A Novel Synthesis Route of Mesoporous γ-Alumina from Polyoxohydroxide Aluminum

Felipe Módolo Segal*, Michelle Fidelis Correa*, Rebeca Bacani*, Bruna Castanheira*, Mario José Politi*, Sergio Brochsztain*, Eduardo Rezende Triboni**

*Departamento de Engenharia Química - DEQ, Escola de Engenharia de Lorena da Universidade de São Paulo, Estrada Municipal do Campinho, s/n, CEP 12.602-810, Lorena, SP, Brazil
**Departamento de Ciências Exatas e da Terra, Universidade Federal de São Paulo - UNIFESP, Rua São Nicolau, 210, CEP 09913030, Diadema, SP, Brazil

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Mesoporous gamma-aluminas (γ-Al₂O₃) were synthesized starting from an unusual precursor of polyoxohydroxide aluminum (POHA). This precursor was obtained from aluminum oxidation in alkaline water-ethanol solvent in the presence of d-glucose that induces the formation of a gel, which leads to the POAH powder after ethanolic treatment. Precipitated POHAs were calcined at different temperatures (300, 400, 700 and 900 °C) resulting in the metastable γ-Al₂O₃ phase. Whereas at 300 °C no γ-Al₂O₃ phase was formed, unexpectedly, mesoporous γ-Al₂O₃ was obtained at 400 ºC having a high specific surface area (282 m²/g) and a narrow pore size distribution. At higher temperatures, the aluminas had the expected decrease in surface area: 166 m²/g (700 °C) and 129 m²/g (900 °C), respectively. The structural change from POHA to alumina calcined at 400 °C occurs directly without the need to isolate the hydroxide or oxyhydroxide aluminum precursors. Both POHA and transition aluminas were characterized by Fourier Transform Infrared spectroscopy (FTIR), X-ray diffraction (XRD), N₂ sorption and Scanning Electron Microscopy (SEM). These findings show an alternative route to produce high standard aluminas.

Keywords: aluminum and d-glucose, EtOH-H₂O alkaline medium, chemical preparation, mesoporous gamma-Al₂O₃.

1. Introduction

The control of morphology and crystallinity in materials is very important due to its close relationship between structure and function. Thus, the search for synthetic routes for obtaining new selected materials with the desired properties is aimed1-5.

Alumina compounds are known to present exceptional structural stabilities and quite large specific surface areas, one of the reasons why these compounds are widely used for catalysis and adsorption processes6-12. The narrow connection that exists between the structure of the starting material and that of the target can be exemplified in the preparation of several types of aluminas such as corundum (α-Al₂O₃) and several transition aluminas (χ-, K-, γ-, δ-, ε-, η-Al₂O₃) commonly synthesized at different temperatures by calcination of their trihydroxide and oxyhydroxide precursors13-20. Renewed interest in a novel and facile synthesis methods of aluminum oxides using these precursors are thus envisaged.

*γ-Alumina (γ-Al₂O₃) is a very important transition alumina since it has acidic sites and it is widely used in the petrochemical industry21. This alumina is used as well as a catalyst scaffold allowing the dispersion of several active phases as metals and metallic oxides for important organic reactions and several advanced technological applications22-25,30-32. The main precursor for the synthesis of γ-alumina commonly used is the aluminum oxyhydroxide (Boehmite), γ-AlOOH. A peculiar characteristic observed in this process is that during the calcination the dehydration has been related as a topotactic reaction26. By other hands, Bayerite (β-AlOOH) and Gibbsite (α-AlOOH) precursors could be used but the phase transformation pathway has different outcomes13,37-35.

Up to date literature highlights the effect of hydroxylated compounds directing the precipitation of aluminum hydroxide and as well on the alumina phase formation36-38. Obrenovic et al. investigated the precipitation of aluminum hydroxides from diluted Bayer's liquor in the presence and absence of d-glucose obtaining boehmite and bayerite phases, respectively. These starting compounds are then calcined for obtainment...
of mesoporous aluminas. In these contexts, a previous work on aluminum oxidation in alkaline alcohol-water 3:1 yielded a paramagnetic organic-bayerite material. It was shown that the high ethanolic fraction to the precipitation of the bayerite.

In this work, we present a novel method to obtain γ-Al$_2$O$_3$ from polyoxohydroxide aluminum ion (POHA) precipitated with d-glucose as an inductor additive. The synthesis of POHA was carried out under ultrasonic condition to promote the formation of elemental aluminum as K OH in ethanol-water with the addition of d-glucose. The POHA powders were calcined and a novel tandem reaction was taken into account to the transformation where the POHA ion changes straightforward to γ-Al$_2$O$_3$ without the need to obtain previously the trihydroxide or oxyhydroxide precursors. γ-Al$_2$O$_3$ was formed at the temperatures of 400, 700 and 900 °C. Calcination at 400 °C resulted in γ-Al$_2$O$_3$ having a surface area of 282 m$^2$/g and a narrow pore volume. These features highlight the importance of a synthetic method by simple precipitation, whereas in most current methods it is necessary to prepare the (pseudo-)boehmite or bayerite precursors.

2. Experimental

2.1 POHA powder synthesis

Aluminum powder (99.9% Reagent) and ethanol (Mallinkrodt) were used as received. Water was doubly distilled and further purified via a Millipore Milli-Q system, others reagents were of the best available grade (Aldrich). The d-glucose was purchased from Merck and used without further purification.

Aluminum powder, Al (400 mg), KOH (1.5 g) in 40 mL ethanol:water 3:1 (v:v) ratio and 50.0 mg d-glucose were added to an Erlenmeyer flask and the suspension was sonicated in an ultrasonic bath (output of 125 W/20 KHz). After the total dissolution of the aluminum, it was verified the formation of two phases with a gel at the bottom of the flask. The gel was separated by decantation and 100 mL ethanol dropped stepwise under stirring, the resulting solid (1.5 g) was filtered out and thoroughly washed with water and ethanol and following dried in an oven at 70 °C. Resulting powders were calcined for 2 hours at 300, 400, 700, and 900 °C, in a muffle furnace under air.

2.2 POHA powder characterization

XRD diffraction patterns of the samples were obtained on an X-Ray Diffractometer Rigaku Miniflex (30 kV/15 mA), using a Cu tube, K$_\alpha$ ($\lambda=1.5418$ Å) with Ni filter. MDI Jade 6.5 software was used to access PDF database and indexing. The as-synthesized and calcined samples were also characterized by Fourier Transform Infrared Spectroscopy (FTIR) with a Bomen model MB 100 using KBr pellets in the range 4000 to 500 cm$^{-1}$. The surface morphology was evaluated by scanning electron microscopy (SEM) using a Hitachi 3400N instrument. Nitrogen adsorption/desorption isotherms were measured with a Quantachrome Nova 2200e. The samples were pretreated by degassing at 55 °C for 24 hours. The specific surface area was obtained using the Brunauer Emmett Teller (BET) method; the pore size distribution (PSD) was derived from the adsorption branches of the isotherms using the BJH method. The microporosity was estimated using the t-plot method.

3. Results and Discussion

3.1 FTIR spectroscopy

Figure 1 shows the FTIR spectra of POHA, before and after calcination. In Fig. 1(a) the peaks at 3434 and 1642 cm$^{-1}$ can be assigned to vibrational (bending and stretching, respectively) modes of the hydroxyl group of adsorbed water. The overlapped band centered at 620 cm$^{-1}$ presenting two shoulders at 520 cm$^{-1}$ and at 720 cm$^{-1}$ represents a very important feature of the POHA structure. These peaks are related to pseudo-spinel gels and also with those of the transition aluminas that consist of tetrahedrally (AlO$_4$) and octahedrally (AlO$_6$) coordinated aluminum. The AlO$_6$ peaks can be assigned to Al-OH and Al-O stretch modes at 620 cm$^{-1}$ and 520 cm$^{-1}$ respectively, while the peaks at 720 cm$^{-1}$ and 870 cm$^{-1}$ are related to AlO$_2$ stretching modes. The spectrum also shows peaks at 1507 and 1400 cm$^{-1}$ assigned to d-glucose that is entrapped into the as-synthesized POHA inner structure. The pseudo-spinel structure formed in aluminate solutions are metastable structures which could provide more organized trihydroxide (Al(OH)$_3$) and oxyhydroxide (AlO(OH)) phases by aging and treatment in appropriate pH.

Speciation studies showed that in conditions where OH$^-$/Al molar ratio values are below 4, there was a high tendency of spinel polymeric aluminum species formation, which would be made by the coalescence of monomeric, dimeric and oligomeric (like Al$_{13}$ species) in solution. Herein, since the experimental start condition has an OH$^-$/Al molar ratio value of approximately 1.3 it should be an ideal or a more favorable condition to obtain a pseudo-spinel solid. The general and oversimplified formula of this polymeric structure is γ-Al$_2$O$_3$·xH$_2$O·yOH with its structure bearing the oxo and hydroxo bridges as well as edge hydroxyl subunits, therefore it was named as poly oxo-hydroxy aluminate, POHA. Figure 1(b) shows a general infrared spectrum of the γ-aluminas obtained from POHA powders after calcination. The peaks at 3464 and 1643 cm$^{-1}$ are attributed to stretching and bending modes of strongly adsorbed water. The intense bands centered at 793 and 578 cm$^{-1}$ are assigned to AlO$_2$ and AlO$_3$ coordinate aluminum that are typical of γ-Al$_2$O$_3$. The calcination process triggered the decomposition of the d-glucose.
3.2 X-Ray Diffraction

The Figure 2 shows the XRD results of the as-synthesized powder (as-POHA). Figure 3 depicts the diffractogram of the samples calcined at different temperatures.

The peaks of the as-POHA powder in which are identified the crystallographic planes corresponding to potassium aluminum oxide hydrated species (PDF 19-0927 and 40-0703). Also, there were peaks corresponding to bayerite phase (PDF 20-0011 for Al(OH)3) and oxo hydroxy aluminum species (PDF 05-0355 for AlO(OH))41. After calcination at 300 ºC, there are peaks corresponding to bayerite, boehmite and also some of the γ-Al2O3 phase. The arrows in fig. 3(A) indicate also the presence of some non-stoichiometric aluminum oxide hydrate (PDF 22-1119). The samples calcined at 400, 700 and 900 ºC showed sharp peaks at 2θ of 46.2° and 67.2°, referring to the (400) and (440) peaks of γ-alumina, respectively (PDF 10-0425). The increase in the calcination temperature did not change the position of the peaks, thus indicating that there is no change of the structure9. The small band around 2θ < 75-80° could be referred to the vacancies of the octahedral sites that are characteristic of these spinel structures. Accordingly, in this work, the threshold temperature to achieve the active phase of γ-alumina was 400 ºC.

3.3 Nitrogen physisorption

The nitrogen adsorption/desorption isotherms and particle size distributions of the samples are illustrated in Figure 4. Table 1 presents the textural results from BET and BJH methods.

The samples calcined at 300, 400 and 700 ºC exhibited type IV isotherms with hysteresis loop between H1 and H2 type, characteristic of cylindrical or spherical pores and regular pore size distribution. Whilst the powder obtained at 900 ºC, which showed type II isotherm with hysteresis loop type H3, indicating the presence of disordered slit or wedge pore structures44. There is no indication of micropores since the isotherms did not present the usual “knee” at the beginning of the adsorption branch, that also can be indicated by the t-plot graph (fig. 4(c)), which has a negative intercept on the volume axis.

All samples’ isotherms did not show a plateau when P/ P0 < 1 probably due to some macroporous presence that was not completely filled or interparticle porosity45. All samples showed a pore size distribution within the mesoporous range. As expected, the increase in temperature causes annealing of the grains that result in a decrease in the specific surface area and a broader distribution of pore sizes (especially for 900 ºC)44. The calcination of the POHA at 400 ºC presented the best textural properties taking into account the specific surface area, pore size distribution and pore volume. The lack of micropores shows that this material could be more selective to adsorptive applications.

The high surface area mesoporous aluminas are commonly achieved through the use of structure driving agents (SDA) such as pluronic block copolymers, ionic surfactants, fatty acids, and long chain amines46-50. Recently, the use of glucose was considered to replace SDAs39. Compared with other methods of direct precipitation16-18,37, the current synthetic route brings a gain in order to produce γ-Al2O3 without the
Figure 3. X-ray diffraction results for each calcination temperature: A: 300 °C, B: 400 °C, C: 700 °C and D: 900 °C.

Figure 4. (a): Nitrogen isotherms of calcined POHA; (b): Pore size distribution (PSD) obtained from the adsorption branch using BJH method of calcined POHA. (c) t-plot detail revealing lack of micro-pores.

Table 1. Textural properties from nitrogen sorption measurements: specific surface area (SBET), pore volume (Vpore) and pore diameter (Dpore), for each calcination temperature of the POHA powders.

<table>
<thead>
<tr>
<th>T calcination (°C)</th>
<th>S_BET (m²/g)</th>
<th>V_pore (cm³/g)</th>
<th>D_pore (nm)</th>
</tr>
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<tbody>
<tr>
<td>300</td>
<td>72</td>
<td>0.13</td>
<td>3.5</td>
</tr>
<tr>
<td>400</td>
<td>282</td>
<td>0.26</td>
<td>6.2</td>
</tr>
<tr>
<td>700</td>
<td>166</td>
<td>0.26</td>
<td>4.0</td>
</tr>
<tr>
<td>900</td>
<td>129</td>
<td>0.24</td>
<td>10.3</td>
</tr>
</tbody>
</table>

use of SDAs leading to a large surface area gamma alumina of easy work-up. Studies are being made to expand the production scale and to further increase the surface area.

3.4 SEM images

The Figure 5 presents the SEM micrograph for calcined samples. In fig. 5(a), calcination at 300 °C it is possible to
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Figure 5. SEM images of the POHA powders after calcination; (a): 300 °C; (b): 400 °C; (c): 700 °C; (d): 900 °C.

notice that for this temperature there is no formation of uniform particle shape. After 400 °C calcination temperature, there are mostly spherical particles with an average diameter of 1.2 µm. The sample calcined at 700 °C showed more agglomeration and particles with an average diameter less than 1 µm and larger aggregates. After the calcination at 900 °C, there is a densification of the system which showed particles with sizes greater than 2 µm.

3.5 Synthetic Approach

For the formation of the heterogeneous gel mixture, a high ethanol fraction (EtOH:H₂O 3:1) is needed for aluminum consumption. Assays with different proportions of H₂O-EtOH (v:v), KOH and d-glucose as the additive, showed different behavior. With a higher water fraction, the gel was not formed and slow precipitation of common polymorphic aluminum oxide hydrates was verified. On the other hand, with higher ethanol amount, the formation of the gel was faster and the best condition was found to be H₂O-EtOH 1:3 (v:v). These results point to similar pathway to those found in a previous work about ripening (dissolution-precipitation) of elemental aluminum in water-ethanol mixtures. The aluminum consumption is dependent upon its own concentration, pH, nature, and type of base and its counter-ion, and stability of the aluminate species in the reaction media. In this process, the hard oxide shell covering the aluminum is dissolved with the metal becoming free and active to be leached. Thereby, the aluminum speciation in solution reveals the presence of monomeric and oligomeric aluminates ranging from 6- to 5- and 4-coordination numbers. The aluminum coordination in solution has been considered as an important feature for phase structure when organic additives or solvents are employed. As mentioned above (section 1), the aluminum oxidation in H₂O-EtOH under sonication with a higher fraction of ethanol in aqueous mixture (i.e. 3:1, v:v) was essential to the faster precipitation of the aluminum trihydroxide (bayerite). As highlighted, the presence of d-glucose had a fundamental influence to achieve the POHA material since the bulk condition was the same, i.e., 1:3 water-ethanol. Since the d-glucose is capable of making hydrogen bonds, it could get in coordination with the interlayers of the initial oligomeric structures or even with the fresh aluminum cation and then favor the early aggregation of the aluminate species analytically found. These results evidence the d-glucose and ethanol are serving as targeting agents. The interference of hydroxyl compounds on the precipitation of aluminum hydroxides
and oxides has been noted in other studies\textsuperscript{37,36}. In parallel, the sonochemical route showed to be more efficient than the stirring one for the aluminum oxidation. The complete aluminum dissolution occurred in a shorter time. Once sonication gives rise to cavitation on the surface, the aluminum surface is activated faster. The sonicated reaction affording the heterogeneous gel was three times faster than the stirred reaction.

Lastly, an important point is the direct change from POHA to the γ-alumina without a previous preparation of common trihydroxide or oxyhydroxide precursors. Despite the XRD peaks assignment of bayerite and boehmite in the calcined powder at 300 °C, these intermediates do not interfere with the formation of the γ-alumina phase. Thus the decisive factor appears to be the pre-aggregation of ionic aluminum oligomers with pseudo-spinel arrangements that induces the formation of the respective alumina on heating. This could be related to a Tandem process in which the common intermediates of reaction steps are not isolable.

4. Conclusion

The use of the as-synthesized POHA powder with d-glucose for the preparation of γ-alumina is a new method due to the decrease in the overall synthesis time and temperature. Since there was no requirement of an aging process for any aluminum hydroxide precursor, the γ-alumina phase was obtained at a lower temperature compared to other methodologies. It is very likely that the POHA changes towards the γ-Al\textsubscript{2}O\textsubscript{3} phase at lower temperature it can be assigned as a tandem transformation. The heating treatment at 400 °C proved to attain the best textural properties, such as high specific superficial area and a narrow pore size distribution. These alumina are used hereafter as catalyst supports for ZnO nanoparticles for promoting photooxidation reactions in our laboratory.

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6. References

2. Davis ME. Ordered porous materials for emerging applications. Nature. 2002;417:813-821. DOI: 10.1038/nature00785
16. Elbadzadeh T, Asadian K. Microwave-assisted synthesis of nanosized α-Al\textsubscript{2}O\textsubscript{3}. Powder Technology. 2009;192(2):242-244. DOI: 10.1016/j.powtec.2009.01.001


