The influence of ageing in pseudoboehmites synthesis

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Abstract. The developing of nanosystems has been intensely studied because of their efficiency when applied to pharmaceutical excipients, frequently called as drugs delivery systems. Sol-gel obtained pseudoboehmite, a fine synthetic ceramic precursor of alumina, shows itself as very promising due to its adsorption/desorption properties with pharmaceutical molecules. The use of factorial planning of two levels is very effective in preliminary studies about the possible influence of specific factors in the reagent conversion to a product. A method of pseudoboehmite obtainment was adopted, that has been already reported. The factorial planning 2^3 used for the pseudoboehmite synthesis involved three variables of synthesis: temperature (A), the aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) concentration (B) and the ageing time (C). The X-ray diffraction data shows that the aging time has influence in the crystalinity of the synthesis product.

Introduction

Pseudoboehmite is an aluminium oxyhydroxide that can be prepared by sol-gel synthesis. This is a very important material with application in the thermally induced transformation to γ-alumina used as catalyst. Owing to its large surface area, γ-alumina is a catalyst support often used. The phase transformations of pseudoboehmite with the increase of temperature are the same of boehmite [2]. The sequence of phase transformations is:

$$\text{boehmite} \rightarrow \gamma\text{-alumina} \rightarrow \delta\text{-alumina} \rightarrow \theta\text{-alumina} \rightarrow \alpha\text{-alumina} \quad \text{(eq. 1)}$$

Due to the importance of γ-alumina as catalyst, several preparations use the sol-gel process, which allows possibility to control the pore size and surface area of the synthesis product. Pseudoboehmite can be also used in ceramic nanoparticles production. Ceramic nanoparticles preparation method, including sol-gel process, has been proved to be convenient for inorganic systems with porous characteristics that have recently emerged as drug vehicles [1]. Because these particles can be easily engineered with the desired size and porosity, growing interest has emerged to use ceramic nanoparticles as drug delivery systems. These biocompatible ceramic nanoparticles such as silica, titania and alumina can be used in cancer therapy. However, one of the main concerns is that these particles are non-biodegradable, as they can accumulate in the body, thus causing undesirable effects.

Experimental

The planning of the experiments was realized using factorial experimental design. In a factorial design the influences of all experimental variables, factors, and interaction effects on the response or responses are investigated. If the combinations of k factors are investigated at two levels, a factorial design will consist of 2^k experiments. The levels of the factors are given by − (minus) for low level and + (plus) for high level [3]. Three experimental variables were studied: concentration of aluminum nitrate solution, Temperature of precipitation and ageing time at 100^o C. The parameters used in the reactions are showed in Table 1.

Table 1: Studied parameters in the reactions

Variables	level (-)	level (+)
A - $Al(NO_3)_3.9H_2O$ concentration	900 g/L	450 g/L
B - Synthesis temperature	25°C	-9°C
C - Aging time	24 horas	0

The matrix of the experiments of the 2^n factorial experimental design is showed in Table 2.

Table 2: Matrix of the full factorial 2^3 experimental design.

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

The used reagents were: aluminum nitrate solution obtained using $Al(NO_3)_3.9H_2O$ and ammonium hydroxide (NH_4OH) water solution (28wt%). The aluminium nitrate solution was dropped into an ammonium hydroxide solution. All chemicals used in the experiments are of analytical purity and used directly without any further purification. All the solutions were prepared with deionized water. All the eight experiments were carried using batch technique. The products of each reaction were filtered and washed with water during filtration. Thereafter the product of filtration was dried at 70^o C for 24 hours in air.

Characterization of the samples:

The pseudoboehmites obtained in the 8 different conditions were characterized by several techniques. The specific surface area was obtained at IPEN and the other analysis was obtained at Mackenzie University.

Thermal analyses: The thermogravimetric analysis (TG) and differential Scanning calorimetry (DSC) were performed in Netzsch-STA409C equipment; heating from room temperature to 1300^o C, with 20^o C min^{-1} heating rate and $50cm^3/min$ N_2 flow.

X-rays powder diffraction: The samples dried at 70^o C were analyzed by x-ray diffraction. For the 8 samples were collected diffraction data with a Rigaku MultiFlex difractometer with a fixed monocromator. The experimental conditions were: 40kV, 20mA, $20^o \leq 2\theta \leq 80^o$, $\Delta 2\theta = 0.02^o$, $\lambda_{CuK\alpha}$, divergence slit = 0.5^o, reception slit = 0.3 mm and step time 2 s.

Specific surface area: The specific surface area was measured with a Quantachrome NOVA 1200 Brunauer–Emmett–Teller BET surface analysis instrument, based on adsorption of N_2.

Scanning electron microscopy: Scanning electron microscopy (SEM) images were taken with a Jeol equipment JSM 6510, using secondary electron detector and EDS detector. The powder was placed upon SEM stubs covered with double-face tape and covered with gold in an Edwards Sputter Coater model S150B. The images were registered under several magnifications.

Results and discussion

Thermal analysis

The results of differential scanning calorimetry indicate that in the aged samples the phase transformation to γ-alumina was at a temperature of 327.1ºC and in α-alumina at approximately 1.188.9°C (Figure 1). A higher temperature was necessary for the transformation to α-alumina of the not aged samples. The obtained results were similar to those, published previously [4]. When calcined, pseudoboehmite can result in the crystalline phases described in equation 1.

X-rays powder diffraction: The aged samples 5 and 8 showed a increase in the cristalinity with well defined peaks in the x-ray diffraction data. The factorial analysis shows that the ageing time and the interaction effect of the aluminum nitrate concentration and temperature of synthesis influence the cristalinity of the product. The X-ray diffraction data are similar to those published by MOROZ et al [5]. Figure 2 shows the x-ray diffraction data for sample 4 (not aged sample) and the result for sample 5 (aged sample).

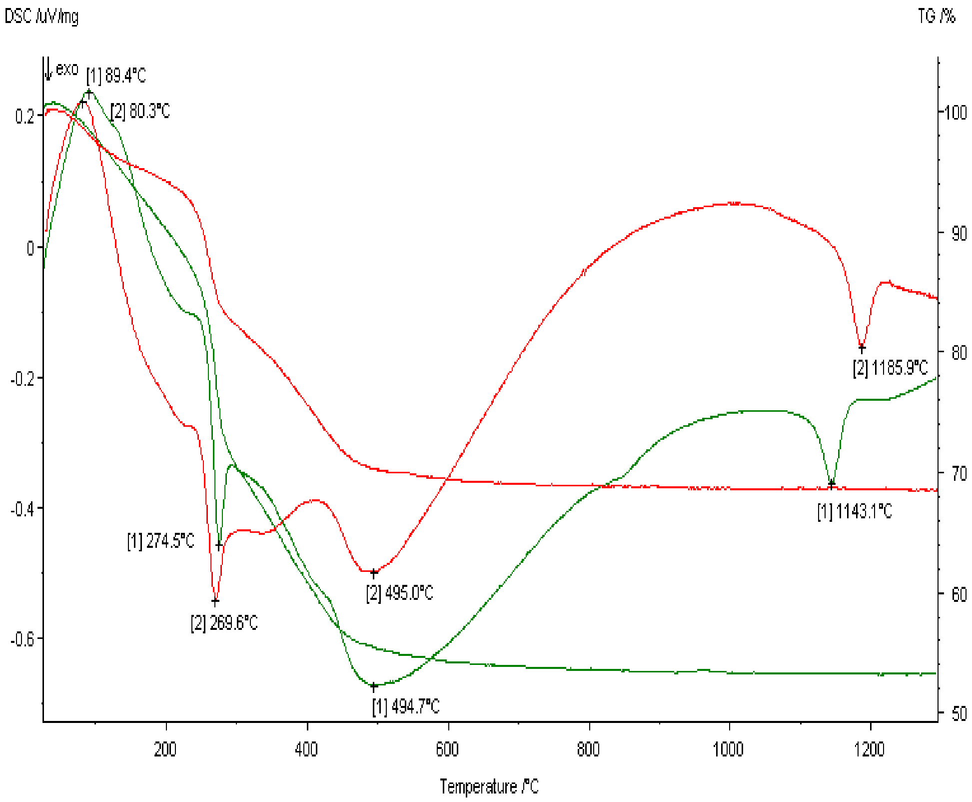
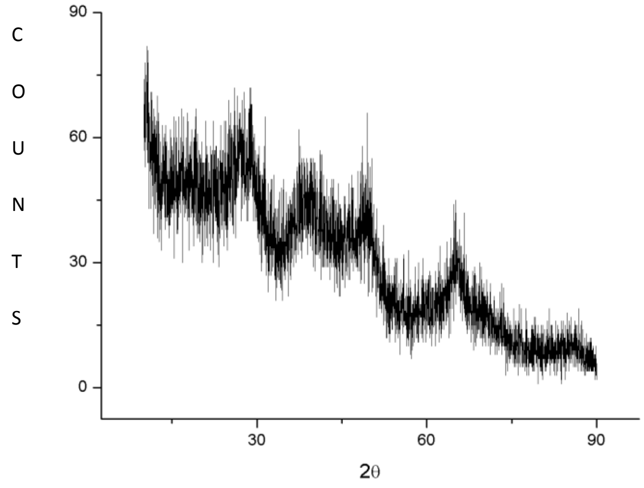


Figure1: DSC and TG curves of the aged sample 8 (top) compared with the curve of not aged sample 4 (bottom).

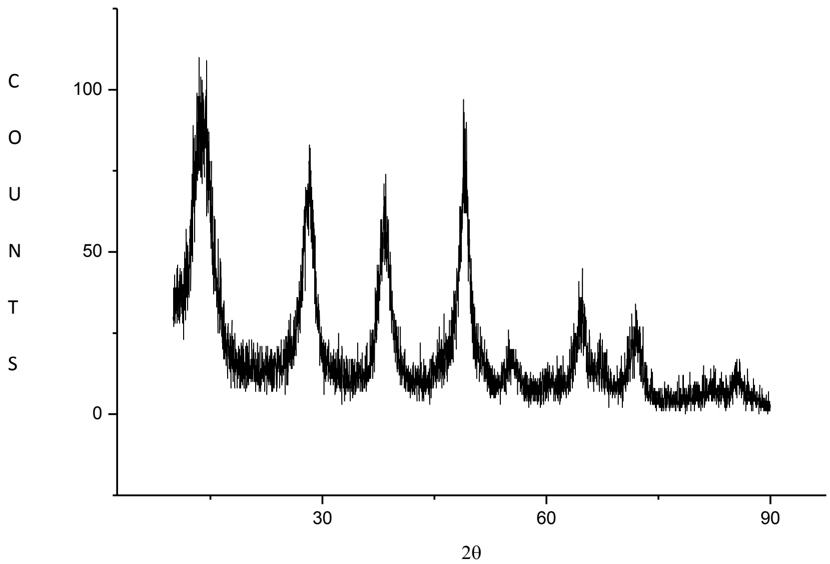
Specific surface area: Table 3 shows the results of the specific surface area of the eight samples. The Factorial 2^n experimental design calculation shows that no variables can influence the specific surface area of the pseudoboehmites. Besides the calculations of the 2^n factorial experimental design demonstrate the aging time has no influence in the specific surface area, the medium value of the specific surface area for the not aged samples is 42 m^2/g and for the aged samples is 100 m^2/g.

Table 3. Specific surface area results

Sample	Specific surface area (m^2/g)
1	0.4
2	140.5
3	20.2
4	8.6
5	220.3
6	34.4
7	52.7
8	92.2



(a)



(b)

Figure 2: XRD-data of sample 04 (a) and sample 05 (b).

Scanning electron microscopy: the scanning electron microscopy of the samples 4 and 8 obtained using secondary electron detector is showed in Figures 3, 4 and 5. Figure 4 and 5 shows a presence of fibers in the surface of the aged sample.

Figure 6 shows the results of EDS detector for sample 8 The small peak of the EDS spectra is due the sputtering of the sample with gold. Table 4 shows the results of EDS analysis of sample 4. As expected there is the presence of only aluminum and oxygen according with the pseudoboehmite formula (AlOOH). The results of table 4 show 1 atom of aluminum for 2 atoms of oxygen.

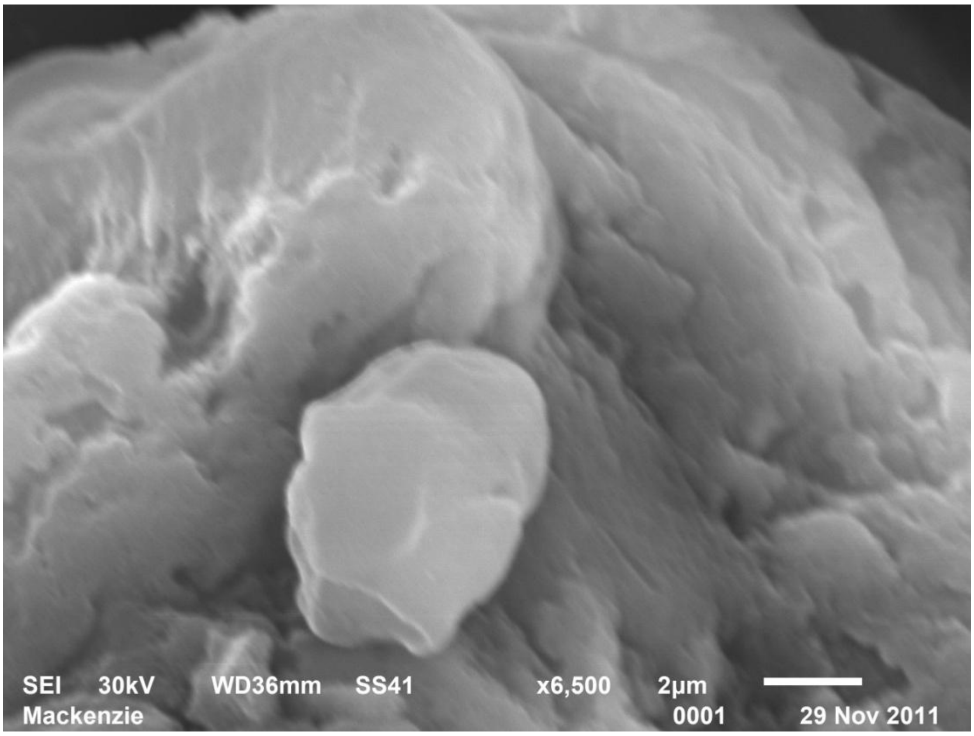


Figure 3. SEM of fample 4.

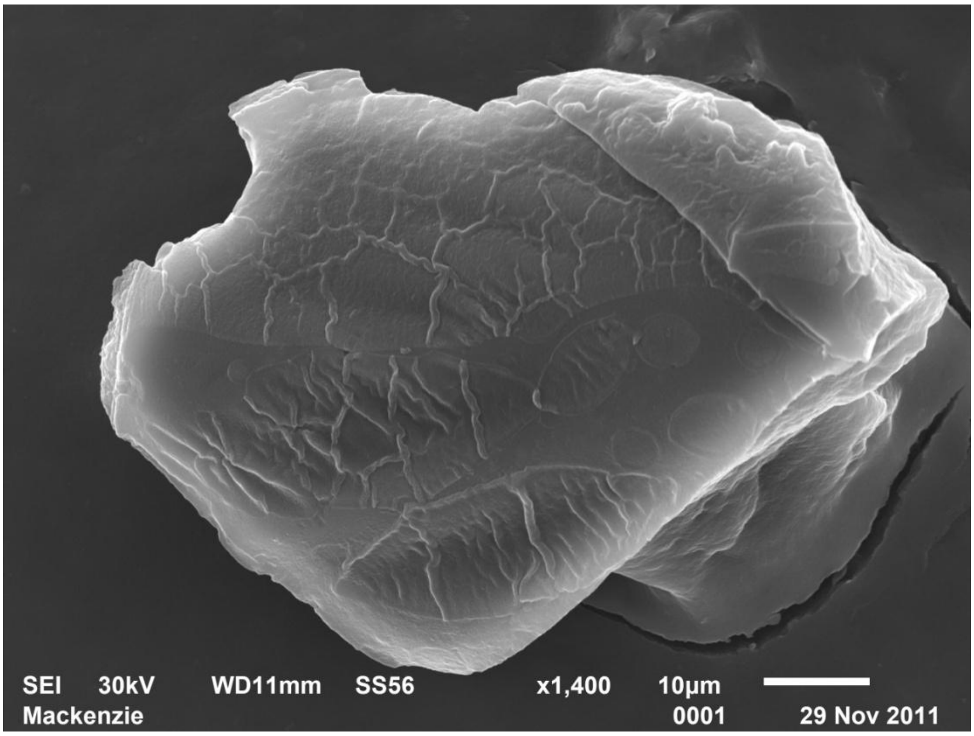


Figure 4. SEM of sample 8. Magnifications of 1400X.

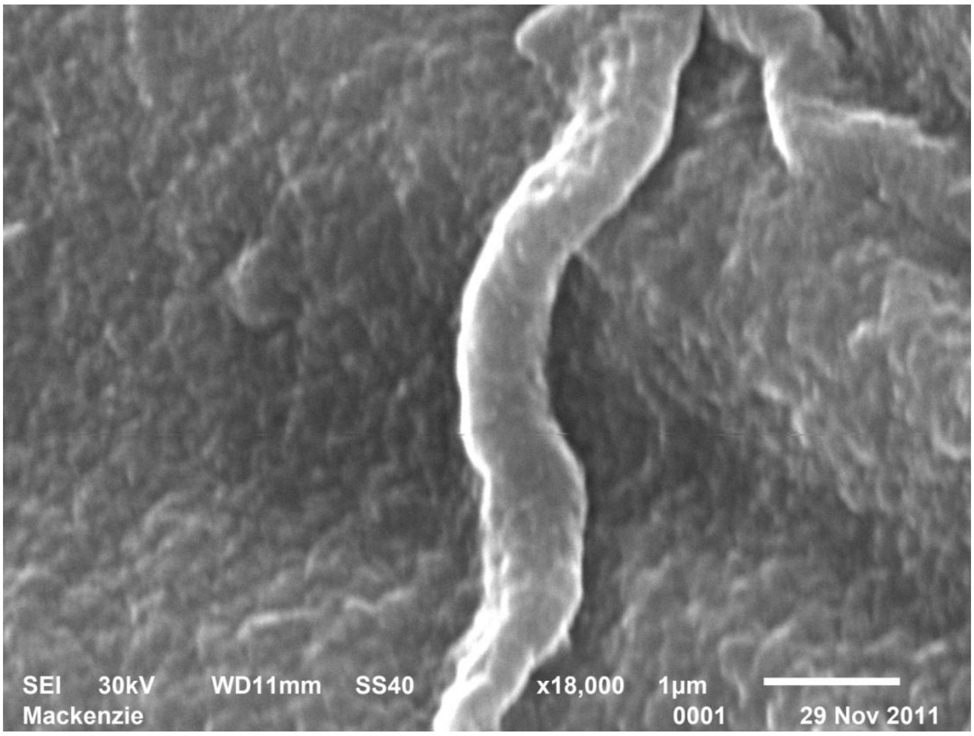


Figure 5. SEM of sample 8. Magnifications of 18000X

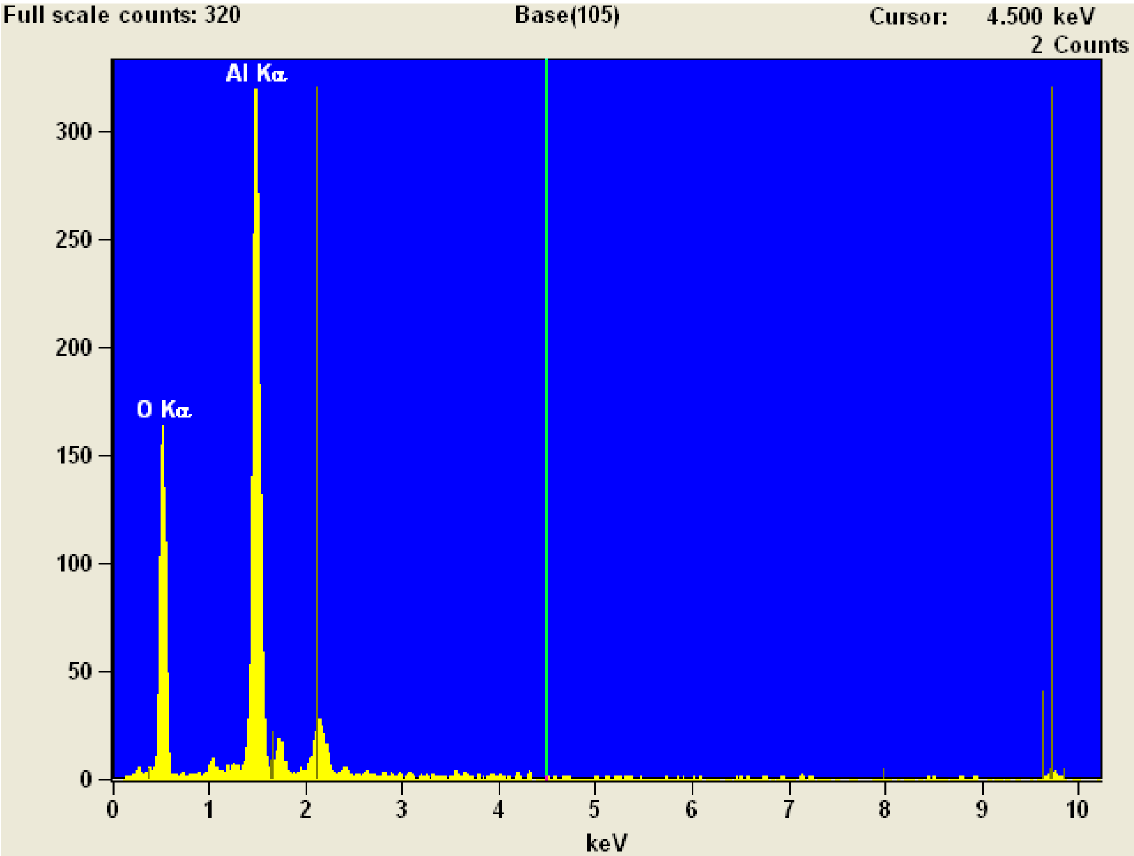


Figure 6. Results of EDS spectra of sample 8.

Table 4. Results of EDS analysis of sample 8

Element Line	*Net Counts*	*Weight %*	*Atom %*
O K	906	54.92	67.26
Al K	2298	45.08	32.74
Total		100.00	100.00

Conclusions:

The results show that the ageing time increases the cristalinity of the material. The results indicate that for the aged samples the specific surface area is bigger than the not aged samples. The thermal behavior of the sample is similar to the reported in the literature. The sample contains aluminum and oxygen according with the pseudoboehmite formula (AlOOH). The aged samples show the presence of fibers in the sample.

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