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Nanostructure of Gamma-Alumina Prepared by a Modified Sol-Gel Technique

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Abstract—Nanoporous γ-Al_2O_3 samples were synthesized via a sol-gel technique, introducing changes in the Yoldas´ method. The aim of the work was to achieve an effective control of the nanostructure properties and morphology of the final γ-Al_2O_3. The influence of the reagent temperature during the hydrolysis was evaluated in case of water at 5 ºC and 98 ºC, and alkoxide at -18 ºC and room temperature. Sol-gel transitions were performed at 120 ºC and room temperature. All γ-Al_2O_3 samples were characterized by X-ray diffraction, nitrogen adsorption and thermal analysis. Our results showed that temperature of both water and alkoxide has not much influence on the nanostructure of the final γ-Al_2O_3, thus giving a structure very similar to that of samples obtained by the reference method as long as the reaction temperature above 75 ºC is reached soon enough. XRD characterization showed diffraction patterns corresponding to γ-Al_2O_3 for all samples. Also BET specific area values (253-280 m^2/g) were similar to those obtained by Yoldas's original method. The temperature of the sol-gel transition does not affect the resulting sample structure, and crystalline boehmite particles were identified in all dried gels. We analyzed the reproducibility of the samples' structure by preparing different samples under identical conditions; we found that performing the sol-gel transition at 120 ºC favors the production of more reproducible samples and also reduces significantly the time of the sol-gel reaction.

***Keywords*—**Nanostructure alumina, boehmite, sol-gel technique, N_2 adsorption/desorption isotherm, pore size distribution, BET area.

I. INTRODUCTION

POROUS γ-alumina has been extensively used in many different industrial applications such as catalysis and membrane separation processes. This material is highly appreciated due to its high thermal stability, chemical and microbiological resistance and high surface area [1]-[3].

Synthesis of γ-Al_2O_3 by the sol gel technique originally developed by Yoldas through a low temperature process, yields high purity materials with small pores and narrow pore size distributions [2], [4], [5]. Basically, Yoldas´ method consists in four steps: 1-hydrolysis of aluminum alkoxide, 2-peptization of the hydroxide to boehmite sol, 3-sol-gel transition and 4-thermal treatment of the dried gel to alumina [4]-[7].

Many efforts have been made in the past to control the morphology of γ-Al_2O_3 during the sol-gel process. It is well known that water/alkoxide and acid/alkoxide molar ratios and temperature of the hydrolysis reaction are the most important factors affecting the structure and morphology of the final product [4], [6], [7]. Several studies have been reported on synthesis conditions; such as type of acids [4], use of cationic exchange resins [1], acid concentration [4], [5], and also hydrothermal treatment on boehmite films [2]. These works demonstrated how some of the different synthesis conditions modified the nanostructure of the final γ-alumina.

In our laboratory, γ-alumina has been traditionally synthesized by the original Yoldas´ method. Aluminum sec-butoxide is hydrolyzed to get a sol of boehmite, which is then peptized by adding nitric acid, to give place to a stable particulate sol. The sol gel transition is conducted in an oven at 120ºC and afterwards the xerogel of boehmite is treated at 600°C for 4 h to yield nanoporous γ-Al_2O_3 with high surface area.

The aim of this work was to introduce some modifications in the traditional γ-Al_2O_3 synthesis in order to improve the control of structure parameters such as surface area, total pore volume, porosity and pore size distribution of the samples.

II. EXPERIMENTAL

The present work was focused on the hydrolysis and sol-gel transition steps. For this purpose, hydrolysis reaction was performed with reagents, i.e., both water and alkoxide, at different temperatures. Gelation reaction was conducted at room temperature and 120 ºC.

A. Sample Preparation

Fig. 1 shows a scheme of the general procedure. As indicated, aluminum-tri-sec-butoxide diluted with sec-butanol, was used as precursor of the hydrolysis reaction; a mass ratio: 1/2 alkoxide/dry alcohol was used.

Hydrolysis was carried out by addition of the alkoxide/alcohol solution into an excess of Milli-Q water (100 water/alkoxide molar ratio). Initial temperature of the hydrolysis reagents and the temperature of the gelation process were different in the preparation of each sample. A reference sample was prepared by following the standard Yoldas´ method (REF).

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The alkoxide/alcohol solution was cooled down to -18 °C for the synthesis of all samples but the reference one, which was prepared with that solution at 20 ºC. The solution was hydrolyzed in boiling water for samples A98RT and A98TC; samples A5RT and A5TC were prepared using water at 5 ºC.

Hydrolysis reaction was performed at a temperature above 75 ºC for 30min, while briskly stirring. The reaction temperature was reached within 2h after mixing the reagents (alkoxide/alcohol – water). Table I summarizes the conditions of sample preparation.

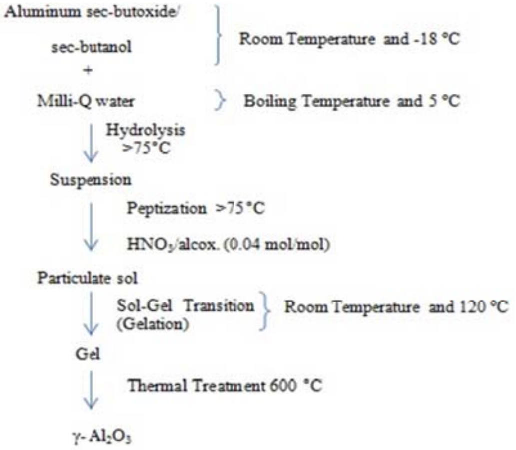

Fig. 1 Sol-gel technique by Yoldas´ method and modifications introduced

Peptization was performed by adding nitric acid (7.38 N) into the reaction solution (0.04 acid/alkoxide molar ratio); heating and stirring conditions were maintained for 2-3h, until a clear boehmite sol was obtained.

Sol-gel transition was carried out at room temperature (RT) in air flow, taking several days to complete the process, and at 120 ºC (TC), getting a dried gel in a few hours.

Thermal treatments were conducted at 600 °C, during 4 h, in air flow, with a heating rate of 10 ºC/min, in order to transform boehmite into γ-Al_2O_3. Samples were ground, afterwards, before their characterization.

Samples were named using the following code: A for alumina; XX water temperature and RT or TC as defined before. Three different samples were prepared under identical conditions in case of A98RT, A5RT and REF, whereas in case of TC´s conditions two samples were synthesized.

TABLE I
CONDITIONS OF SAMPLES PREPARED[1]

Sample Name	Hydrolysis		Gelation
	Initial Temperature(ºC)		Temperature (ºC)
	alkoxide/alcohol	water	
A5RT	-18	5	Room
A5TC	-18	5	120
A98RT	-18	98	Room
A98TC	-18	98	120
REF	20	98	120

[1] The temperature of hydrolysis reaction was 75 ºC and the samples were calcinated at 600 ºC for 4h.

B. Characterization

Transition phases from boehmite to α-Al_2O_3 were characterized by means of Differential Thermal Analysis and Thermogravimetry (DTA/TGA) in a Netzsch STA 409 Instrument. The samples were heated up to 1200ºC with a heating rate of 10ºC/min, in a flow of dry air. The crystalline phase of samples was determined by X-Ray Diffraction (XRD) experiments with a PANalytical Empyrean Phillip Difractometer (Start-End Angle: 10-90º; Time: 150:450; Step Size: 0.026).

Nanostructure of γ-Al_2O_3 was characterized by means of nitrogen adsorption/desorption isotherms at 77K acquired with an ASAP 2020 instrument; samples were previously degassed at 400 °C for 2 h. The adsorption/desorption isotherms were processed according to BJH algorithm. This model is based on straight, non-interconnected, cylindrical pores closed off at one end. The pore size distributions are calculated by evaluation of the derivative of the pore volume adsorbed and desorbed with respect to the pore size, the latter related to the relative pressure through the Kelvin equation. Surface areas were calculated by BET equation, and porosities were obtained considering two values for the material density: 3.5 and 3.9 g/cm^3.

III. RESULTS AND DISCUSSION

A. Differential Thermal Analysis and Thermogravimetry (DTA/TG)

All samples showed similar thermal behavior, regardless the hydrolysis or gelation conditions. Fig. 2 represents a typical DTA/TG plot from our boehmita samples. DTA first peak, at a temperature below 200°C, is due to the removal of water from the xerogel, and has associated a 10-20% weight loss in the corresponding TG curve. The second broad structure that appears in the region between 300 and 600 °C, is related to the dehydroxylation transition of boehmite to the γ-Al_2O_3, and coincides with a 20-25% weight loss. The presence of the third peak is associated to a crystalline transformation to α-Al_2O_3 at a temperature higher than 1000°C, which occurs without any mass change (constant TG curve).

The thermal behavior of all samples was consistent with identical crystalline boehmite structures in agreement with the results reported by Quattrini et al. [2]. These authors indicated that the width of the DTA-second peak and the presence of a third peak might be related with the grade of crystallinity of the boehmite gel. The conditions of sol-gel transition in our experiments do not modify the crystallinity of the boehmite gel. Moreover, the thermal shock caused by the different reagent temperatures does not affect the particle crystallinity. We expected, however, that thermal shock would affect the rate of hydrolysis and, consequently, the structure of the materials with respect to the traditional Yoldas´ method [8]. Our results show that temperature modifications do not produce any effect on the particle crystallinity.

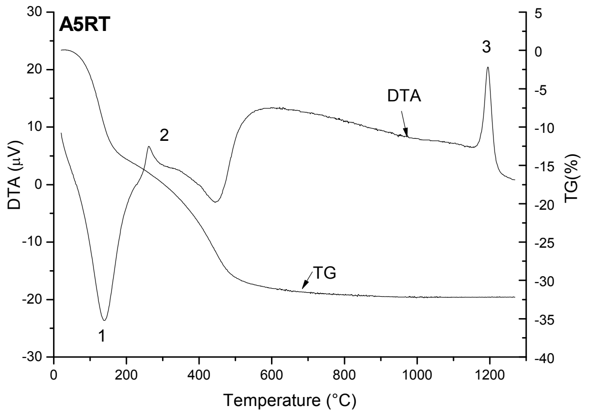

Fig. 2 DTA/TG curves of boehmite gel samples

B. X-Ray Diffraction (XRD) Patterns of the γ-Al_2O_3 Samples

In Fig. 3, XRD patterns from boehmita gel samples are compared. It is well known after Yoldas′ studies that hydrolysis performed with hot water (> 80 °C) gives place to formation of crystalline boehmite whereas with cold water, produces an amorphous hydroxide. This hydroxide can transform to boehmite when heated at temperatures above 80 °C for 3 or 4 h, or to bayerite when is kept at lower temperature [4], [6], [7]. In our case, the heating of reagents started immediately after mixing the reagents and the reaction temperature (>75 ºC) was reached before 2h.

All XRD patterns showed structures consistent with boehmite phase; thus indicating that if the reaction temperature (>75 ºC) is reached soon enough after mixing, the gel phase can be controlled independently of the original reagent temperatures. This result demonstrates that the initial temperature of the reagents is not the determining parameter of the product of the hydrolysis.

Using cold water however prevents any explosion reaction because of the lower thermal shock between reagents. Moreover, the lower vapor production when water is not boiling, avoids that hydrolysis occurs before the alkoxide reached the liquid water. That facilitates the alkoxide addition into the reactor vessel.

The XRD patterns of all samples shown in Fig. 4 are consistent with the gamma-alumina phase. This fact gives further evidence to the conclusion that the product obtained in all hydrolysis was boehmite. The identical width of the primary peaks (46º and 67º) in all γ-Al_2O_3 samples indicates the presence of crystallites with similar size, according to the Scherrer equation.

C. Nitrogen Adsorption Characterization of Nanostructure of γ-Al_2O_3

The nitrogen adsorption/desorption isotherms of the γ-Al_2O_3 samples are presented in Fig. 5. These isotherms correspond to type IV under BDDT classification, and show capillary condensation in the mesopore range (20-500 Å). Hysteresis loops are type H2 (p/p_0 = 0.4-0.9) that represents a *globular* morphology, where big cavities are connected to the outside by small throats, known as *ink-bottle* pores. These results are in agreement with those of Quattrini et al. [2]; the authors found that the crystallinity of the boehmite, that determined the pore morphology of the γ-Al_2O_3, is related to the temperature of the sol-gel transition. In our experiments, both RT and TC conditions, gave place to low-crystalline boehmite (Fig. 2), which is responsible of the *globular* morphology found (Fig. 5).

TABLE II
NANOSTRUCTURE PROPERTIES OF γ-Al_2O_3 SAMPLES

Sample	Results	BET (m^2/g)	Pore Total Volume (cm^3/g)	Mean Pore Size (A)	Porosity (%) (*)	
					a)	b)
A98RT	Average	269	0.38	56.78	57	60
	SD	28	0.03	0.94	3	2
A5RT	Average	280	0.38	54.05	57	59
	SD	38	0.03	4.85	2	2
A98TC	Average	253	0.39	61.17	57	60
	SD	6	0.01	0.08	1	1
A5TC	Average	253	0.39	61.17	57	60
	SD	5	0.01	0.18	0.4	0.4
REF	Average	263	0.39	59.75	58	61
	SD	2	0.02	3.96	2	2
	Media	263	0.38	58.58		
	SD	12	0	3		
	CV (%)	4	1	5		

(*) Porosity a) was calculated considering δ= 3.5 g/cm^3 and b), δ= 3.9 g/cm^3.

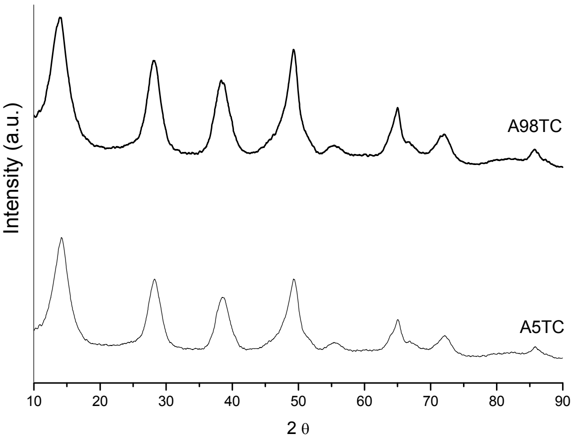

Fig. 3 XRD patterns of boehmite obtained with hot (98 ºC) and cold (5 ºC) water

The nanostructure properties of all γ-Al_2O_3 samples are listed in Table II. A comparative analysis of the values of BET area, pore total volume and mean pore size show that the differences among all samples are less than 5%, and porosity ranges 57-60%. This little deviation of the results for all different preparations, suggests that the modifications introduced in this work have no appreciable effects in the final γ-Al_2O_3 nanostructure.

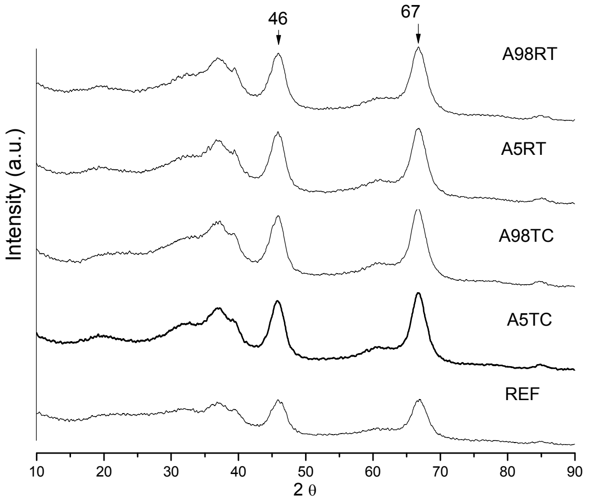

Fig. 4 XRD patterns of the γ-Al_2O_3 samples

Values of all properties and their standard deviations of Table II refer to the mean value and dispersion of the two (or three) samples prepared under identical conditions as it was explained in the experimental description. Mean and standard deviation values of BET surface areas are plotted in Fig. 6. The standard deviation of BET areas for samples A5RT and A98RT is one order of magnitude higher than that for samples A5TC, A98TC and REF. This difference could be related with water evaporation when the sol-gel transition proceeds at 120°C, which would give more stable reaction conditions than room temperature and consequently more reproducible results. Therefore, BET surface area is sensitive to the temperature of sol-gel transition.

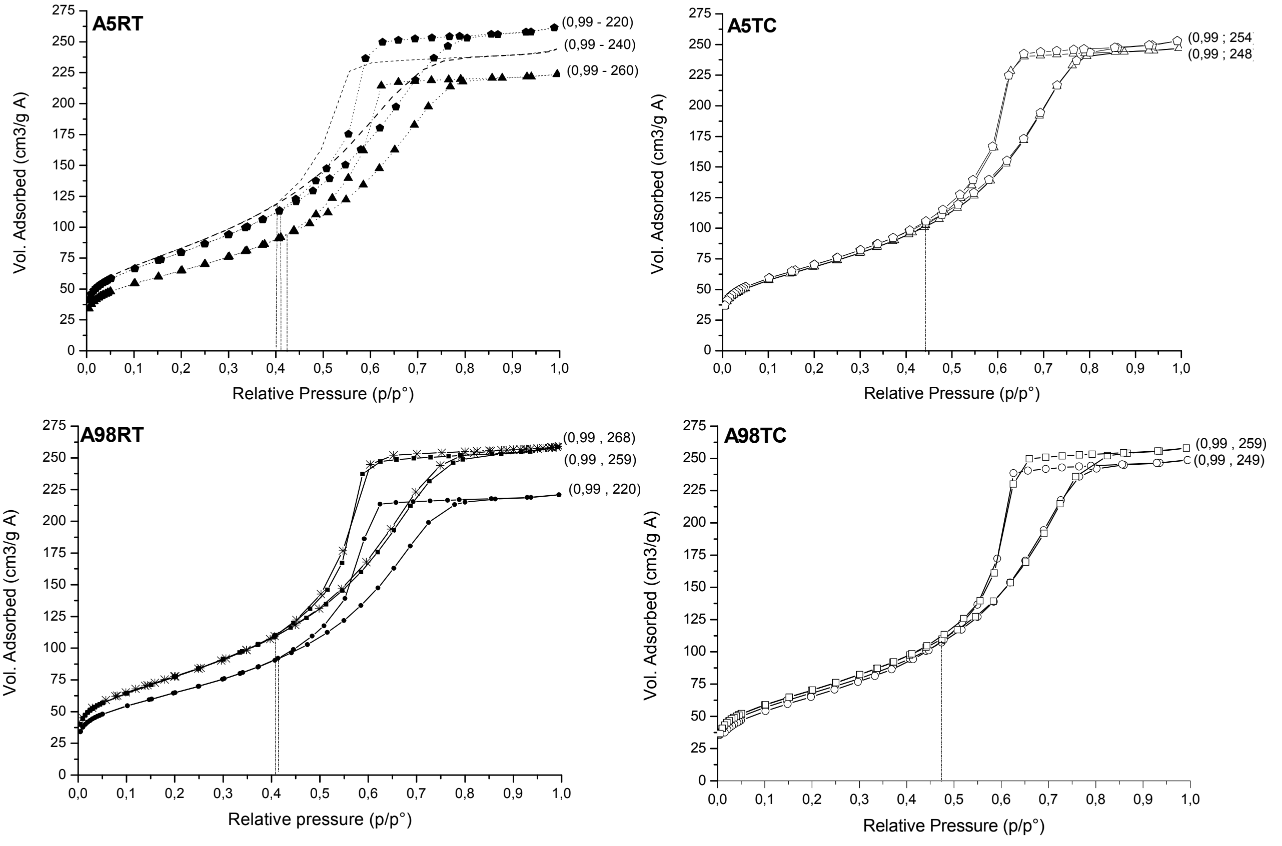

Fig. 5 Adsorption/desorption N_2 isotherm of γ-Al_2O_3 samples

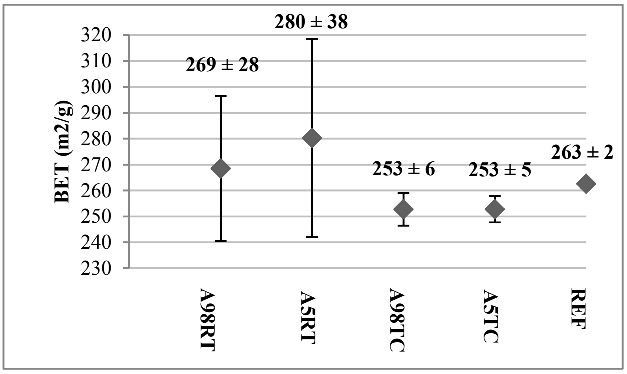

Fig. 6 Statistics results of BET surface area of samples

Pore size distributions, calculated by derivation of the pore volume adsorbed or desorbed with respect to the pore size, are represented in Figs. 7 and 8. As the morphology of the pores is ink-bottle-like, the pore size distributions obtained from the adsorption branch of the nitrogen isotherm (Fig. 7) are broader than those obtained from the desorption branch (Fig. 8). Moreover, the differences in pore size distribution among different samples prepared under identical conditions, are more evident in desorption than in adsorption. Our BET surface area results indicated that those differences are more important for RT that TC samples.

The higher reproducibility observed for TC samples regarding BET area and pore size distribution could be explained by the effect of capillary pressure on the obtained xerogel and subsequently on the pore structure of the final γ-Al_2O_3. As capillary pressure exerted by water evaporation is directly related to the temperature, the system would evolve in a more controlled way when the reaction proceeds at 120 ºC. If the xerogel is constituted by uniform particles, TC conditions could be useful to control the particle network, thus achieving a more uniform pore distribution when comparing samples prepared under equivalent conditions [8].

The use of cold reagents facilitates handling and prevents the reaction being initiated by the presence of boiling water vapor outside the liquid phase. This provides an operational advantage and does not alter the final nanostructure of γ-Al_2O_3, as long as the reaction temperature above 75 ºC is reached soon enough.

Our results showed that although γ-alumina structure is not affected by sol-gel transition temperature, performing the reaction at 120 °C improves the reproducibility of the samples and significantly reduces the time of the sol-gel reaction.

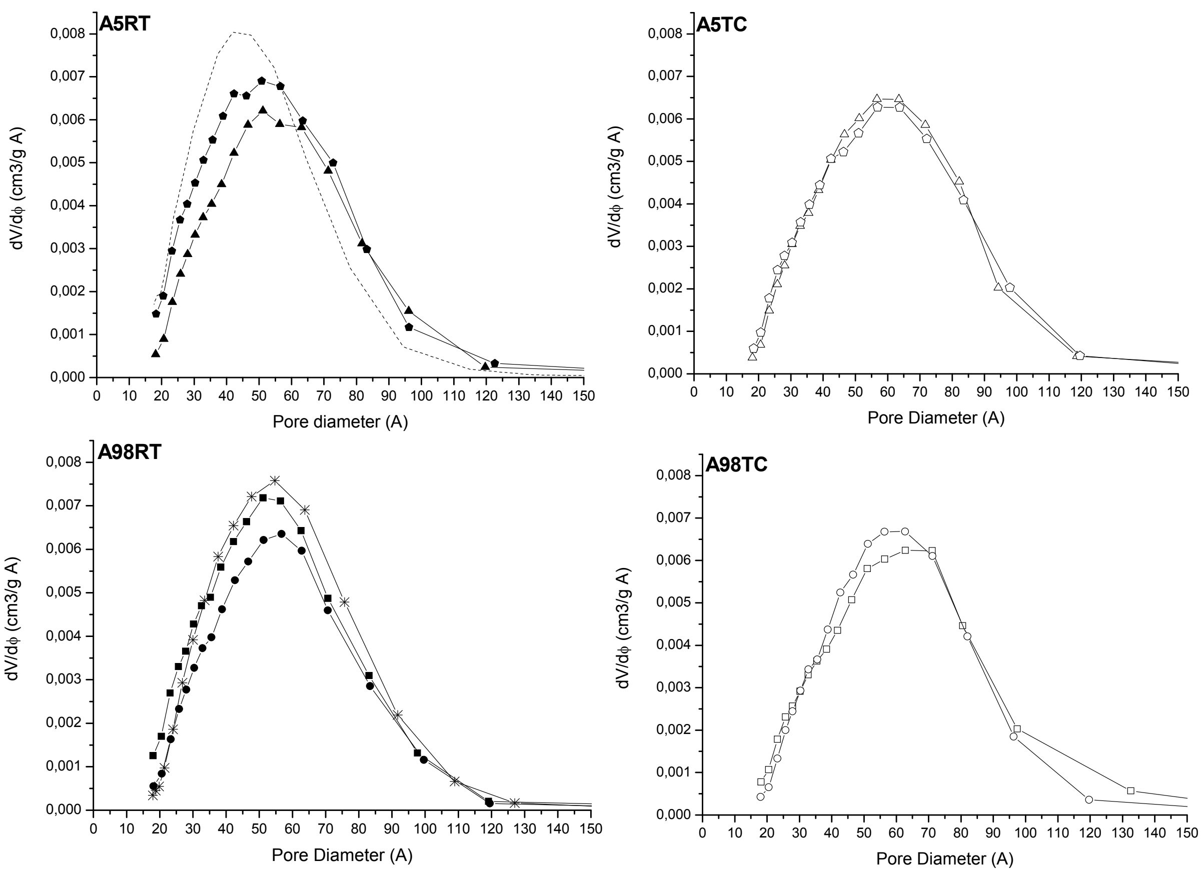

Fig. 7 Pore size distribution of γ-Al_2O_3 samples from adsorption branch

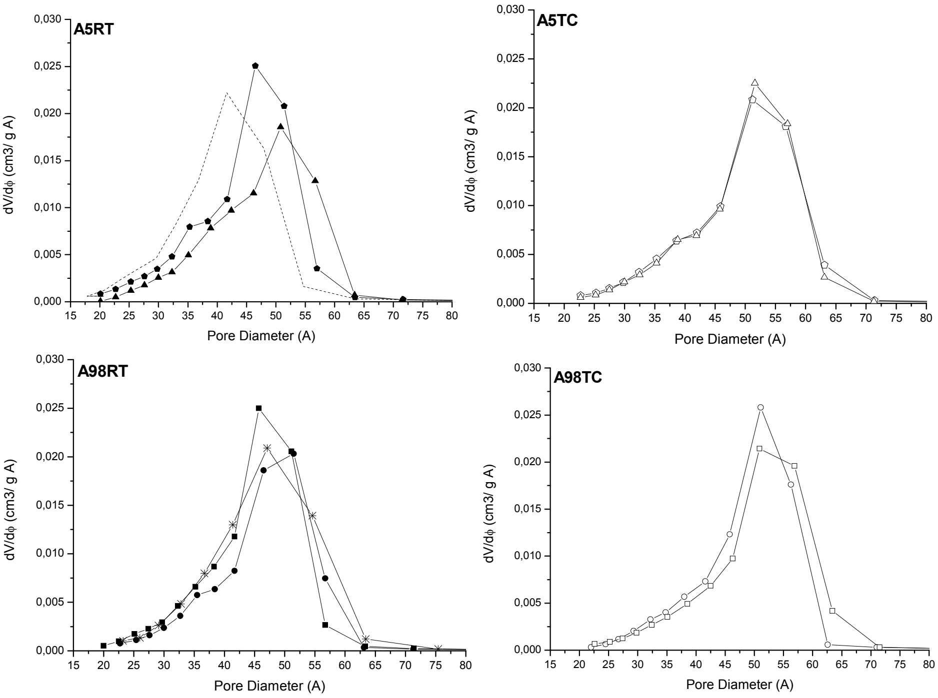

Fig. 8 Pore size distribution of γ-Al_2O_3 samples from desorption branch

IV. CONCLUSIONS

We have studied the influence of the temperature in two steps of Yoldas´ method for synthesis of γ-Al_2O_3 on the nanostructure of both the intermediate gel and the final alumina.

Our results showed that the initial temperatures of alkoxide/alcohol solution and water as well as the sol-gel transition temperature have no significant effects on the γ-Al_2O_3 nanostructure. The nanostructure of all γ-Al_2O_3 samples presented similar properties such as BET surface area and pore size distribution.

Handling the reagents at low temperature represents an experimental advantage during hydrolysis and does not affect the formation of boehmite if the reaction temperature is reached within two hours.

Although the temperature of the sol-gel transition does not affect the final alumina structure, performing the reaction at 120ºC has proved to produce more reproducible samples and to reduce the sol-gel reaction time.

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