Synthesis of pseudoboehmite – effect of acetate ion

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Pseudoboehmite (AlOOH.xH₂O) is one of the precursors of alumina. Its calcination produces different phases of alumina and at 1200°C the most stable phase, α-alumina, is formed. The synthesis of pseudoboehmite by the sol-gel process results in a product with high purity, high specific surface area, and high reproducibility. The aging of the pseudoboehmite at temperatures above room temperature results in pseudoboehmites with distinct properties. In this work we report the synthesis of pseudoboehmite by the sol-gel process, using aluminum nitrate and aluminum chloride as precursors, and investigate the effect of acetate ion on crystallinity, adsorption capacity, particle morphology, thermal properties and specific surface area. The X-ray diffraction data of the synthesized pseudoboehmites in the presence of the acetate ion revealed high quality nanoparticles.

Keywords: Pseudoboehmite, acetate ion, powder synthesis, factorial experimental design, sol-gel.

1. Introduction

Pseudoboehmite (AlOOH.xH₂O) is an aluminum compound of the synthetic fine ceramic type, precursor of alumina. It has an orthorhombic structure (a = 0.366936 nm, b = 1.221 nm, c = 0.288679 nm), in which it is formed by two octahedra layers of oxygen partially filled by aluminum cations. Its unit cell is slightly larger than that of the boehmite and this occurs due to the large incorporation of water.

Several papers in the literature report the importance of this material in catalysis, drug delivery system including DOX, a typical chemotherapeutic anticancer drug and nanocomposites. The presence of pseudoboehmite in the catalyst Pt/HZSM-48+ pseudoboehmite for the synthesis of benzene through methycyclcopentane shows that pseudoboehmite increases the total amount of acid sites and weakens the acid strength, compared to those of the Pt/HZSM-48 catalyst. Lewis acid sites were more abundant than Brønsted acid sites over the Pt/(HZSM-48+pseudoboehmite) catalysts resulting in the increase of selectivity to the ring-enlargement reaction over to the ring-opening reaction. It is difficult to overestimate the importance of alumina in today’s catalysis. Therefore, from this point of view, undertaking research on the preparation of pseudoboehmite is most justified.

By its calcination α-alumina is obtained, which is the most stable phase of alumina. The transformation of aluminum oxide to the more stable hexagonal form of alumina, α-alumina, does not occur directly. Starting from the boehmite (ALOOH) or the pseudoboehmite, the transformation process goes through a series of metastable phases, following the order presented in Equation 1.

\[
\text{AlOOH.xH}_2\text{O} \rightarrow \gamma - \text{Al}_2\text{O}_3 \rightarrow \delta - \text{Al}_2\text{O}_3 \rightarrow \theta - \text{Al}_2\text{O}_3 \rightarrow \alpha - \text{Al}_2\text{O}_3
\]

(1)

The production of pseudoboehmite can be carried out by the sol-gel process using aluminum chloride or nitrate, for instance. This process consists in the use of a suspension of fine particles of colloidal dimensions (sol) that under certain conditions transform into a continuous network (gel), thus generating a semi-rigid mass for later drying. The particle size and specific surface area of pseudoboehmite influences the temperature of transformation of pseudoboehmite in the transitional alumina and into α-Al₂O₃. Previous reports describe the use of acetate ion in the synthesis of pseudoboehmite. It has been argued that the presence of the acetate ion in the alkaline reaction medium would be essential for obtaining thick plates morphology (near “2D” crystals). The synthesis of pseudoboehmite using aluminum nitrate and aluminum chloride as precursor using acetate in reaction synthesis has not been reported thus far. In this paper we study the influence of acetate ion in the synthesis of pseudoboehmite using aluminum nitrate, aluminum chloride, ammonium hydroxide, and sodium hydroxide.

Two-factor factorial experimental design is very useful in experimental procedures, in which the influence or interaction of variables on the expected outcome is desired. This procedure is performed, specifying the factor to be studied and assigning to it, +1 coefficients, for higher levels and -1, for lower levels. A two-level factorial design for the study of three variables is represented as 2³, resulting in
eight tests arranged in a matrix of experiments. Thus, after a statistical calculation of the effects, it is possible to interpret the influences and/or interactions of the variables studied in the experimental process\textsuperscript{14,15}.

2. Experimental

2.1 Sample preparation

The pseudoboehmite was obtained by precipitating a solution of aluminum salts in the presence of acetate ions in a basic solution, according to the upper and lower levels listed in Table 1. The precipitations were performed at room temperature, adopting after the synthesis, for all samples, the aging time of 96 h, at the boiling temperature. For the synthesis of pseudoboehmites, 8 trials were obtained, organized in a factorial experimental design of $2^3$, in which the variables are the reagents themselves, classified as Aluminum Salt (A), Acetate (B) and hydroxide (C), all divided into (+1) and lower levels (-1), in order to analyze its effects on the properties of obtained product. Table 2 shows the matrix of experiments with the eight synthesis conditions. Note that the eight synthesis conditions are different.

The tests were carried out using the following molar ratio for the use of acetate: 1 mol of Al: 1 mol acetate (CH$_3$COONa or CH$_3$COONH$_4$): 50 mol H$_2$O. Thus, a solution of nitrate or chloride salt (AlCl$_3$, 6H$_2$O or Al(NO$_3$)$_3$, 9H$_2$O) and acetate (CH$_3$COONa or CH$_3$COONH$_4$) was dripped in an basic solution (NaOH or NH$_3$OH) to give the pseudoboehmite gel.

In the factorial experimental design, the error can be estimated using the interactions of 3 orders. The error of the effects without the realization of repetitions can be estimated using the interactions of 3 orders. The error of the effects considered as non-significant. The equation that gives the variance of the effects can be estimated by Equation 2, where $ef$ is the interaction effects considered as experimental errors, $V(ef)$ is the variance and $l$ is the total number of effects considered, being also the number of degrees of freedom.

$$V(ef) = \Sigma(ef)^2 / l$$

(2)

Table 1. Experimental variables and levels.

| Variables                  | Lower level (-1) | Higher level (+1) |
|----------------------------|------------------|-------------------|
| A aluminum precursor       | AlCl$_3$, 6H$_2$O| Al(NO$_3$)$_3$, 9H$_2$O |
| B acetate addition         | CH$_3$COONa      | CH$_3$COONH$_4$   |
| C hydroxide used in the synthesis | NaOH             | NH$_3$OH          |

Table 2. Matrix of experiments.

| Sample number | A  | B  | C  |
|---------------|----|----|----|
| 1             | -  | -  | -  |
| 2             | +  | -  | -  |
| 3             | -  | +  | -  |
| 4             | +  | +  | -  |
| 5             | -  | -  | +  |
| 6             | +  | -  | +  |
| 7             | -  | +  | +  |
| 8             | +  | +  | +  |

After the synthesis, the pH of the solution was kept alkaline and the product was aged for 96 h under reflux at the boiling temperature of the mixture in which the glass flask coupled to the condenser was kept under heating using a thermal mantle. After that the gel was vacuum filtered and dried to obtain a powder by freeze-drying. The dry powder was characterized by x-ray diffraction, thermal analysis (thermogravimetric analysis and differential thermal analysis), nitrogen adsorption isotherm, specific surface area by the B.E.T. method and by scanning electron microscopy (SEM) using secondary electron and energy dispersive spectroscopy (EDS) detector.

2.2 Characterization of the samples

X-ray diffraction analysis was performed using a Rigaku MultiFlex powder diffractometer with CuK$_\alpha$ radiation ($\lambda = 1.542$ Å) under operating conditions at 40 KV voltage and 20 mA current. The scanning angle (20) was varied from zero to 90° at 2° min$^{-1}$ scanning speed.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed using a Netzsch equipment, model STA 449F3-Jupiter. A quantity of 0.013 g of sample was placed in open alumina crucible and the DTA-TG measurements were carried out simultaneously. Samples were heated from ambient temperature to 1300°C at a rate of 10°C min$^{-1}$ using a 60 mL min$^{-1}$ nitrogen flow.

Nitrogen adsorption and desorption isotherms were determined using a Belsorp max equipment. The samples were previously outgassed at 100°C for a period of 24 h. The specific surface area was determined by the Brunauer Emmett Teller method\textsuperscript{16} from the nitrogen adsorption isotherms data acquired at 77K temperature.

SEM images were obtained using a JEOL JSM-6510 microscope. Samples used for SEM analysis were placed on stubs and coated (using the sputtering technique) with a thin film of gold. Secondary electron detection and an EDS detector were used in our SEM analysis.

3. Results and Discussion

3.1 X-ray diffraction data

Figure 1 shows the x-ray diffraction patterns of samples 1 to 8. All samples exhibited the X-ray diffraction peak position characteristic of pseudoboehmite, with a pattern consistent with previous published results\textsuperscript{17}. The boehmite phase presents enlarged peaks showing that they have very low average crystallite size and it is difficult to differentiate this phase from pseudoboehmite, beta boehmite and alpha boehmite. So, it was adopted in a generic way as boehmite (ICDD 83-2384). The diffraction patterns of samples 2, 4, and 7 exhibited another phase besides pseudoboehmite at 20 ~20° and 20-40°. This second phase is attributed to bayerite (ICDD 77-117). However, the intensity of the second phase diffraction peaks are smaller than that of pseudoboehmite mainly in samples 2 and 4. The peaks of bayerite were marked as by in Figure 1.
3.2 Differential thermal analysis and thermogravimetric analysis

The results of the thermal analysis of sample 1 are presented in Figure 2 where one can observe the standard peaks associated with the pseudoboehmite\textsuperscript{18,19}.

An endothermic peak at \(~105.4\) °C in DTA was observed and it corresponds to the loss of adsorbed water; the endothermic peak at \(~434.1\) °C (observed in the second derivative thermogravimetry, 2\textsuperscript{nd} peak DTG), corresponds to the transformation of the pseudoboehmite into \(\gamma\text{-Al}_2\text{O}_3\).

The exothermic peak at DTA for the final transformation into \(\alpha\text{-Al}_2\text{O}_3\), the most stable alumina phase, occurs at \(~1220.5\) °C. We determined a mass loss of 21.71 wt%, from room temperature to 1300 °C.

Figure 1. X-ray diffraction data of samples (sample 1 (a), sample 2 (b), sample 3 (c), sample 4 (d), sample 5 (e), sample 6 (f), sample 7 (g), sample 8 (h). by = peaks attributed to bayerite.

Figure 2. DTA and TG analysis of sample 1.
Table 3 shows the results from the DTA and TG analysis. The analyzed data was: the peak of the 1st DTG (associated with the loss of water), 2nd peak DTG (associated with the transformation of pseudoboehmite into $\gamma$-Al$_2$O$_3$) and last peak in DTA (temperature of $\alpha$-Al$_2$O$_3$ formation). The other phases transformation ($\gamma, \delta, \theta$) were not observed at DTA. The probable temperature of formation of the other phases according to the literature is shown in Figure 2.

The results listed in Table 3 were treated using the 2$^3$ factorial experimental design and the results are presented in Table 4.

In the 1st peak DTG results the interactive effects were, in increasing order, AC and AB. In the 2nd peak DTG the main effect observed was the alkali ion. According to factorial experimental design results when the NaOH was changed to NH$_4$OH, there was a reduction in the temperature of the pseudoboehmite due to the $\gamma$-Al$_2$O$_3$ transformation. It was also observed that interactive effects were significant, in increasing order, AB, BC and AC. Considering that variable B is related to acetate ions, the interaction of this ions with the aluminum precursor salt and the hydroxide used has a significant influence on pseudoboehmite synthesis. Thus, as the acetate ion appears in two interactions, it can be stated that this variable is the most important in the synthesis of pseudoboehmite.

In the temperature of $\alpha$-Al$_2$O$_3$ formation the interactive effects were also more important than the main effects. The interactive effect with more significance was the AC. Considering that the interaction AB was relevant in the specific area, the interactive effects were, in increasing order, AB, BC and AC. This result is the same for the 2nd peak DTG.

As observed in the thermal analysis results the aluminum precursor and the acetate addition interaction increase the temperature of $\alpha$-Al$_2$O$_3$ formation.

### 3.3 Nitrogen isotherms and specific surface area

The specific surface area data are presented in Table 5. The values of the specific surface area are very high when compared to the data reported in the literature. There is no significant difference in the specific surface area among the investigated samples. The crystallite size of boehmite and pseudoboehmite, and the specific surface area, has a strong correlation with the formation temperature of $\gamma$-Al$_2$O$_3$ and the phase transition temperature of $\theta$- to $\alpha$-Al$_2$O$_3$. But comparing previous results with the listed data in Table 5, the differences of the values in Table 5 were so small that they promote no change in the temperature of the pseudoboehmite to $\gamma$-Al$_2$O$_3$ and the $\theta$- to $\alpha$-Al$_2$O$_3$ phase transformation. The phase transformation diminishes the value of specific surface area with the increase of temperature. In literature the only exception is the carbon coated alumina that hinders the sintering of the $\delta$-Al$_2$O$_3$.

According to the data and taking the calculations for factorial planning we determined the corresponding specific surface area results which are listed in Table 6. Note that the variables A and C, individually, are not significant in relation to the specific area, but again the interactions are significant for the specific surface area results. In the specific surface area, the interactive effects were, in increasing order, AB, BC and AC. This result is the same for the 2nd peak DTG. As observed in the thermal analysis results the aluminum precursor and the acetate addition interaction are significant for the specific surface area results.

$N_\text{ads}$ adsorption-desorption isotherms of the samples show that they correspond to type IV of the International Union of Pure and Applied Chemistry (IUPAC) classification, which indicates that the pores of the samples are composed of mesopores and macropores. Figure 3 shows the adsorption and desorption isotherms obtained for all samples.

### Table 3. DTA and TG results.

| Sample | 1st peak of DTG | 2nd peak of DTG | Temperature (°C) of $\alpha$-Al$_2$O$_3$ formation in DTA |
|--------|-----------------|-----------------|--------------------------------------------------------|
| 1      | 96.1            | 434.1           | 1220.5                                                 |
| 2      | 84.9            | 438.8           | 1267.4                                                 |
| 3      | 101.1           | 421.9           | 1284.6                                                 |
| 4      | 95.7            | 418.6           | 1260.2                                                 |
| 5      | 93.2            | 413.3           | 1256.0                                                 |
| 6      | 85.0            | 324.4           | 1293.0                                                 |
| 7      | 90.9            | 395.3           | 1235.3                                                 |
| 8      | 103.4           | 395.3           | 1235.3                                                 |

### Table 4. Factorial 2$^3$ experimental design results for the 1st and 2nd DTG peaks and the temperature of $\alpha$-Al$_2$O$_3$ formation.

| Medium effects and interactions | 1st peak DTG | 2nd peak DTG | $\alpha$-Al$_2$O$_3$ formation |
|---------------------------------|--------------|--------------|--------------------------------|
| Medium                          | 93.8         | 405.8        | 1263.7                         |
| Main effect, A                  | -3.1         | -23.0        | 0.3                            |
| Main effect, B                  | 8.0          | 6.0          | 9.2                            |
| Main effect, C                  | -1.3         | -45.2        | 11.0                           |
| Interactions between factors    |              |              |                                |
| AB                              | 6.6          | 19.1         | -41.4                          |
| AC                              | 5.2          | -23.7        | -10.9                          |
| BC                              | 0.1          | 22.4         | -19.3                          |
| ABC                             | 3.7          | 23.1         | -5.7                           |
The hysteresis loops may exhibit a wide variety of shapes, and according to Sing et al.\(^2\), they provide the information about the material structure. Adsorption hysteresis arises when the adsorption and desorption of nitrogen curves do not coincide. The hysteresis appearing in the multilayer range of physisorption isotherms is associated with capillary condensation in mesopore materials.

Sample 2 has a hysteresis type H3. According to the literature\(^2\) the Type H3 loop does not exhibit any limiting adsorption at high \(p/p^0\). It is observed in aggregates of primary particles that have a lamellar habit, plate-like particles, and indicate the adsorption of nitrogen in the slit-shaped pores. According to Sing et al.\(^2\), “an agglomerate is defined as an assemblage of particles rigidly joined together and an aggregate as an assemblage of particles which are loosely coherent”.

Samples 1, 3, 4, 6 and 7 have a hysteresis with H1 shape. Type H1 hysteresis is often associated with porous materials known, from other evidence, to consist of agglomerates or compacts of approximately uniform spheres in regular array.

### Table 5. Specific surface area of the samples.

| Sample | Specific surface area (m\(^2\)/g) |
|--------|----------------------------------|
| 1      | 304.68                           |
| 2      | 331.26                           |
| 3      | 311.51                           |
| 4      | 299.28                           |
| 5      | 321.99                           |
| 6      | 292.33                           |
| 7      | 343.36                           |
| 8      | 314.98                           |

### Table 6. Full factorial experimental design results for specific surface area.

| Medium effects and interactions | Specific surface area |
|---------------------------------|-----------------------|
| **Medium**                      | 314.9                 |
| **Main effect**                 |                       |
| A                               | -10.9                 |
| B                               | 4.7                   |
| C                               | 6.5                   |
| **Interactions between factors**|                       |
| AB                              | -1.4                  |
| AC                              | -18.1                 |
| BC                              | 17.3                  |
| ABC                             | 10.0                  |

### Table 7. Full factorial experimental design results for EDS analysis.

| Sample | Oxygen | Sodium | Aluminum | Silicon | Chlorine | O/Al ratio |
|--------|--------|--------|----------|---------|----------|------------|
| 1      | 61.98  | 0.68   | 36.65    | 0.91    | 0.47     | 1.7        |
| 2      | 58.10  | 0.68   | 35.51    | 0.91    | 0.47     | 1.6        |
| 3      | 59.25  | 0.68   | 37.89    | 1.86    | 1.00     | 1.6        |
| 4      | 61.31  | 0.68   | 36.94    | 1.75    | 1.00     | 1.6        |
| 5      | 58.16  | 0.68   | 38.95    | 1.35    | 2.54     | 1.5        |
| 6      | 65.97  | 0.68   | 34.03    | 2.00    | 1.00     | 2.0        |
| 7      | 63.80  | 0.68   | 30.80    | 2.80    | 2.60     | 2.1        |
| 8      | 61.45  | 0.68   | 37.62    | 0.93    | 1.6      | 1.6        |
Figure 3. Absorption and desorption isotherms obtained (sample 1 (A), sample 2 (B), sample 3 (C), sample 4 (D), sample 5 (E), sample 6 (F), sample 7 (G), sample 8 (H)).
Figure 4. SEM of the samples 1 to 8.
4. Conclusions

The pseudoboehmite was obtained by precipitating a solution of aluminum salts (aluminum nitrate and aluminum chloride) in the presence of acetate ions (ammonium acetate and sodium acetate) in a basic solution (sodium hydroxide or ammonium hydroxide). In eight different synthesis conditions pseudoboehmite was obtained, confirmed by x-ray diffraction experiments and EDS analysis.

For the conditions and reagents studied it was observed that the use of acetate ion in the synthesis of pseudoboehmite has no influence alone in the temperature of phase transformations and in the specific surface area of the product. The interaction of the acetate with the aluminum precursor and the hydroxide used in the synthesis has a significant effect in the properties of the synthesized product.

The analysis of the DTA and TG data using the $2^3$ factorial experimental design shows that the interactions between the studied variables are more important in the temperature of pseudoboehmite to alumina transformations than the main effects. The interaction of aluminum precursor and acetate addition was relevant in the temperatures of phase transformation of pseudoboehmite to alumina. This interaction increases the temperature of the 1st and 2nd peaks of DTG and promoted the reduction of the $\alpha$-$\text{Al}_2\text{O}_3$ formation.

Using the $2^3$ factorial experimental design for the analysis of the specific surface area it was observed also that the interactions are more important than the main effects. For the alumina phase transformations observed in thermal analysis the variable associated with ion acetate appears in two interactions of the $2^3$ factorial experimental design.

The analysis of the 8 different samples using nitrogen adsorption isotherm and scanning electron microscopy using secondary electron detector shows that all samples has high porosity and contain mesopores and macropores. The nitrogen adsorption/desorption isotherm indicates that one sample contain aggregates of plate like particles.

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