td>( \gamma)-\text{AlOOH}-D</td>
<td>36.1</td>
</tr>
</tbody>
</table>

*Percentage extraction values are based on triplicate analysis

Also, the presence of silicon (Si), calcium (Ca) and iron (Fe) in small quantities in the four samples were reported. Furthermore, the results of the as-synthesized samples of pseudoboehmite are also given in Table 1, and which exhibit a higher concentration of Al and O. This is consistent with the chemical formula of γ-AlOOH. The presence of 0.4 wt.% of S in the sample γ-AlOOH-A was also observed, attributed to ammonium sulfate ((NH₄)₂SO₄) as a residue generated during the synthesis process. Besides that, the presence of Mg decreased, which is attributed to the fact that the 0.2 wt.% was removed during the synthesis process and washes.

3.2. X-ray powder diffraction (XRD)

The phase structure and purity of the aluminum salts of the as-synthesized samples were examined by XRD. The XRD patterns of the aluminum sources are shown in Figure 1a), and the XRD patterns of the as-synthesized samples in Figure 1b). The salts of Al₂(SO₄)₃-A and B show signals of peaks at 2θ of 12.51°, 21.06°, 25.55°, 30.76°, 33.73°, 40.99°, 44.38° and 46.81°, which are in line with those reported by other authors [23, 24]. No impurities-related signals were detected in Al₂(SO₄)₃-A and γ-AlOOH-A as Mg, attributed to a homogeneous dispersion in the structure. The AlCl₃-C salt diffraction pattern agrees with its crystallographic card (JDCPS card No. 44-1473) corresponding to AlCl₃·6H₂O, with the main peaks at 20 = 15.07°, 27.19°, 27.52°, 35.05°, 39.01°, 41.38°, 43.33° and 51.94° with rhombohedral geometry [25, 26]. On the other hand, the Al(NO₃)₃-D diffractogram shows the crystalline phase corresponding to Al(NO₃)₃·9H₂O presenting similar characteristic peaks as previously reported by Paceswca [27] and Karimi [28]. The different aluminum precursors have different degrees of crystallinity. These aluminum precursors exhibit the following order: Al(NO₃)₃-D > AlCl₃-C > Al₂(SO₄)₃-A > Al₂(SO₄)₃-B. The above indicates that the size of crystals present in the aluminum sulfate hydrate is finer than the other aluminum sources.

Figure 1b) shows the XRD patterns of the samples synthesized in this research. All diffraction peaks of the pseudoboehmite nanoparticles corresponded to the (020), (120), (140), (131), (200), (160), (151), (071), (022) and (251) planes of the orthorhombic pseudoboehmite, respectively. The orthorhombic structure of γ-AlOOH is proved by comparing the XRD pattern with those reported in the literature [7, 10]. X-ray diffractograms of samples γ-AlOOH-C and γ-AlOOH-B show characteristic peaks of γ-AlOOH. However, it also shows four peaks at 2θ (19.05, 20.05, 41.0 and 53.0°) which do not correspond to the pseudoboehmite phase, indicating that the materials exhibited an additional crystalline phase of bayerite. This result indicates an impure γ-AlOOH phase [31].

Fig. 1. X-ray powder diffraction of a) aluminum source and b) as-synthesized samples
Previous studies have reported that when AlCl₃ and Al(NO₃)₃ salts are used to obtain pseudoboehmite, the formation of additional crystalline phases such as gibbsite and bayerite can appear. The presence of these crystalline phases is due to experimental parameters that were directly influenced by the pH and the precursors [32]. It has been reported that bayerite Al(OH)₃ formation could be obtained at alkaline pH values (pH 11), together with a weak XRD peak assigned to boehmite from nitrate precursors. On the other hand, at lower pH, the crystalline phase in the samples changed to pseudoboehmite, whose peaks became broader [33]. This work showed a similar behavior with aluminum salts (nitrate or chloride) which reached pH 11 during the synthesis process, but not for aluminum sulphate salts with a pH 9. It is known that the physicochemical properties can be very different for low- and well-crystallized pseudoboehmite, even though their crystal structure is just the same. Furthermore, there is an evident shift of the diffraction lines of γ-AlOOH-C and γ-AlOOH-D, which suggests that the layers are rotated or displayed due to the change of pH or aluminium salt. It is noteworthy, that compared with the XRD pattern of γ-AlOOH-B, the sample γ-AlOOH-A demonstrated wider peaks; this represents an increase in the lattice parameter values. The increase in the spacing confirms that Mg is present in the framework of γ-AlOOH-A. This attribution is made due to the contribution of other authors, where they mention that the incorporation of Mg generates the formation of Mg–O bonds with lengths longer than that of the Al–O bonds, resulting in a mesostructural expansion [22].

3.3. Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis of γ-AlOOH is characterized by prominent OH stretching and bending modes associated with the interlayer hydrogen bonds of the structure in terms of vibration intensity and frequency [32]. Figure 2 shows the infrared spectra of synthesized samples of γ-AlOOH. In general, all the FTIR spectra are similar regardless of the slight difference in intensities of some peaks, and one additional peak for the synthesized samples from aluminum salts (nitrate or chloride). The FTIR spectra demonstrate the typical spectra of pseudoboehmite [32, 34]. Firstly, for the samples γ-AlOOH-A and γ-AlOOH-B, intensive bands at 3443 and 3090 cm⁻¹ are observed, while for the samples γ-AlOOH-C and γ-AlOOH-D bands are observed at 3650, 3575, 3443 and 3090 cm⁻¹. All bands belong to the ν₆(A1)O=H and ν₆(A1)O–H stretching vibrations or O–H stretching mode [34–37]. The band at 3443 cm⁻¹ for the samples γ-AlOOH-A and γ-AlOOH-B dominates this region and prevents the observation of the features corresponding to the structural OH groups for the pseudoboehmite phase. The weak band at 2095 cm⁻¹ is the combination band [35, 36]. The weak band at 1638 cm⁻¹ can be assigned to the stretching and bending modes of the adsorbed water molecules and this absorbance in the spectra of γ-AlOOH nanoparticulates is very weak for γ-AlOOH-C and γ-AlOOH-D, indicating a very small amount of physically adsorbed water molecules. This result is consistent with the XRD patterns (Figure 1b), because it exhibits a major crystalline structure compared to γ-AlOOH-A and γ-AlOOH-B. It has been reported that the bands at around 1420 and 1510 cm⁻¹ are due to the amorphous surface structure existing in nanocrystalline pseudoboehmite. This explains the vibrations observed at ~1389 and 1507 cm⁻¹ in our synthesized pseudoboehmite [36]. While the sharp peak at 1072 cm⁻¹ and small shoulder at 1171 cm⁻¹ are assigned to the angle bending of the H bonds in the octahedral structure of pseudoboehmite (HO–Al=O) and the angle deformation (wagging) of the H bonds in the octahedral structure of pseudoboehmite (HO–Al=O), respectively [32, 36, 37]. The bands at 750, 625 and 490 cm⁻¹ are ascribed to the vibration modes of AlO₆, while a band at 882 cm⁻¹ is ascribed to the stretching mode of AlO₄ [32, 34, 36, 37]. The main bands are listed in Table 2, together with their assignment, and compared with those reported in the literature.
Table 2

<table>
<thead>
<tr>
<th>Pseudoboehmite band position (cm⁻¹)</th>
<th>Assignment (from reported [32–37])</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>From reported</td>
</tr>
<tr>
<td>3650</td>
<td>3628</td>
</tr>
<tr>
<td>3575</td>
<td>–</td>
</tr>
<tr>
<td>3443</td>
<td>3440, 3445, 3460</td>
</tr>
<tr>
<td>3090</td>
<td>3080, 3095, 3098</td>
</tr>
<tr>
<td>2095</td>
<td>2091, 2092</td>
</tr>
<tr>
<td>1638</td>
<td>1630, 1634, 1635, 1638, 1640</td>
</tr>
<tr>
<td>1507</td>
<td>1510, 1520</td>
</tr>
<tr>
<td>1389</td>
<td>1384, 1387, 1389, 1400, 1420</td>
</tr>
<tr>
<td>1171</td>
<td>1156, 1160, 1170</td>
</tr>
<tr>
<td>1072</td>
<td>1065, 1072, 1073, 1075</td>
</tr>
<tr>
<td>882</td>
<td>884</td>
</tr>
<tr>
<td>750</td>
<td>720, 746, 747, 760</td>
</tr>
<tr>
<td>625</td>
<td>631, 633</td>
</tr>
<tr>
<td>490</td>
<td>480, 491</td>
</tr>
</tbody>
</table>

3.4. N₂ adsorption-desorption

Figure 3 shows the N₂ adsorption–desorption isotherm measured at 77 K and the corresponding pore size distributions curves (inset) calculated via the Barrett-Joyner-Halenda (BJH) of the synthesized pseudoboehmite samples. All samples exhibit IV-type isotherm (definition by IU-PAC) [32, 36] and, as indicated by the convex curvature of the isotherms at the sub-monolayer range and by the occurrence of a narrow hysteresis loop at high P/P₀ range, it shows that these pseudoboehmites were mesoporous materials [36]. The appearance of a type H₂ hysteresis loop in the isotherm indicates the presence of ink-bottle type pores in the mesoporous pseudoboehmite. This indicates that they have good pore connectivity [32]. Table 1 lists the results of specific surface area (SSA), pore volume (V_p) and average pore diameter (D_p) of the synthesized γ-AlOOH nanostructures, values reported in the literature, and preparation conditions. These results show that the source of aluminum is crucial to the preparation of γ-AlOOH by the hydrolysis-precipitation method. It can be seen that the pore sizes for all synthesized samples were located between 2–17 nm, respectively.

All samples synthesized have a high surface area (327–350 m²/g), which could be ranked in the following order: γ-AlOOH-A > γ-AlOOH-D > γ-AlOOH-C > γ-AlOOH-B. The samples synthesized by nitrates and chlorides did not show significant changes in the surface area, even with their greater crystalline structure and the presence of bayerite as an additional phase, as shown in Figure 1b). On the other hand, the γ-AlOOH-A sample exhibited a higher specific surface area (350 m²/g). Nonetheless, the obtained textural properties for sample γ-AlOOH-A is comparable and higher than other pseudoboehmites and boehmites reported in the literature, as shown in Table 3.
Until now, few reports are available on the direct synthesis of mesoporous Mg-AlOOH composite oxyhydroxides of low-cost with a long-range mesostructured, high specific surface area and pore volume, and a highly homogeneous presence of MgO as an impurity. These results suggest that aluminum precursors with a considerable degree of impurities are a more economical, easy, environmentally friendly and convenient synthesis procedure with better textural properties for mesoporous pseudoboehmite particles. In general, larger specific surface area and pore volume are favorable for many applications such as catalyst support, and absorbance.

### Table 3

<table>
<thead>
<tr>
<th>As-synthesized powder</th>
<th>Temperature (°C)</th>
<th>Solution pH range</th>
<th>SSA (m²/g)</th>
<th>V_p (cm³/g)</th>
<th>D_p (Å)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-AlOOH-A</td>
<td>65 ± 2</td>
<td>9–10</td>
<td>350</td>
<td>0.77</td>
<td>85</td>
<td>This work</td>
</tr>
<tr>
<td>γ-AlOOH-B</td>
<td>65 ± 2</td>
<td>9–10</td>
<td>327</td>
<td>0.74</td>
<td>80</td>
<td>This work</td>
</tr>
<tr>
<td>γ-AlOOH-C</td>
<td>65 ± 2</td>
<td>10–11</td>
<td>335</td>
<td>0.62</td>
<td>80</td>
<td>This work</td>
</tr>
<tr>
<td>γ-AlOOH-D</td>
<td>65 ± 2</td>
<td>10–11</td>
<td>340</td>
<td>0.30</td>
<td>62</td>
<td>This work</td>
</tr>
<tr>
<td>C-5</td>
<td>180</td>
<td>5</td>
<td>48</td>
<td>0.37</td>
<td>166</td>
<td>[32]</td>
</tr>
<tr>
<td>C-11</td>
<td>180</td>
<td>11</td>
<td>39</td>
<td>0.35</td>
<td>280</td>
<td>[32]</td>
</tr>
<tr>
<td>N-5</td>
<td>180</td>
<td>5</td>
<td>48</td>
<td>0.35</td>
<td>287</td>
<td>[32]</td>
</tr>
<tr>
<td>N-11</td>
<td>180</td>
<td>11</td>
<td>46</td>
<td>0.27</td>
<td>300</td>
<td>[32]</td>
</tr>
<tr>
<td>ATG1-25</td>
<td>25</td>
<td>10.8–12</td>
<td>393</td>
<td>0.29</td>
<td>29</td>
<td>[36]</td>
</tr>
<tr>
<td>ATG2-25</td>
<td>25</td>
<td>9.5–10.8</td>
<td>350</td>
<td>0.5</td>
<td>28</td>
<td>[36]</td>
</tr>
<tr>
<td>Synthetic Boehmite</td>
<td>95</td>
<td>–</td>
<td>198</td>
<td>–</td>
<td>40</td>
<td>[38]</td>
</tr>
<tr>
<td>Boehmite</td>
<td>180</td>
<td>8.5</td>
<td>98.6</td>
<td>–</td>
<td>–</td>
<td>[31]</td>
</tr>
<tr>
<td>LP</td>
<td>60</td>
<td>9.7</td>
<td>273</td>
<td>0.66</td>
<td>75</td>
<td>[20]</td>
</tr>
<tr>
<td>AlO(OH)-NR</td>
<td>70</td>
<td>9–10</td>
<td>448</td>
<td>–</td>
<td>20</td>
<td>[39]</td>
</tr>
<tr>
<td>Pseudoboehmite</td>
<td>–</td>
<td>10.5</td>
<td>350</td>
<td>0.49</td>
<td>53</td>
<td>[40]</td>
</tr>
<tr>
<td>AlOOH</td>
<td>80</td>
<td>–</td>
<td>385</td>
<td>0.28</td>
<td>28</td>
<td>[15]</td>
</tr>
<tr>
<td>γ-AlOOH</td>
<td>150</td>
<td>–</td>
<td>225</td>
<td>0.45</td>
<td>56–82</td>
<td>[41]</td>
</tr>
</tbody>
</table>

#### 3.5. Field-emission scanning electron microscopy (FESEM)

The microstructure of the synthesized γ-AlOOH nanoparticles was studied using FESEM. Figure 4 shows the representative images of a) γ-AlOOH-A, b) γ-AlOOH-B, c) γ-AlOOH-C, and d) γ-AlOOH-D, respectively. According to FESEM images, different sources of aluminum have a fundamental effect on the morphologies of as-prepared γ-AlOOH by the hydrolysis-precipitation route. The obtained images indicate that the γ-AlOOH-A, γ-AlOOH-B and γ-AlOOH-C samples have a sponge-like morphology, while the γ-AlOOH-D sample showed irregular crystalline agglomerates (not nanostructured). Furthermore, obvious agglomeration phenomena can be observed in the samples due to the effect of surface functional groups and quantum size [42]. This fact evidences the differences between the samples obtained by hydrolysis-precipitation method, showing amorphous nanofibrous agglomerates for the samples (a, b and c) due to their high surface energy, so generating a high porosity. However, regarding sample (d), it exhibits a high degree of crystallinity, (Fig. 1b) and, thus, has many small pores, causing a low pore volume and diameter (Table 3). The reason leading to this phenomenon may be that the pore structures were occupied by water during the polymerization process. The fibers’ length is approximately 100 nm and the diameter approximately 20 nm. This means that the crystals grew faster in the longitudinal direction than in the diametrical direction. The nano-fibers are tangled with a smooth surface. It can be appreciated that the formed nanoparticles for γ-AlOOH-A, γ-AlOOH-B, and γ-AlOOH-C samples possess uniform pore size distribution and are homogeneous without preferentially oriented shapes, while the γ-AlOOH-D sample indicate a totally different ...
morphology (small plate-like structures). Due to this structure, there are lots of defects on secondary particles, inducing a larger amount of pores between primary crystallites, and these pores are very small. This is why sample γ-AlOOH-D has a high SSA. When the primary crystallites are well crystalline, the corresponding secondary particles have few defects and most pores arise from the packing spaces between secondary particles. Nevertheless, it has been observed that the structure and physicochemical properties not only depend on the aluminium source, but also that they are strongly influenced by the synthesis method and its conditions.

3.6. Transmission electron microscope (TEM)

TEM micrographs of aluminum oxyhydroxide nanoparticles are given in Figure 5. All particles exhibit similar shapes and morphologies. However, slight changes in the morphological nano-fibrillar messy substructure were observed: a length of approximately 100 nm for the γ-AlOOH-A sample and 80 nm for γ-AlOOH-B, while for γ-AlOOH-C, a nanofibrillar length of 60 nm can be observed. Finally, the γ-AlOOH-D sample has very small nanofibers of about 33 nm in length. The results show that the length and thickness plays a key role in the textural and crystallinity properties. The shorter nanofibers induce a greater crystallinity, and therefore, reduced textural properties due the overlap and the closely spaced nanofibers. The textural properties and X-ray diffraction analysis back up these results obtained by TEM analysis. The results obtained by the TEM analysis for nanofiber lengths presented the following order: γ-AlOOH-A > γ-AlOOH-B > γ-AlOOH-C > γ-AlOOH-D, which are in accordance with those obtained in the pore size distribution (Fig. 3).

![Fig. 4. FESEM images of pseudoboehmite samples, a) γ-AlOOH-A, b) γ-AlOOH-B, c) γ-AlOOH-C, d) γ-AlOOH-D](image-url)
The role of the aluminum source on the physicochemical properties of γ-AlOOH nanoparticles


4. CONCLUSIONS

In this paper, the simple synthesis of pseudoboehmite nanostructures using diverse aluminum sources at low temperature has been reported. The above mentioned was done, without using any surfactant or template. It is possible to obtain the pseudoboehmite phase from Al$_2$(SO$_4$)$_3$ technical grade, of low-cost, through the hydrolysis-precipitation route. The mesoporous pseudoboehmite shows a high specific surface area (350 m$^2$/g) which is comparable with other materials fabricated using analytical grade precursors. The possible use of a low-temperature, mild and environmentally friendly synthesis, with high impact regarding the costs of precursors and energy consumption during the production of γ-AlOOH nanopowders, is presented as an alternative. The advantages of these nanostructures include their simplicity, low-cost and versatility with a wide range of applications in ceramics, adsorption, catalyst and catalyst supports and moreover, complex apparatus is not needed.

Acknowledgements. The authors gratefully acknowledge the support provided by the National Council on Science and Technology (CONACYT); LICAMM UG: Laboratory of research and characterization of minerals and materials, for providing access to XRF and XRD equipment and to the University of Guanajuato, México. We also thank the Michoacán University of San Nicolas of Hidalgo (UMSNH), Morelia, Michoacán, México, for providing access to SEM and TEM equipment facilities.

Conflict of interest. The authors declare that they have no conflict of interest.

REFERENCES


doi:https://doi.org/10.1016/j.jallcom.2018.05.356


The role of the aluminum source on the physicochemical properties of γ-AlOOH nanoparticles

DOI: https://doi.org/10.1016/S0167-577X(01)00461-X

DOI: https://doi.org/10.1016/j.bsecv.2017.06.002

DOI: https://doi.org/10.1016/j.tnf.2014.07.014

DOI: https://doi.org/10.1016/j.apradiso.2016.01.026

DOI: https://doi.org/10.1016/j.jhazmat.2019.121373

DOI: https://doi.org/10.1016/j.ceramint.2018.04.103

DOI: https://doi.org/10.1016/j.clay.2019.105207

DOI: https://doi.org/10.1016/j.materresbull.2013.08.072

DOI: https://doi.org/10.1016/j.apcata.2018.12.017

DOI: https://doi.org/10.1021/ie3017626

DOI: https://doi.org/10.1016/j.ceramint.2015.11.079

DOI: https://doi.org/10.1016/j.ijleo.2017.09.093