Specific surface area and structures of aluminas from fibrillar pseudoboehmite

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ABSTRACT

By heating powders of the aluminum monohydroxide fibrillar pseudoboehmite from 200°C to 1400°C several high surface area aluminas are prepared and characterized by X-ray diffraction and electron optical methods. Aqueous sols with pseudoboehmite fibrils of different lengths were dried by two methods: at room temperature and spray-dried. The following aluminas were obtained after treatment of the powders at increasing temperatures and having a range of specific surface areas: γ–Al_2O_3 (470°C – 770°C; 179 m^2/g – 497 m^2/g); δ-Al_2O_3 (770°C – 930°C; 156 m^2/g – 230 m^2/g); θ-Al_2O_3 (930°C – 1050°C; 11 m^2/g – 200 m^2/g); α-Al_2O_3 (1050°C – 1400°C; 2 m^2/g – 17 m^2/g). Spray-dried powders, fired at the same temperature than the ground powders, showed higher specific surface areas. The higher surface area alumina have values of the same order of magnitude of the commercial "ad-cat" aluminas.

Keywords: pseudoboehmite, transition aluminas, active aluminas, specific surface area.

1   INTRODUCTION

By pseudobohemite it is meant "poorly crystallized" Al^{3+} compound of composition $Al_2O_3.xH_2O$ (2.0 > x > 1.0) with interplanar spacings increased in the [020] direction to 0.67nm (6.7Å) in comparison with 6.12Å for boehmite – AlOOH or $Al_2O_3.1H_2O$ (Krivoruchko *et al.*, 1978). Fibrillar pseudoboehmite (FPSB) is the name proposed by Bugosh *et al.* [1] for the elongate microcrystals of poorly crystallized boehmite formed by aging non-crystalline aluminum hydroxide gels in pHs between 5.0 and 7.4 [2]. Pseudoboehmite is the solid component of the "bad gel" formed as by-product in the linear alcohol production by the Ziegler process (hydrolysis of aluminium alcoxides) [3, 4]. The thermal transformation of fibrillar pseudoboehmite microcrystals was characterized by transmission electron microscopy (TEM), selected area electron diffraction (SAED) and X-ray diffraction (XRD); the observed sequence of crystalline phases is:

$$PSB \rightarrow gamma\text{-}alumina \rightarrow delta\text{-}alumina \rightarrow theta\text{-}alumina \rightarrow alpha\text{-}alumina.$$

That fibrillar pseudoboehmite aqueous sol was prepared by thermal aging of the gel formed by reaction between aqueous acetic acid solution and Al-secbutoxide or Al-isopropoxide [5]. Later, another method of preparation of fibrillar pseudobohemite sols was developed by reacting aqueous acetic acid solution with amalgamated aluminum foils, followed by thermal aging for a longer time up to 500 hours [6].

The highly viscous sols, after evaporating on flat polystyrene surfaces, produced symmetric pseudobohemite membranes [7, 8]; in these, the fibrils are side by side, parallel to their lengths, forming an ordered structure. These sols are excellent to prepare membranes and channeled spheres for immobilization and growth of *Saccharomyces cerevisae* [9]. On the other hand, yet it was not found a drying method to obtain powders constituted by free pseudoboehmite microfibrils: always they were ordered side by side or in bundles or into a network. So, always a part of al the fibrils cannot contribute to its free surface area.

The purpose of this paper is to compare the effect of the ordering of fibrils on alumina formation from the thermal treatment of the same fibrillar pseudoboehmite sol, dried either as in a membrane or as a spray-dried powder.

2   MATERIALS AND METHODS

2.1   Reagents: Aluminium Powder and Acetic Acid

The aluminium powder used was type 123 produced by Alcoa, Poços de Caldas, MG. Particle size: (a) 100% minus ABNT number 100 sieve; (b) 99.9% minus number 200 sieve; (c) 96.6% minus number 325 sieve (44μm aperture). Chemical analysis: Al = 99.84%; Si = 0.04%; Fe = 0.09%. Acetic acid used was A.R. grade product from Labsynth, Diadema, São Paulo, Brazil.

2.2   Equipments

The reaction was conducted in a Pyrex two-liter three-neck round bottom flask equipped with: (a) automatic stirrer in central neck; (b) thermometer with thermostatic control; (c) water-cooled condenser; (d) electric heating mantle.

The differential thermal analysis (DTA) was conducted in an equipment made by BP Engenharia, Campinas, SP, operating with a temperature rising rate of 10°C/min, in air.

The X-ray powder diffraction (XRD) was conducted in a Philips X-Ray Diffractometer X'PERT MPD model (PW3050/10), using Cu-Kα radiation operating at 40kV and 40mA between 1^{o}(2θ) and 90^{o}(2θ).

Scanning electron microscopy (SEM) was made in a JEOL model JSM 840A. Transmission electron microscopy (TEM) was made in a Philips CM200 equipment at 200kV. The same microscope was used as a diffraction camera for obtaining the selected area electron diffraction (SAED) for the identification of the crystalline structures of the various phases. The fired ground samples for membranes were sprinkled onto a microscope grid for TEM and SEM characterization.

Surface area of the powders was measured by using the BET low temperature nitrogen adsorption method [10]. About 300mg of the dried powders were placed in the sample holder of the Micromeritics model ASAP 2010 BET adsorption apparatus. The previous drying was carried out at 120°C under vacuum in the pre-treatment unit of the equipment; six hours were the minimum time for the drying. The heating was interrupted when the chamber pressure lowered to 10^{-5} mm of mercury. In the adsorption measurements, ultra-pure nitrogen (99.995%) from Air Liquide was used.

2.3   Operation

The reaction was conducted in the following steps: (a) the acetic acid solution was introduced in the flask and the three necks closed; (b) the heating and stirring were started until the temperature of 90°C ($\pm$ 1°C) was attained and the maintained; (c) the aluminium powder was introduced opening the neck having the condenser; the powder was added slowly, in 1-2 portions, in order to avoid an intense production of hydrogen froth; (d) the temperature raised some degrees and the heating had to be discontinued to avoid too much frothing; cooling the free surface of the flask was enough to decrease the frothing, which ended after one hour; (e) the suspension was kept stirred at 90°C ($\pm$ 1°C) for 168 hours; (f) after 168h of heating, the system was cooled and the flask contents a viscous white fibrillar pseudobohemite sol.

2.4   Al/Acid/Water Ratios

The preparation method described in this paper was developed during studies on the aqueous linear condensation polymerization of non-crystalline or amorphous aluminium hydroxide into colloidal fibrillar pseudoboehmite for the preparation of concentrated sols [6]; in these estudies, the same Al^{3+} concentration was used as in the early stages of polymerization of $Al(OH)_3$ by several authors [11, 12]; therefore, always the $1Al:50H_2O$ was used, that is, 27g of Al powder and 900mL distilled water. The ration Al / Acetic Acid (Ac) adequate to produce the fibrillar pseudoboehmite was found to be 1.0 / 0.5 Ac [6]. These proportions produced the concentration of 70g of AlOOH / L of sol. The study was conducted on a mixture of six batches, with a total volume of 5.4L.

2.5   Drying the Sol Like a Membrane

The sol was air-dried at room temperature in polystyrene molds with 10.0cm diameter and 0.5cm high; the air-dried fibrils formed disk-shaped continuous symmetric membranes, 9.0 cm diameter. The membranes were ground in a corundum mortar to minus #100 ABNT sieve (0,143mm) for characterization, thermal treatment and experiments.

2.6   Spray-Drying of the Sol

It was conducted in a spray drier model APV-ANHYDRO, from the Laboratory of Food Engineering of the Chemical Engineering Department of Escola Politécnica, University of São Paulo. The drying air temperature was 120°C-140°C. The spindle velocity was 6200rpm. The white dried powder was free-flowing. The majority (about 95%) of the powder passed #100 sieve; the minus #100 sieve powder was used for the experiments.

2.7   Heating the Powders

5.0 grams of membrane or spray-dried powder were heated in an electric furnace at 10°C/minute in oxidative atmosphere and were kept 3 hours at the maximum firing temperature (residence time). The samples were naturally cooled and kept in closed flasks fo characterization. The temperature range was 200°C to 1400°C with 100°C intervals, or smaller when necessary. The fired samples were characterizad by XRD and their specific surface area was measured by the BET method. The XRD crystalline structure characterization of the aluminas was made from Wefers and Misra [13] and Souza Santos *et al.* [14].

3   RESULTS

3.1   Composition

The sol (50mL) was dried at 105°C / 110°C to constant weight and the solid calcined at 1100°C to constant weight. Its calculated formula is $Al_2O_3 \cdot 1.12\ H_2O$, which is in agreement with the pseudoboehmite definition [15].

3.2   TEM of the Sol

Figure 1 shows an TEM electron micrograph of the sol: it contains exclusively long microfibrils, as it would be expected from fibrillar pseudoboehmite. The fibrils present a tendency to align in bundles when the sol is dried on the support of TEM.

3.3   XRD of the Dry Powders

Figure 2a,b presents the XRD curves of the powders of the ground membranes and the spray-dried sols, respectively. Both curves are typical of pseudoboehmite with d(020) = 6,19Å for membrane and 6,23Å for spray-dried; this difference may be due to larger parallel ordering of the fibrils in the membranes; the existence of the 36Å reflexion in the "membrane curve" and absence in "spray-dried" is a result of that ordering.

Figure 1: TEM of the 168h aged sol showing the mesh pseudoboehmite fibrils, many ordered into bundles.
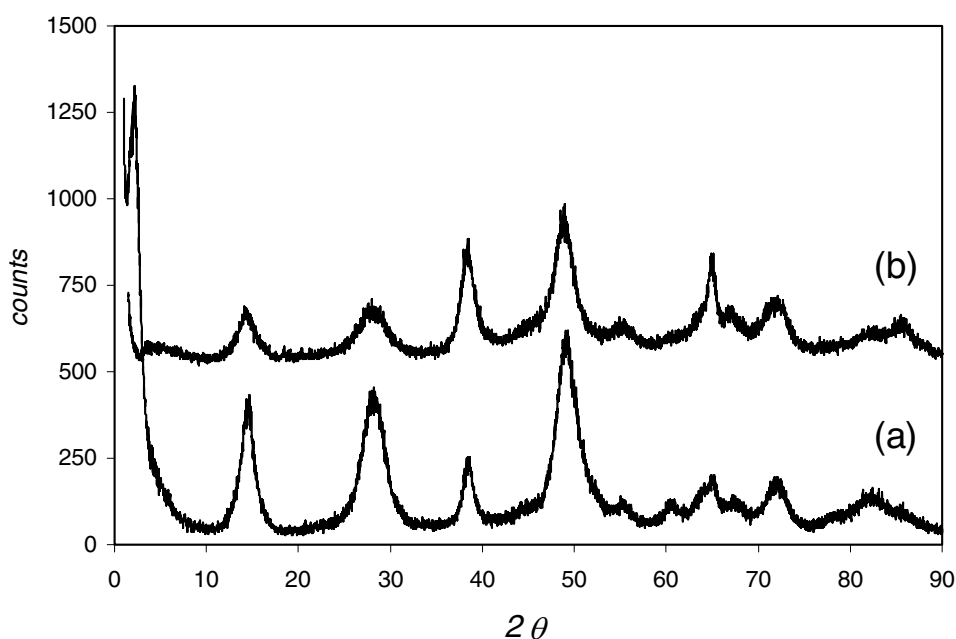

Figure 2: (a) XRD curve of the ground membrane of the 168h aged sol (pseudoboehmite); (b) XRD curve of the same 168h aged spray dried sol (pseudoboehmite).

3.4   SEM of the Dry Powders

Figure 3 shows an scanning electron micrograph of the ground powder from membrane. The parallel ordering of pseudoboehmite fibrils into layers is very clear. Figure 4 shows a micrographs of the spray-dried powder: it is constituted by hollow, shell-like particles or spheres of fibrillar pseudoboehmite. The examination of the "shell" shows that the fibrils are only partially ordered, due to the high rate of drying of the sol drops (Figure 5). According to Messing *et al.* [16], the morphologies of the hollow particles of Figure 4 is due to the low surface permeability of the drying sol drops. The hollow, shell-like structure of the 168

hours spray dried particles is different from the compact structure of the particles obtained by Varma *et al.* [17] in 48 hours aged sol.

Figure 3: Scanning electron micrograph of the ground powder: membrane showing layers and bundles of pseudoboehmite fibrils.
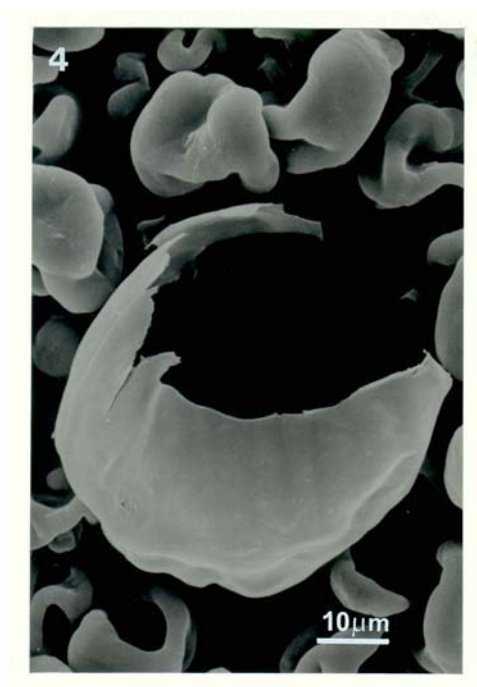

Figure 4: Scanning electron micrograph of the spray-dried powder: hollow sphere showing the broken shell constituted by pseudoboehmite fibrils.

Figure 5: Scanning electron micrograph of the broken border of the sphere from Figure 4: the partial disordering of the pseudoboehmite fibrils is clearly visible.

3.5   DTA

Figure 6 shows the DTA curve of the membrane powder: there is a large endothermic peak, starting about 300°C with maximum at 450°C; two small exothermic peaks (or "humps", according to Mackenzie [18] about 750°C and 950°C; a large and a small endothermic peaks occur at low temperatures (under 300°C). The interpretation of the peaks is based on the alumina phases formed by heating the powders and characterized by XRD and SAED using ICDD data.
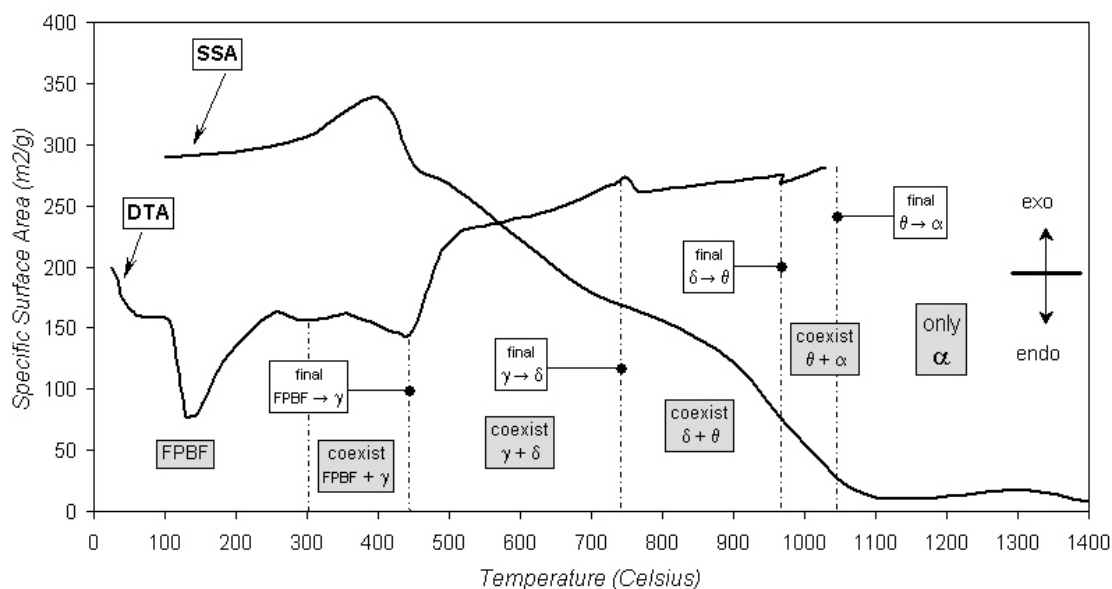

Figure 6: DTA curve of the membrane ground powder; specific surface area (SSA) of the membrane heated powders. Temperature ranges and transition temperatures of the aluminas.

3.6   XRD of Aluminas

By heating, pseudoboehmite dehydrates into the transition gamma-alumina (cubic symmetry); with further heating, delta-alumina (orthorhombic) and theta-alumina (monoclinic) are formed; at high temperatures, the thermodinamically crystalline stable alpha-alumina phase (rhombohedral) is formed; its melting point is 2050^oC.

The XRD curves for the three transition aluminas are very similar and their intensities are much lower than alpha-alumina reflexions. That is the reason why they are not presented. The phase characterization needs the detailed comparison of the reflexions and their intensities; also a search program can be used on the XRD data from the reference quoted [14] or from the ICDD (International Center for Diffraction Data).

The most important $\underline{d}$ values for characterization of gamma, delta and theta-aluminas are shown in Table 1.

The differences are better shown by SAED than by XRD. The similarities between some of the strong d values of the three transition aluminas are due to the relatively fixed arrangement of oxygen anions in their crystalline lattices. The different distribution of the Al^{3+} cations within a more-or-less constant close-packed cubic oxygen network make possible the three different structural arrangements. The gamma to delta to theta transformations are topotactical and therefore are low energy reactions. All three share the same c.c.p. oxygen sub-lattice which has to change to the hexagonal close packed (h.c.p.) oxygen lattice in alpha-alumina structure. This transformation has been object of investigation since 1960, specially on its mechanism.

Wefers and Misra [13] presented the following transition temperatures of the aluminas from firing "well crystallized" boehmite (B):
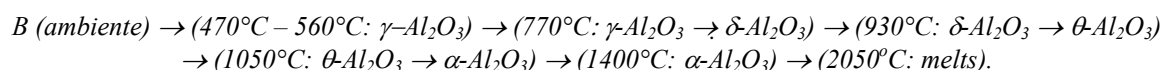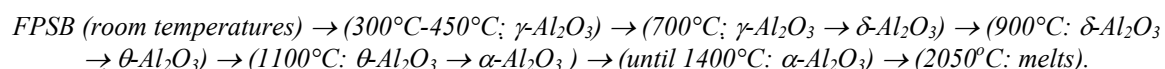
$$B \text{ (ambiente)} \rightarrow (470°C – 560°C: \gamma–Al_2O_3) \rightarrow (770°C: \gamma-Al_2O_3 \rightarrow \delta-Al_2O_3) \rightarrow (930°C: \delta-Al_2O_3 \rightarrow \theta-Al_2O_3) \rightarrow (1050°C: \theta-Al_2O_3 \rightarrow \alpha-Al_2O_3) \rightarrow (1400°C: \alpha-Al_2O_3) \rightarrow (2050^oC: melts).$$

Table 1: Most important $\underline{d}$ reflexion values of γ, δ and θ-Al_2O_3

Gamma (Å; I/I_0)	Delta (Å; I/I_0)	Theta (Å; I/I_0)
2.80 (20)	----	2.84 (80)
2.39 (80)	2.40 (10)	2.44 (60)
1.98 (100)	1.99 (75)	1.95 (5)
1.40 (100)	1.40 (100)	1.39 (100)

SAED and XRD characterization of the membrane and spray-dried fired samples indicated the following transition temperatures:

$$FPSB \text{ (room temperatures)} \rightarrow (300°C-450°C: \gamma-Al_2O_3) \rightarrow (700°C: \gamma-Al_2O_3 \rightarrow \delta-Al_2O_3) \rightarrow (900°C: \delta-Al_2O_3 \rightarrow \theta-Al_2O_3) \rightarrow (1100°C: \theta-Al_2O_3 \rightarrow \alpha-Al_2O_3) \rightarrow (until\ 1400°C: \alpha-Al_2O_3) \rightarrow (2050^oC: melts).$$

Only at 1000ºC a difference was observed: the ground membrane presented θ and the six more intense reflexions of α-Al_2O_3, while spray-dried presented only the θ-Al_2O_3 reflexions.

Therefore, the transiton temperatures of fibrillar pseudoboehmite are a little smaller than those of well crystallized boehmite, but the existence temperature ranges of each of the three transiton aluminas, gamma, delta and theta are larger. These temperature ranges of the transition aluminas are marked in the DTA curve of the membrane ground powder (Figure 6).

3.7   TEM of Aluminas

Figures 7 to 10 are transmission electron micrographs of particles of the ground membranes after fired at four temperatures to show that: (a) the fibrillar pseudoboehmite to gamma-Al_2O_3 transformation is

pseudomorphic, that is, the single fibrils shape and the organization in parallel bundles are maintained (Figure 7); (b) each fibril is broken into small platy crystals of γ-Al_2O_3 which remains aligned in the pseudomorph (Figure 7; 700°C); (c) the fibrills pseudomorphism and parallel arrangement is mainteined in the delta (Figure 8, 900°C) and theta (Figure 9a,b, 1000°C) transformations; there is a continnous increase in diameter or coarsening in γ- to δ- to θ-Al_2O_3 transformation, clearly observables from Figures 7 to 9; (d) from 1100°C (Figure 10a,b,c) to 1400°C there is sintering of the platy crystals of the newly formed alpha-alumina; unfortunately, it has not been possible yet to observe directly in the MET the nucleation from the θ-Al_2O_3 platy crystals of Figure 9 to α-Al_2O_3 in order to contribute with information to the two existing theories of that transformation: preferential α-Al_2O_3 phase nucleation at the necks between crystals or diffusion controlled growth of the θ-Al_2O_3 microcrystals followed by synchro-shear martensitic type transformation of θ- to α-Al_2O_3 [19, 20].

3.8 Specific Surface Area of Aluminas

Table 2 shows the BET specific surface área, pore volume and average pore diameter of ground membrane and spray dried sol after heating between 200°C and 1400°C, and based on the results of this table, the following observations can be made:

- The specific surface areas after heating between 200°C and 950°C of both samples are always higher than 100m^2/g; so, according to Oberlander [21] these fired samples are "high surface area aluminas".
- Both samples present maximum values of specific surface area (423 and 338 m^2/g) after fired at 400°C and both have gamma-alumina structure.
- For the same temperature of firing, the transition aluminas from the spray-dried sol have higher specific surface areas than the ground membranes; the cause is due to the smaller ordering of the spray-dried fibrils shown by the micrograph of Figure 5; as more fibril surface is free, the specific surface area is larger.
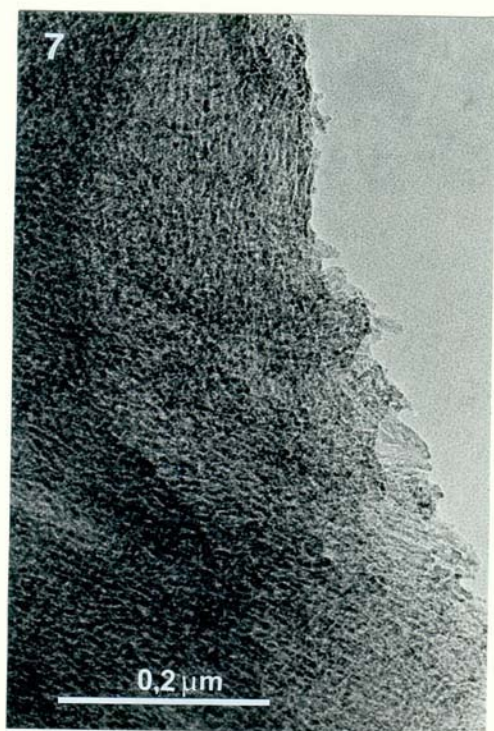

Figure 7: TEM of the γ-Al_2O_3 pseudomorphs from 700°C heated 168 hours aged pseudoboehmite fibrils.
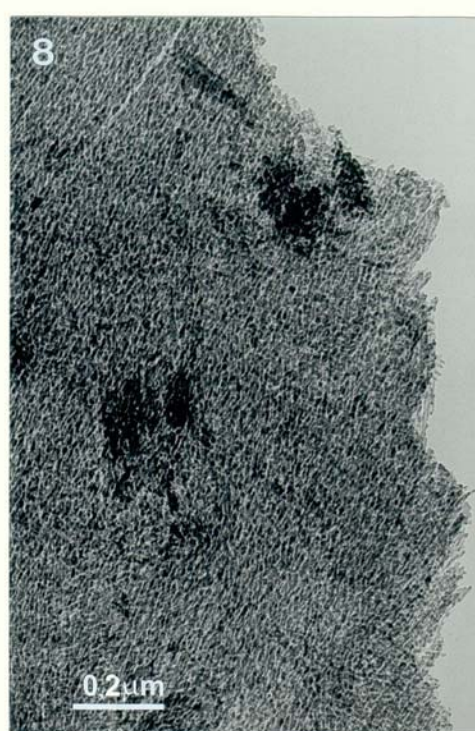
Figure 8: TEM of the δ-Al_2O_3 pseudomorphs from 900°C heated 168 hours aged pseudoboehmite fibrils.
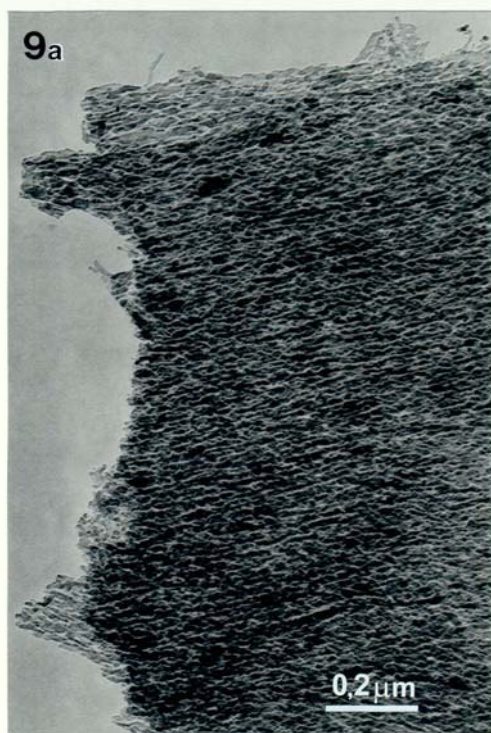
Figure 9a: TEM of the θ-Al$_2$O$_3$ pseudomorphs from 1000°C heated 168 hours aged pseudoboehmite fibrils.
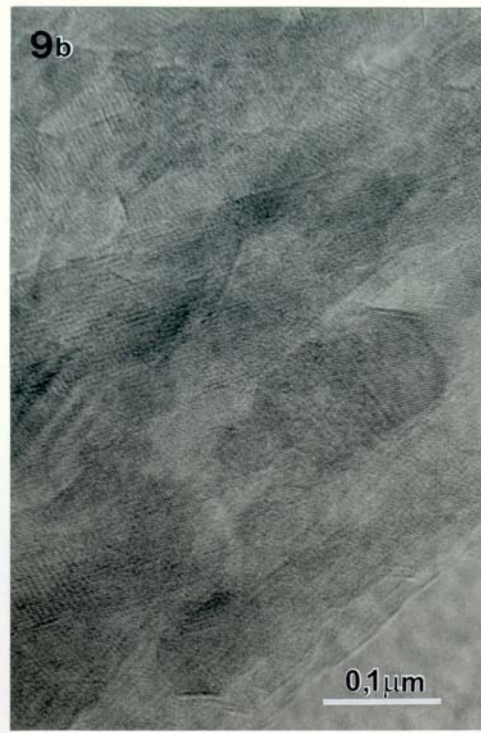
Figure 9b: Lattice image of θ-Al$_2$O$_3$ crystals.
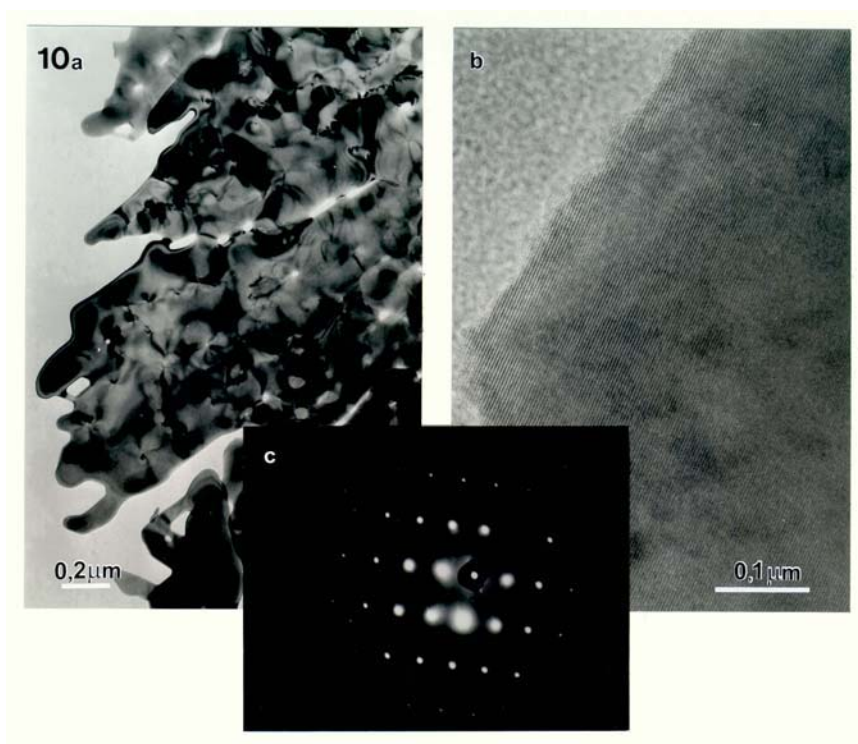
Figure 10: (a) TEM of the α-Al$_2$O$_3$ pseudomorphs from 1100°C heated 168 hours aged pseudoboehmite fibrils; (b) lattice of α-Al$_2$O$_3$ crystals; (c) SAED of α-Al$_2$O$_3$ crystals.

- The values of the specific surface area of the ground membrane powder are also plotted in Figure 6 with the DTA curve; it can be observed that the temperature of the maximum value of the specific surface area is smaller than the temperature of the peak of the dehydroxilation reaction :

$$2\ AlOOH\ \rightarrow\ gamma\text{-}Al_2O_3\ +\ H_2O$$

- At 900ºC, both samples have theta-alumina structure, but the specific surface area of the spray-dried is 1.3 times higher. At 1000ºC, ground membrane has alpha-alumina structure while spray-dried still is theta-Al_2O_3, but with a specific surface area 2.51 times higher. It seems that the higher specific surface area of the spray-dried alumina at 900ºC gave stability to the transformation theta $\rightarrow$ alpha at 1000ºC, that is, preserved the theta structure at 1000ºC.
- Specific surface areas from alpha-alumina samples from 1100ºC to 1400ºC are the lowest due to the sintering of the crystals as shown by MET.
- Pore volumes also presented maximum values, however at different temperatures: ground membrane – 0.332cm^3/g at 450ºC and spray-dried – 0.334 cm^3/g at 800ºC. No correlation could be found with the structural and morphological changes that could be observed by TEM, SEM and SAED along the increasing temperatures.
- The average pore diamenter increased with temperature until α-Al_2O_3 formation and decreased due to sintering of the crystals. Both maxima occurred at 1100ºC.

Table 2: Values of Specific Surface Área, Total Pore Volume and Average Pore Diameter of fired samples.

Temp (º C)	BET Specific Surface Área (m^2/g)		Pore Volume (ϕ < 781 Å) - cm^3/g		Averare Pore Diameter (Å)	
	membrane	spray	membrane	spray	membrane	spray
200	294	331	0.216	0.203	29	25
300	307	348	0.231	0.247	32	28
400	338	423	0.312	0.315	37	30
450	283	nd	0.332	nd	47	nd
500	268	320	0.317	0.317	47	40
600	222	265	0.309	0.325	56	49
700	179	232	0.314	0.321	70	55
800	156	209	0.298	0.334	77	64
900	122	159	0.265	0.311	87	78
950	103	nd	0.253	nd	104	nd
1000	55	138	0.173	0.292	131	85
1100	11	nd	0.029	nd	105	nd
1300	17	nd	0.042	nd	98	nd
1400	8	nd	0.012	nd	64	nd

4   DISCUSSION

The most significative result from the experiments is the fact that the long fibrillar length of pseudoboehmite fibrillar crystals (Figure 1) is a strong factor for parallel ordering, the packing into bundles and membrane formation in the slow drying of the sol. As consequence, the ground membrane powder has smaller specific surface area than the same spray dried sol powder compared at the same firing temperature. The faster spray-drying avoids some of the parallel ordering of the fibrils and leaves some free surface which will increase the specific surface areas of the aluminas. So, it is reasonable to put the question if shorter spray dried pseudoboehmite fibrils could produce higher specific surface area transition aluminas.

Identical sols to the 168 hours aged pseudoboehmite sols were prepared, only 24 and 48 hours aged at 90ºC to produce shorter microfibrils. TEM comproved that as shown in Figures 11 (24 hours) and 12 (48 hours). BET specific surface areas were measured of the ground membranes and spray-dried sols. Values of the specific surface areas for the sols aged for 24, 48 and 168 hours are in the Table 3.

Data in the literature for aluminas for adsorbents and catalysts ("ad-cat aluminas") give the following values for specific surface areas: Alcoa: 210 m^2/g and 390 m^2/g [22]; Oberlander: gamma-aluminas (typically 150-300 m^2/g); delta- and theta-aluminas (100-150 m^2/g); gibbsite-aluminas (320 – 400 m^2/g) [21]; Almatis AC: surface areas of over 400 m^2/g due to micropores [23].

Considering the temperature ranges of the transition aluminas (Figure 6) as gamma (200^oC – 700^oC), delta (700^oC – 800^oC), theta (900^oC – 1100^oC) and alpha (1200^oC – 1400^oC), from Table 3 it can be concluded that a variety of different specific area aluminas can be prepared by the procedures described in this paper: (I) γ-Al_2O_3 : 497 m^2/g – 179 m^2/g; (II) δ-Al_2O_3 : 230 m^2/g – 156 m^2/g; (III) θ-Al_2O_3 : 200 m^2/g – 11 m^2/g; (IV) α-Al_2O_3 : 17 m^2/g – 2 m^2/g.

Figure 11: TEM of the 24 hours aged pseudoboehmite fibrils.

Figure 12: TEM of the 48 hours aged pseudoboehmite fibrils.

Table 3: Comparison of the Specific Surface Areas (m^2/g) of Membrane and Spray-Dried Powders, Aged at 90^oC for 24h, 48h and 168h.

Temp (^{o} C)	24h aged		48h aged		168h aged	
	membrane	spray	membrane	spray	membrane	spray
200	313	391	270	497	294	331
300	430		336	454	307	348
400	384	397	281	359	338	423
500	314	293	271	326	268	320
600	284	295	236	298	222	265
700	218	224	231	273	179	232
800	202	225	191	230	156	209
900	130	187	122	200	122	159
1000	128	120	17	138	55	138
1100	50	nd	17	nd	11	nd
1200	9	nd	9	nd	nd	nd
1300	nd	nd	4	nd	17	nd
1400	2	nd	2	nd	8	nd

5   CONCLUSIONS

It is possible to prepare highly viscous or aqueous sols of fibrillar pseudoboehmite containing 70 g/L of AlOOH. The ordering of fibrils is larger in powders from membranes of the slowly dried sol than in the spray-dried powder from the same sol. Thermal aging of the sols produces longer fibrils as the aging time increases. Firing the powders to 1400°C changes pseudoboehmite to γ-Al_2O_3 to δ-Al_2O_3 to θ-Al_2O_3 to α-Al_2O_3

Varying temperatures and type of drying the following range of values of the specific surface areas can be obtained: (I) γ-Al_2O_3 : 497 m^2/g – 179 m^2/g; (II) δ-Al_2O_3 : 230 m^2/g – 156 m^2/g; (III) θ-Al_2O_3 : 200 m^2/g – 11 m^2/g; (IV) α-Al_2O_3 : 17 m^2/g – 2 m^2/g.

These values are in the same range of the commercial "ad-cat aluminas".

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