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Synthesis and characterization of aluminum carboxylate gels

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Abstract

Aluminum formate and basic acetate gels obtained from commercial pseudoboehmite were synthesized in this work. Phase evolution after successive thermal treatments was studied on the raw material and both gels. In both carboxylates the influence of aging time on the composition, the crystalline structure and the phase transition temperatures was studied by X-ray diffraction (XRD) and differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Two different stages were observed in the thermal decomposition of both carboxylates: the first, corresponding to the decarboxilation and dehydration of the gels, was different for both cases because of the different type of carboxilic acids used; and the second, corresponding to the formation of transition aluminas, was the same whatever the precursor used. However, whenever the aging time was changed on any of the carboxylates, the mechanisms of the thermal transformations were affected.
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1. Introduction

Alumina is an important oxide for the production of technical ceramics and is extensively used in catalysis, microelectronics, refractories and structural applications. Alumina ceramic membranes are new materials technically important in separation processes associated with low requirements of energy, high selectivity and capacity to operate at low and high temperatures. Dip-coating on a porous support is one of the methods used to make microporous membranes. In this method, depending on the membrane pore size required, the precursor particles can be prepared by different techniques [1–6].

The boehmite (AlOOH) is the most common alumina precursor, which undergoes a sequence of transformations with temperature from the transition aluminas (γ, δ, θ) to the α-stable form. Formation of transition alumina phases is a consequence of the relative surface energies associated with the phases. Usually these transformations are simply written as $\gamma \rightarrow \alpha$-$Al_2O_3$, as these phases are the predominant ones, which are also of technical interest. Many authors succeed in getting the α-Al_2O_3 transition at lower temperatures than 1200 °C [7–9].

The membrane synthesis by the dip-coating method using boehmite sols was discussed in many works [9–12]. The preparation of alumina ceramic membranes from aluminum hydrates or salts as precursors

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implies a competition between the obtention of a controlled porosity system with a suitable mechanical strength and the material densification as a consequence of the remaining stable phases after thermal treatment.

Callender et al. [13] made a complete study of the reaction between pseudoboehmite with several carboxylic acids. The synthesis of carboxylate-alumoxanes without aqueous media was studied by Landry et al. [14].

Metal carboxylates are potential precursors for deposition and the following formation of oxides at low temperatures [15]. Other authors study the densification of the gels obtained from aluminum basic acetate with seeding agents [16]. Rajendran and Bhattacharya [15] study the formation of α-Al_2O_3 obtained from commercial carboxylates, observing the transformation sequence and the intermediate phases.

The characteristics and behavior of the aluminum formate and basic acetate gels used to produce membranes by dip-coating were analyzed in this work. Gels were obtained by reaction between pseudoboehmite and formic and acetic acid. The sequence of the different phases which were developed during thermal decomposition could be observed. The aging time influence on the behavior of these gels was also studied.

2. Materials and methods

2.1. Raw materials, methods and equipment used

A commercial pseudoboehmite (γ-AlOOH), whose characteristics will be described in Section 3, was used as starting material for the synthesis of aluminum carboxylate gels. Formic acid, $HCOOH$ proanalysis 98% (w/w) $d = 1.218$ g/ml and glacial acetic acid, $COOHCH_3$ 99.77% (w/w) $d = 1.05$ g/ml, were also used.

Crystalline phases were determined by X-ray diffraction (XRD) with a Philips Pw3710 equipment, Cu Kα, Ni filter, in the $2\theta = 5$–$80°$ region. The cards of the identified compounds correspond to the International Centre for Diffraction Data (ICDD).

Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using a Netzsch STA 409 equipment. Tests were performed with 200 mg of sample on platinum–iridium

crucibles with a heating rate of $10°C/min$ up to $1200°C$, in air atmosphere and using tabular α-Al_2O_3 as reference. Weight losses were calculated from the TGA.

Carboxylates were obtained by stirring mixture of the pseudoboehmite with of each of the acids mentioned. The reaction took place at room temperature.

3. Results

3.1. Pseudoboehmite characterization

The starting pseudoboehmite was characterized by XRD in its original state and as function of thermal treatments. The γ-AlOOH was dried at $100°C$ and then calcined at 800, 1000 and $1200°C$ successively, during 1 min with a heating rate of $10°C/min$. The XRD patterns obtained are shown in Fig. 1.

The diagram of the sample treated at $100°C$ shows peaks that are in accordance with those of the γ-AlOOH (card no.: 21-1307). This material as slightly crystalline; hence it was identified as pseudoboehmite, as reported by Mackenzie [17]. The transformations of the transition aluminas, γ-Al_2O_3 phase (card no.: 10-0425), δ-Al_2O_3 phase (card no.: 16-0394), θ-Al_2O_3 phase (card no.: 35-0121), were observed in the diffractograms of the samples calcined from 800 to $1200°C$. The first traces of the α-phase (card no.: 42-1468) could be appreciated when the samples reached the $1200°C$. It was observed that after a soaking time of 2 h at $1200°C$ the transformation to the α-phase was almost complete, in agreement with Rajendran and Bhattacharya [15].

The TGA and DTA curves obtained for the pseudoboehmite previously dried at $100°C$ are shown in Fig. 2. Two stages of weight losses were observed up to $600°C$ in the TGA curve. The first one extended from 20 to $230°C$ and a loss of 14.1% took place, corresponding to the removal of physically bonded water molecules that are present in the pores of the γ-AlOOH. This stage had an endothermic effect that appeared by DTA at $147°C$. The second lost occurred from 230 to $600°C$ and corresponded to the pseudoboehmite transformation into γ-Al_2O_3, with an endothermic peak at $492°C$ and a weight loss of 14.7%.

The exothermic effects corresponding to the $\gamma \rightarrow \delta$, $\delta \rightarrow \theta$ and $\theta \rightarrow \alpha$-$Al_2O_3$ transitions were not
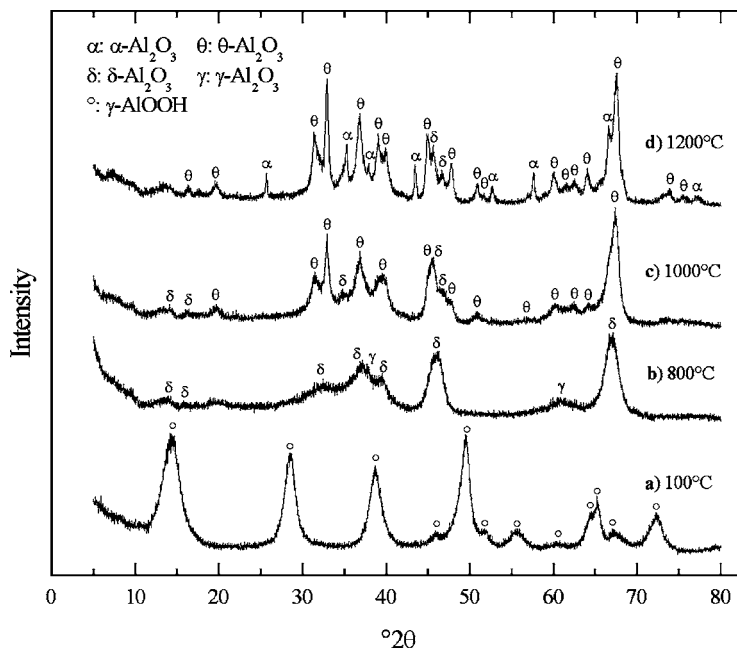
Fig. 1. XRD of γ-AlOOH at different temperatures.

detected in this diagram; however, the existence of these processes was confirmed by XRD.

This sequence of phases as function of temperature was in agreement with what was observed by other authors [15,17].

3.2. Aluminum carboxylates

3.2.1. Synthesis

An amount of 59 ml of formic acid was added to a 30 g of pseudoboehmite sample to obtain aluminum
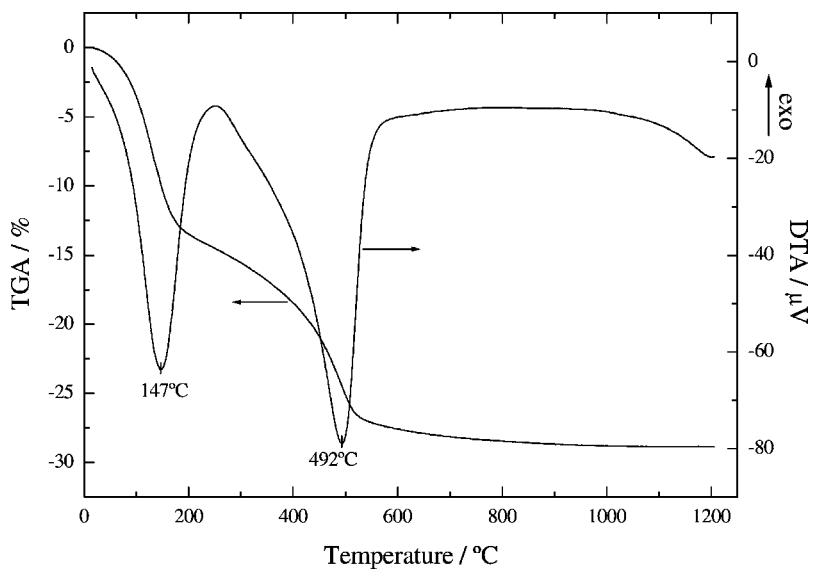
Fig. 2. TGA and DTA of γ-AlOOH.

formate; on the other hand, 95.5 ml of acetic acid were added to another 30 g of γ-AlOOH to obtain aluminum basic acetate. Both samples were made at room temperature, manually stirring the reactives for half an hour. In both cases white color gels were obtained. They were stored in closed containers and set aside at room temperature.

By means of XRD and DTA–TGA, those gels were characterized as regards their evolution under successive thermal treatments. Using these techniques the changes and their behavior in relation with aging were studied.

Landry et al. [14] studied the same reaction between the pseudoboehmite and different carboxylic acids (R = n-C$_{n'}$H$_{2n'+1}$ with $n' = 1$–3 and 13) but under different conditions, that is to say, the authors employed reflux at temperature during 4 days and they obtained in all cases stable compounds known as carboxylate-alumoxanes.

3.2.2. Aluminum formate characterization

XRD patterns for aluminum formate gel samples taken at different stages of aging are shown in Fig. 3. The diffractogram for the gel aged 30 days can be observed in that figure, where well defined peaks that correspond to Al(CHO$_2$)$_3$·3H$_2$O (card no.: 38-0655)

and peaks corresponding to the not reacted γ-AlOOH could be identified. The diffractogram for the gel aged 200 days shows the peaks corresponding to non-hydrated Al(CHO$_2$)$_3$ (card no.: 38-0583) which is the predominant phase, as well as peaks of lower intensity of Al(CHO$_2$)$_3$·3H$_2$O and of γ-AlOOH that did not react.

The DTA obtained for both samples of this gel are shown in Fig. 4. As regards the aged 30 days sample, three endothermic effects were observed. The first one, at 259 °C, was due to the loss of adsorbed H$_2$O by the trihydrate formate. The second one, at 382 °C, was due to the decomposition of aluminum formate to produce γ-Al$_2$O$_3$; and the third one, at 485 °C, caused by the residual γ-AlOOH decomposition.

In the aged 200 days sample an important endothermic effect was centered at 135 °C, due to the adsorbed water loss. The shoulder at approximately 260 °C hardly suggest the trihydrate formate presence. At 365 °C, the effect of the salt decomposition and at 476 °C, the pseudoboehmite conversion to γ-Al$_2$O$_3$, could be observed. These last two effects took place at a temperature slightly lower than that of the aged 30 days sample. In this aged gel two exothermic effects appeared: the first one, at 887 °C, that corresponds to the δ → θ-Al$_2$O$_3$ transition and the second one, at

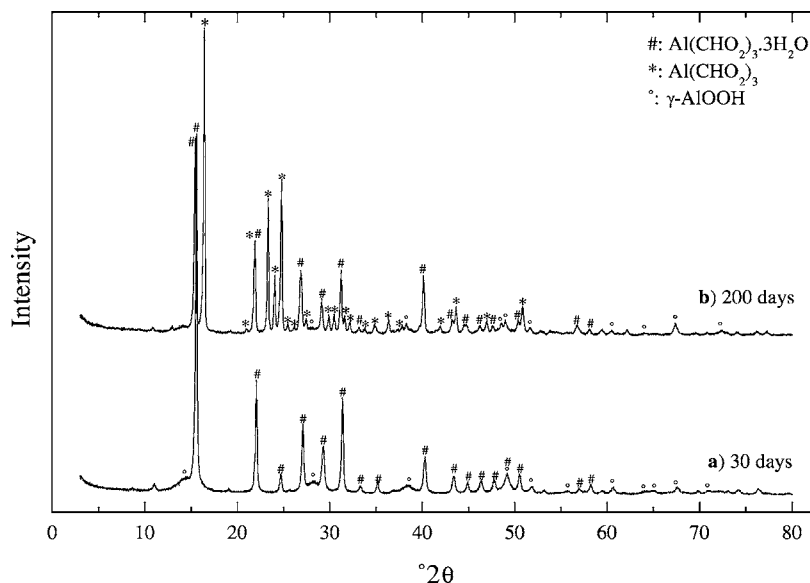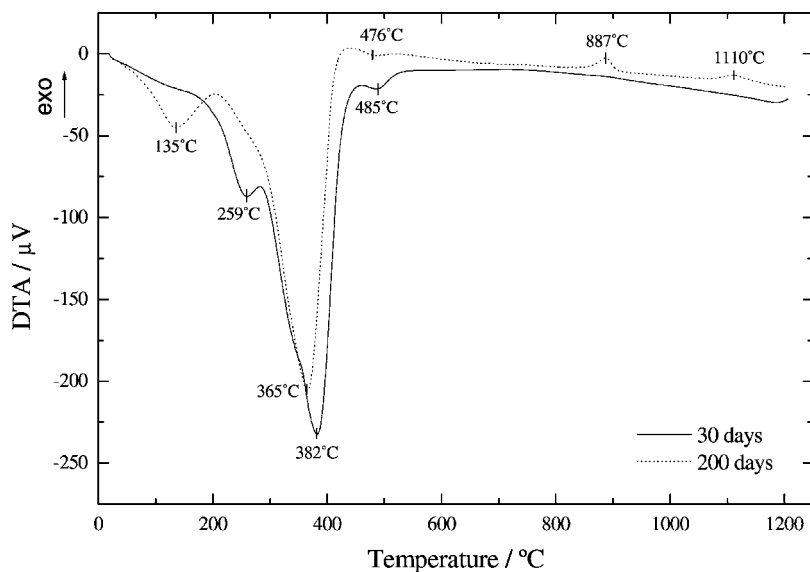Fig. 3. XRD of aluminum formate gel at different aging times.

Fig. 4. DTA of aluminum formate gel at different aging times.

1110 °C, due to the θ → α-Al$_2$O$_3$ transformation. In the aged 30 days gel these exothermic effects did not appear.

Both gels were calcined at three temperatures, 460, 800 and 1200 °C, under the same conditions used for the DTA, and the different crystalline phases were studied by XRD. In theory, the transformations that occurred in the aluminum carboxylates after the salt decomposition were the same as those for the pseudoboehmite.

In these two samples, aged 30 and 200 days, it was observed that those transformations occurred at considerably different temperatures. In both cases, the peaks corresponding to the γ-AlOOH that had not reacted and to the γ-Al$_2$O$_3$ that started to develop were observed at 460 °C. At 800 °C the δ-Al$_2$O$_3$ was identified as the predominant phase and some γ- and θ-Al$_2$O$_3$ traces were observed. The diffractograms of the samples calcined at 1200 °C are shown in Fig. 5. θ-Al$_2$O$_3$ phase and only α-Al$_2$O$_3$ traces were identified in the sample aged 30 days. The peaks observed were wide and of low intensity, indicating a scarce crystalline development of the phases present. In the sample aged 200 days the α-Al$_2$O$_3$ was clearly identified as the predominant phase, with some θ-Al$_2$O$_3$ traces. In this case the peaks were sharp and intense, indicating high crystallinity. These observations were

in agreement with the DTA analysis; in the sample aged 200 days, only the exothermic effects corresponding to the alumina transformations were evident.

The results of the TGA analysis for the aluminum formate gel samples after 30 days of aging (FAl 30D) and those after 200 days of aging (FAl 200D) are shown in Table 1. In all cases, samples were dried at 100 °C before being tested, therefore, the free water was not included in the total mass loss indicated. The stage 1, within the temperature range between 14 and 176 °C, corresponds to the elimination of water molecules physically adsorbed by the gels; and the stage 2, from 176 to 1000 °C, corresponds to the different transformations they underwent.

Table 1
TGA of the studied gels

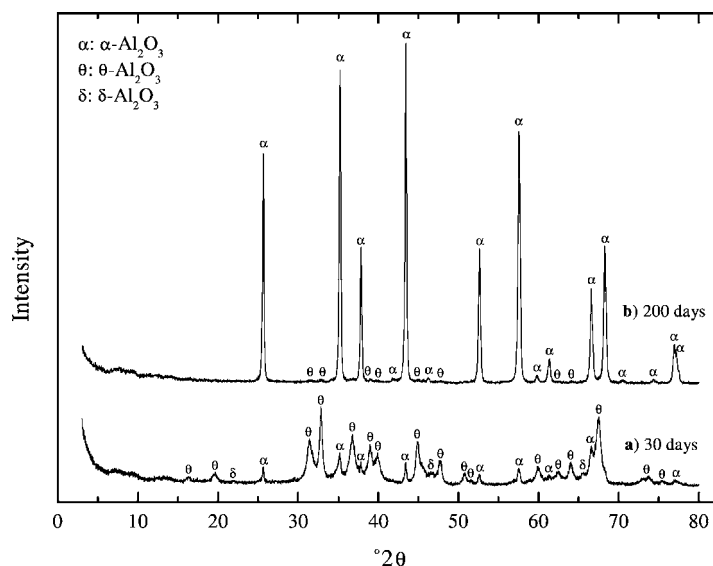| Sample	Stage	Mass loss (%)
FAl 30D	1	2.66
	2	62.68
FAl 200D	1	10.67
	2	53.26
AAl 30D	1	5.5
	2	48.55
AAl 200D	1	2.09
	2	59.9

Fig. 5. XRD of aluminum formate gel at different aging times and calcined at 1200 °C.

In the case of the aluminum formate gel it was observed that the $Al(CHO_2)_3 \cdot 3H_2O$ underwent significant changes during aging, because when time passed, the water molecules that were chemically bonded to the compound, went on being part of the water adsorbed by the gel, generating non-hydrated formate. This loss of the three water molecules of hydration, verified by all the techniques mentioned, implies that this gel is not a stable compound.

Due to the exact coincidence of the XRD peaks with the cards mentioned and to the different results obtained from the DTA diagrams for the compounds studied in this work compared with those synthesized by Landry et al. [14], we consider that the changes mentioned about the synthesis conditions made the product obtained chemically different and consequently having a different behavior. In the carboxylate-alumoxanes the authors mentioned before did not observed changes in the composition, nor in the solubility after several months at room temperature. On the contrary, in the carboxylates obtained by the route explained in this work, focussing on the aluminum formate, changes in the chemical composition were observed.

As a result, we conclude that the aging time on the aluminum formate gel, is an important parameter that determines the composition of this material, the

crystalline structure of the material calcined and the temperatures at which the different transformations take place.

3.2.3. Aluminum basic acetate characterization

The XRD patterns of the aluminum acetate gel samples removed at different aging times can be observed in Fig. 6. Peaks corresponding to the aluminum basic acetate, $Al(C_2O_2H_3)_2(OH)$ (card no.: 13-0833), and peaks corresponding to the γ-AlOOH residual were identified in all cases. It could be observed in this figure that the $Al(C_2O_2H_3)_2(OH)$ presented a peak intensity that continuously increased during the first 150 days, indicating that a crystallization process existed. By contrast, in the samples removed after that period of time, there was not an important variation of crystallinity with the passing of time. It was also observed that the intensity of the peaks corresponding to γ-AlOOH decreased with the passing of time.

The DTA diagrams for the aluminum basic acetate gel samples aged 30 and 200 days are shown in Fig. 7. Both samples presented peaks in similar positions.

The endothermic effects at 125 and 103 °C corresponded to the loss of water adsorbed, the salt decomposition occurred at 363 and 368 °C and the residual pseudoboehmite decomposition took place at 475 and 476 °C, respectively. A final slight exothermic effect
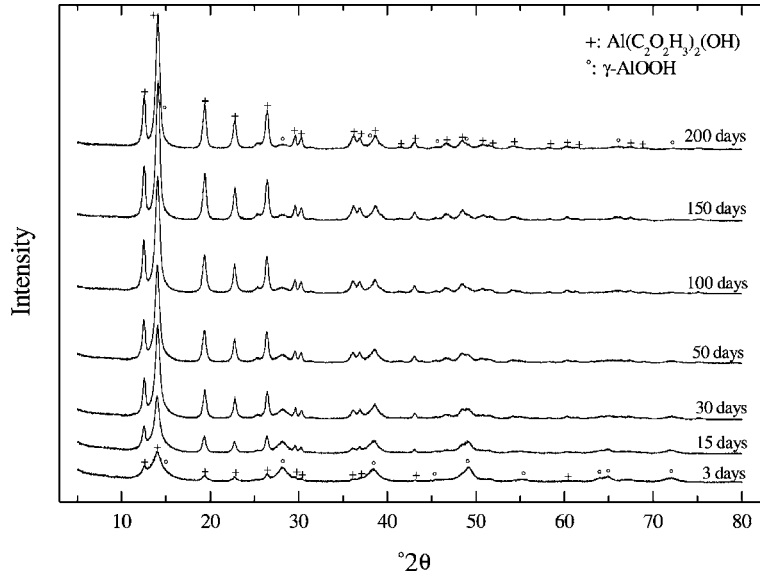
Fig. 6. XRD of aluminum basic acetate gel at different aging times.

that corresponded to the $\theta \rightarrow \alpha$-$Al_2O_3$ transition at 1186 °C for the aged 30 days gel and at 1197 °C for the aged 200 days gel was also observed. The exothermic effect shift to higher temperatures indicates that the crystallinity increases the temperature of $\theta \rightarrow \alpha$-$Al_2O_3$ transformation.

To evaluate the behavior of this gel under successive thermal treatments, a 30 days sample was calcined at four temperatures and then analyzed by XRD. At 570 and 800 °C the γ- and δ-Al_2O_3 presence was detected. At 1000 °C the θ-Al_2O_3 phase was identified with δ- and α-Al_2O_3 traces, whereas at 1200 °C
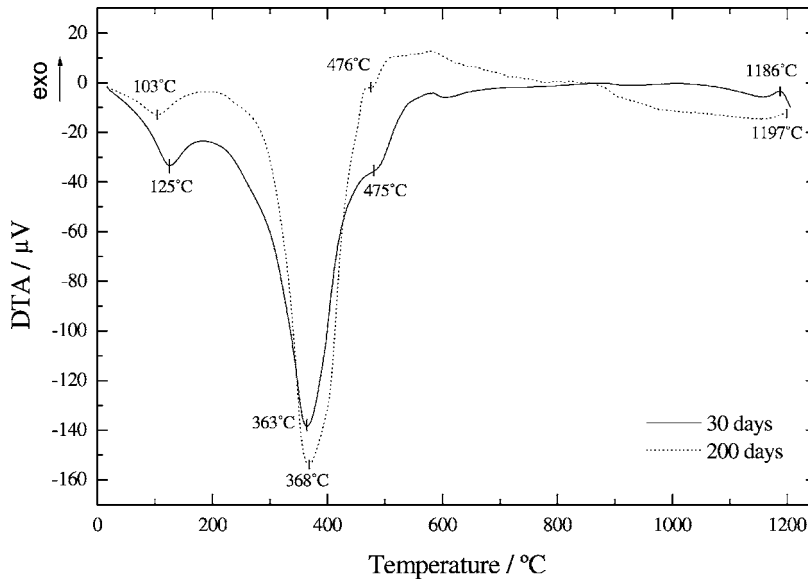

Fig. 7. DTA of aluminum basic acetate gel at different aging times.

the α-Al$_2$O$_3$ was the predominant phase with θ-Al$_2$O$_3$ traces.

From the TGA for the aluminum basic acetate gel samples, aged 30 days (AAl 30D) and aged 200 days (AAl 200D) (Table 1), it was observed that as time passes the amount of water adsorbed by the gel is lower and that the sample aged 200 days presents a greater weight loss in the second stage of mass loss. This may have been caused by the fact that the pseudoboehmite was still reacting with the acetic acid present in the gel and therefore the amount of Al(C$_2$O$_2$H$_3$)$_2$(OH) formed increased as time passed. This can be also explained by the intensity decrease of the peaks corresponding to γ-AlOOH shown in the XRD diagrams of the aged samples.

In relation with the aluminum basic acetate, due to the coincidence of the XRD peaks with the cards mentioned and to the DTA curves that present different peaks (related with different processes) compared with the compounds obtained by the synthesis route studied by Landry et al. [14], we conclude that this work was based on the aluminum carboxylate study while those authors studied the carboxylate-alumoxanes.

In conclusion, the aging time of the aluminum basic acetate gel is an important parameter, but different to that of the aluminum formate gel. In this case, 200 days after the gel synthesis, a crystallinity increase of this material was the most important difference observed, what means a greater temperature for the θ → α-Al$_2$O$_3$ transition.

4. Conclusions

Two stages were observed in the thermal decomposition of: pseudoboehmite, aluminum formate and basic acetate. The first stage corresponds to the decomposition of the compounds, which is different for each of the three cases, due to the different type of phases present. In the second stage, corresponding to the formation of transition aluminas, the formation of γ-Al$_2$O$_3$ followed by the δ → θ → α-Al$_2$O$_3$ transitions was observed for the three materials.

The aging time affected both of the carboxylates prepared, but in a different way.

When aging, the trihydrate aluminum formate gel generated non-hydrated formate, which transforms at 1200 °C almost completely into α-Al$_2$O$_3$, while in the gel without aging, at the same temperature, the θ-Al$_2$O$_3$ was the predominant phase.

On the other hand, in the aluminum basic acetate gel, when aging, an increase of crystallinity was only observed. In this case, a slight temperature increase of the alumina phase transitions took place.

As a conclusion, the aging time affected the chemical composition and properties of the aluminum formate gel, whereas for the aluminum basic acetate this parameter only slightly increased the temperature of the Al$_2$O$_3$ phase transition.

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