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STUDY OF THE EFFECT OF RADIATION IN PSEUDOBOEHMITESOBTAINED BY SOL-GEL PROCESS

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ABSTRACT

The synthesis of pseudoboehmites by sol-gel process is a promising technique for the synthesis of aluminas with high specific surface area and with controlled pore diameter. A pseudoboehmite was obtained by sol-gel process using aluminum nitrate as precursor. The purpose of this work is to study the pseudoboehmite by sol-gel process using different synthesis conditions and the effect of variation the synthesis conditions in the properties of pseudoboehmites and aluminas. A 2^n experimental planning was used to study the effect of the 4 synthesis variables: temperature (room temperature of ~25^{o}C and low temperature of -3oC), concentration of ammonium hydroxide, concentration of the PVAL solution and ionizing radiation. The obtained products of the synthesis with different conditions were characterized by various techniques: scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and infrared absorption spectroscopy. The samples of the different synthesis were calcined at 1100oC during 4 hours and powder diffraction data of the products were collected in order to compare their crystallinity. The difractograms indicate that these products are well crystallized α-alumina.

1. INTRODUCTION

Actually most of the shape selective reactions in industry use zeolites as catalyst. The molecular sieves have pore diameters between 0.5 and 0.6 nm. The pore diameter of the zeolite catalyst can not accommodate the high molecular weight molecules. So it is interesting in the present day to develop heterogeneous mesoporous catalysts (with porous higher than 1 nm and lower than 25 nm) for processing high-molecular-weight hydrocarbons. The sol-gel synthesis is a promising process for obtaining high surface area alumina with controlled pore diameter.

Pseudoboehmite is an amorphous material that can be obtained by sol-gel synthesis using aluminium nitrate($Al(NO_3)_3$) or aluminum chloride ($AlCl_3$) as precursor for example. Freshly aluminium hydroxide, precipitated from aqueous $AlCl_3$ and one alkali at various pH, can

produce pseudoboehmite upon aging [1]. Alumina channeled beads and rough surface membranes prepared from aqueous sols of fibrillar pseudoboehmite are able to immobilize yeasts for ethanol fermentation of sugar solutions [2]. Powders with specific surface areas as high as 710 m^2/g and narrow pore size distributions centered at 20 Å were obtained from calcined pseudoboehmite [3]

2. EXPERIMENTAL

The used reagents were: ($Al(NO_3)3.9H_2O$; 980g aluminium nitrate/1 L water), ammonium hydroxide (NH_4OH) water solution (14 wt% and 28 wt%) and polyvinyl alcohol ($[C_2H_4O]n$) solution (12 wt% in water), which was used to increase the viscosity. The aluminium nitrate solution was mixed with the polyvinyl alcohol and the mixture was dropped into an ammonium hydroxide solution. The product of the 8 reactions was washed during filtration. There after the product of filtration was dried at 70^o C for 24 hours in air. The parameters used in the 2^n full factorial experimental design for study of the reaction are showed in Table 1.

Table 1: Studied parameters in the reactions

Variable	level (-)	level (+)
A – synthesis temperature	-5º C	25º C
B – concentration of ammonium hydroxide solution	14 (wt %)	28 (wt %)
C – radiation dose	0	200kGy

The irradiated samples were submitted to the irradiation with electron beam, from DYNAMITRON electron accelerator, with energy in the order of 1.5MeV and dose rate of 11.3 kGy/s, in the dose of 200 kGy. The reaction medium was irradiated after precipitation of the pseudoboehmite.

2.1 Infrared absorption spectroscopy

The infrared spectrum was obtained using an Perkim Elmer equipament model Spectrum BX.

2.2 Thermal analyses

The thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were performed in a Netzsch-STA409C equipment; the heating was from room temperature to 1300^o C, with 20^o C min^{-1} heating rate and 50 cm^3/min N_2 and synthetic air flow.

2.3 X-rays powder diffraction

For all samples calcined at 1100^o C for 4 hours were collected diffraction data with a Rigaku MultiFlex difractometer with a fixed monocromator. The experimental conditions were: 40kV, 20mA, $20^o \leq 2\theta \leq 100^o$, $\Delta 2\theta = 0.02^o$, $\lambda_{CuK\alpha}$, divergence slit = 0.5^o, reception slit = 0.3 mm and step time 6 s.

2.4 Scanning electron microscopy

Scanning electron microscopy (SEM) images were taken with a Jeol JSM 840A equipment, using secondary electron 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 magnifications of 600X and 6000X.

3. RESULTS AND DISCUSSION

It was observed that Irradiated samples are yellow and non-irradiated samples are white.

3.1 Infrared absorption spectroscopy

The infrared spectroscopy of all non calcined samples shows a characteristic peak (at 980-1020 cm^{-1}) to the bond aluminum-oxygen (see the small box in Figure 1). The spectrum of the irradiated and non-irradiated samples has no difference. For the samples calcined at 500º C it was observed that the irradiated samples have a higher amount of adsorbed water than the non-irradiated one.

In the non irradiated samples calcined at 500º C, it was observed a peak at 1650 cm^{-1} due to the presence of water.

In the irradiated and non irradiated samples calcined at 1100º C (Figure 1) it was not observed the presence of water. It was observed a peak near 2400 cm^{-1} probably due to an impurity present in all samples.Figure 1 shows an infrared spectrum of an irradiated sample.

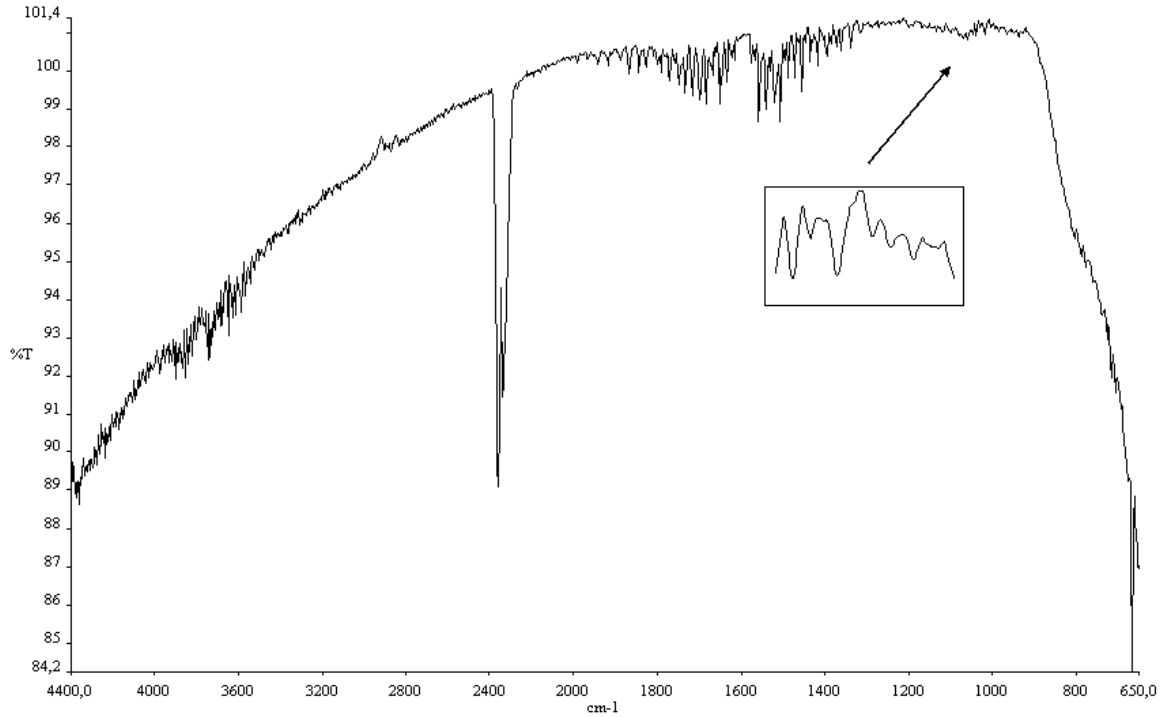

Figure 1. Infrared spectrum of an irradiated sample calcined at 1100º C

3.2 DSC, TG analysis

A typical DSC curve (Figure 2) shows an endothermic curve at 100° C, due to the water vaporization, and an exothermic curve around 300° C due to the beginning of PVAL decomposition. The decomposition of PVAL and the dehydration of pseudoboehmite at the same range temperature of DSC analysis resulted in complex peaks in this region. In the thermal analysis at 1200° C is observed a peak attributed to the transformation of the last metastable phase of alumina to α-alumina. It was observed that the endothermic and exothermic peaks of the irradiated samples occurred at higher temperatures than those of the non-irradiated samples.

For the irradiated samples, the exothermic peak of α-alumina nucleation was observed at 1211.6° C (average of 4 samples) in nitrogen and 1205.7 ° C in air. The same exothermic peak was observed at 1191.1° C and 1189.5 ° C in nitrogen and air respectively, for the non-irradiated samples.

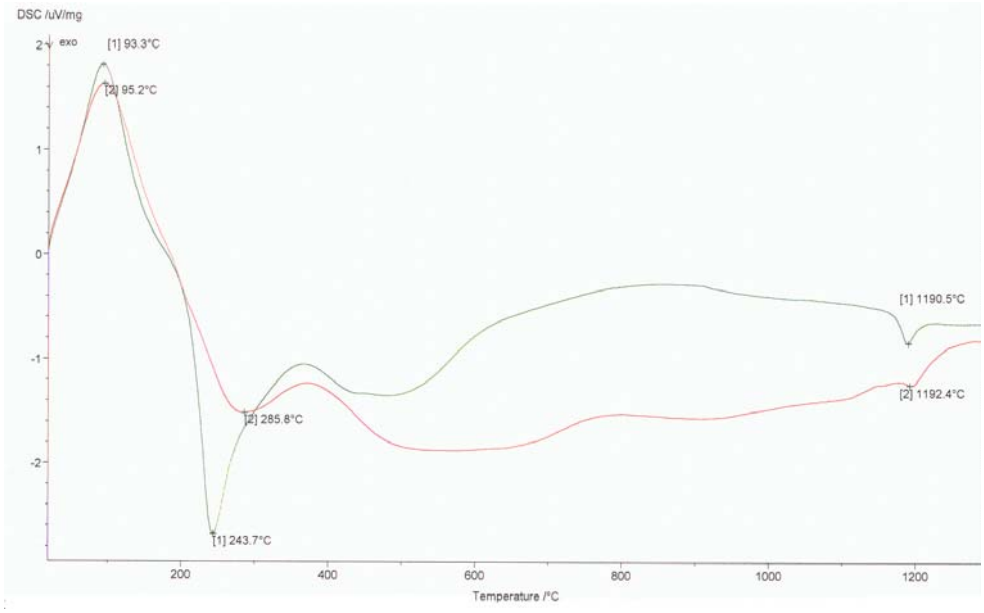

Figure 2 DSC and TG analysis for a typical sample of a non irradiated sample; green (air), red (nitrogen)

3.3 Scanning electron microscopy

From the (SEM) micrographs it is observed that the γ-Al_2O_3 crystallites (samples of pseudoboehmite calcined at 500°C) present anisometric morphology (Figure 3).

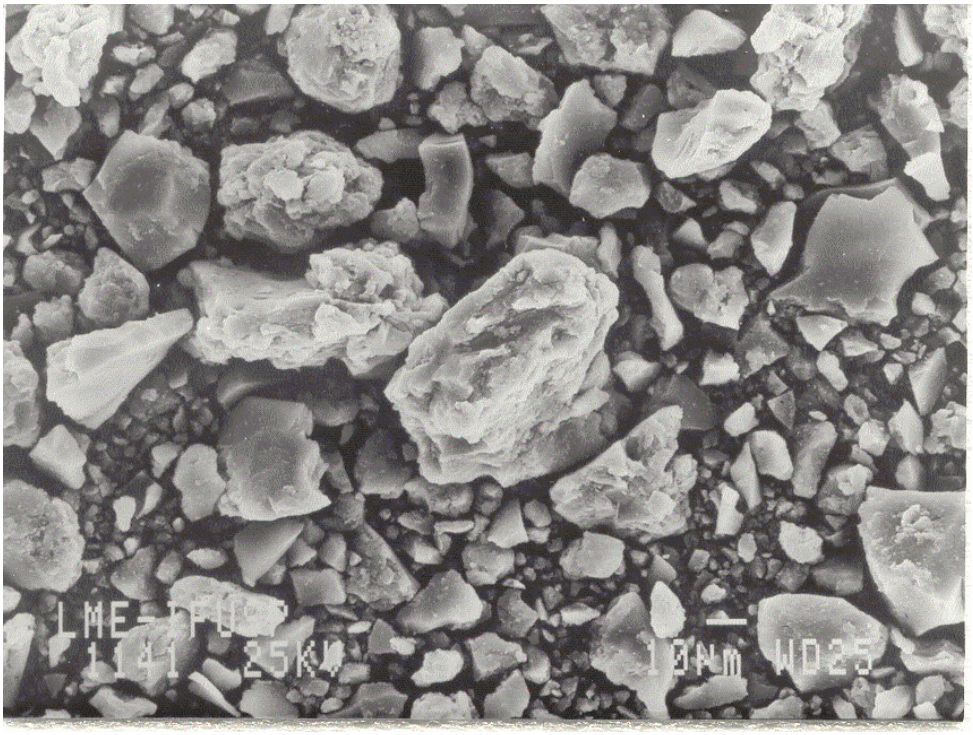

Figure 3. Micrograph of a typical sample obtained with secondary electron detector. Magnification = 600X.

Figure 4 shows a comparison between the crystallites of an irradiated and a non-irradiated sample, where it is observed that the irradiated one presents a higher amount of very small particles randomly distributed on the surface of the crystallite.

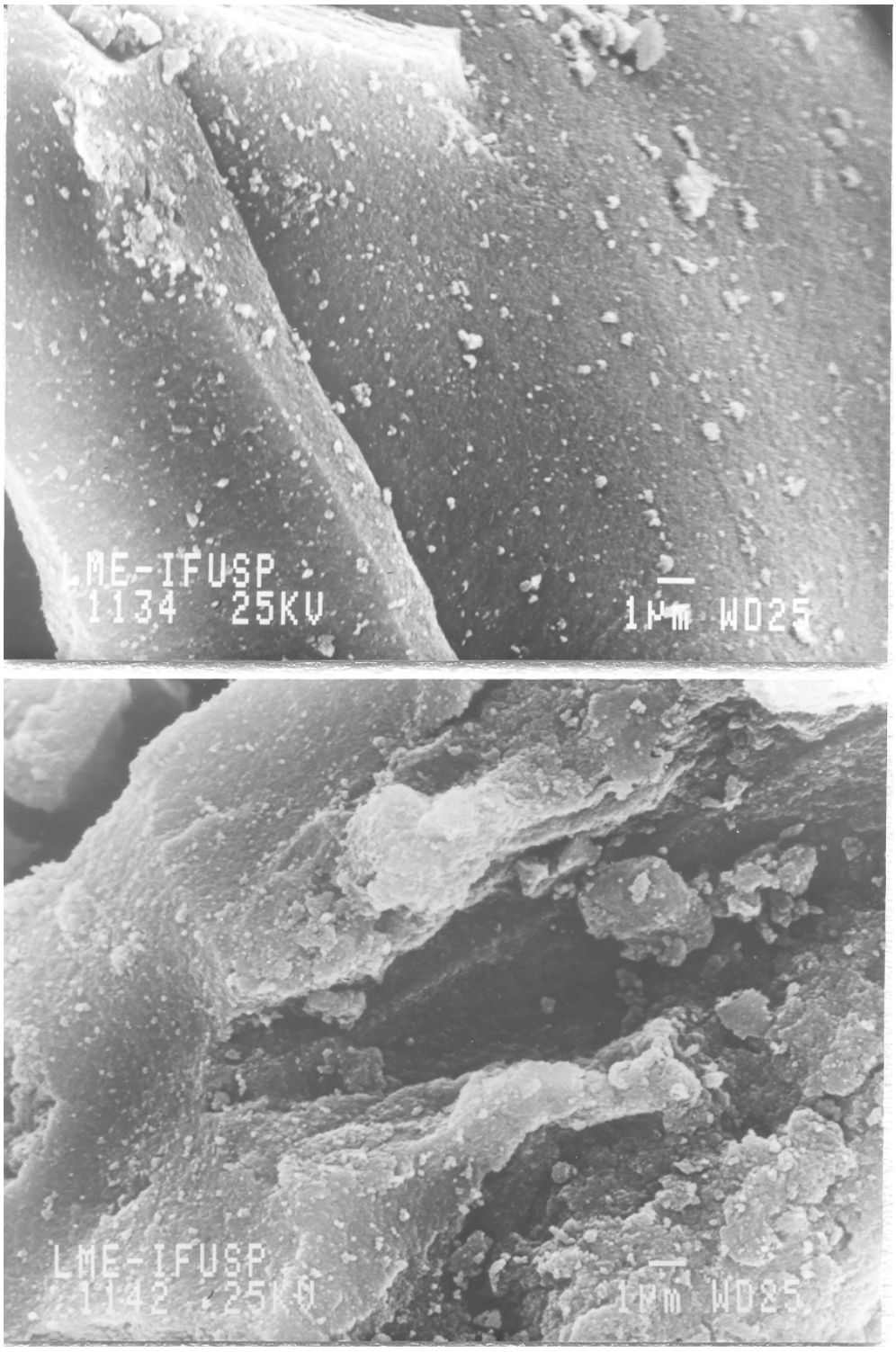

Figure 4. Micrographs of a non irradiated (top) and a irradiated sample (bottom) obtained using secondary electron detector. Magnification = 6000X.

3.4 X-rays powder diffraction

A first comparative overview of powder diffraction data from all samples shows that those calcined at 1100°C present the α-Al_2O_3 structure (ICDD 10-173). It was not observed the

presence of impurities by the X-Ray diffraction data (Figure 5). The average intensity of the irradiated samples is greater (84%) than that of the non-irradiated (69%), which could indicate that the radiation increased the crystallinity (see Table 2).

Table 2: X-ray diffraction data for α-Al_2O_3 samples

Sample	Relative Area	Sample	Relative Area
1	78.6	5	77.1
2	77.1	6	100
3	58.6	7	64.3
4	60.7	8	95

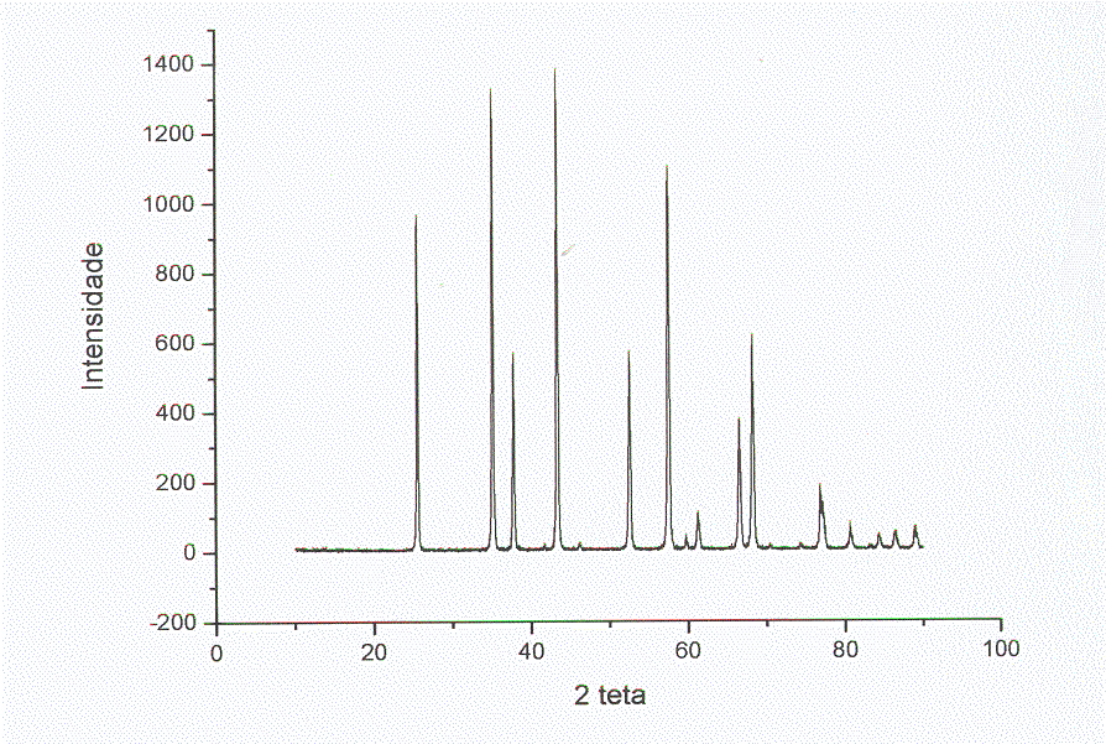

Figure 5. X-Ray diffraction of a irradiated sample calcined at 1100o C.

3. CONCLUSIONS

The infrared data shows that the spectrum of the irradiated samples and the non-irradiated samples has no difference. From the DSC and TG analysis we conclude that the samples of the 8 experiments present a characteristic pseudoboehmite behaviour. From the X-rays diffraction data we conclude that the samples calcined at 1100^o C present the characteristic α-alumina structure. From the full factorial experimental design, we conclude that: The irrradiation of the samples with electrons, the low concentration of ammonium hydroxide in the reaction synthesis and the higher temperature of synthesis increased the crystallinity of the samples. The irradiation of the samples is the principal effect in the increase of their cristalinity. The endothermic and the exothermic transformations of irradiated samples observed in DSC occurred at higher temperatures than the non-irradiated samples.

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