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Structural analysis by the Rietveld method and SEM of irradiated pseudoboehmite and Al_2O_3

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Abstract. The thermally induced transformation of pseudoboehmite via transition aluminas to corundum was recently studied by different techniques [1] [2]. In this work, a pseudoboehmite was obtained by sol-gel synthesis using aluminum nitrate and ammonium hydroxide as precursors. The samples were irradiated with electrons to study the possible effects of radiation in their properties. It was used a full factorial experimental design for studying the effect of the temperature of synthesis, the concentration of ammonium hydroxide during the reaction and the radiation dose in the product of sol-gel synthesis. The product of the synthesis was calcined at different temperatures and studied by scanning electron microscopy (SEM) and X-rays powder diffraction. Thermo gravimetric analysis (TG) and differential scanning calorimetry (DSC) were used to analyze the loss of mass and the endothermic and exothermic transformations. The SEM results show that the temperature of sol-gel synthesis has a strong effect in the morphology of the obtained pseudoboehmite. A well crystallized α-alumina was obtained at 1100°C and the X-ray powder diffraction data of the irradiated samples were used to refine the structures by the Rietveld Method with GSAS. The refinement results allowed an analysis of the effects of variations in the synthesis method in the structural and micro structural parameters.

Introduction

Actually most of the shape selective reactions in industry use zeolites as catalyst. The molecular sieves have pore diameters between 0.5 and 0.6nm. 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. γ-alumina is also an important support as inert carrier for the metal catalysts. The preparation of α-alumina by heating aluminium hydroxides can produce a finely divided powder constituted by micrometer sized particles.
One of the sol-gel-synthesis methods uses ultrasound to break the weak bindings, which are responsible for the aggregates formation at room temperature [3]. One important method of obtaining aluminas by sol-gel process using alcoxides was developed by Yoldas [4,5]. Aluminas obtained by this method present high specific area [6]. The use of organic additives as polyvinyl alcohol and oxalic acid to obtain the gel was studied by Kunze[7].
The irradiation of materials with electrons, especially polymers, is growing recently[8]. So the aim of this paper is to study the effect of a huge radiation dose of 200 kGy in the gel of pseudoboehmite. We report the study of the effect of irradiation in the characteristics of aluminas obtained from irradiated pseudoboehmite. We did not found any previous report in the literature about characterization of pseudoboehmite irradiated with electrons.

Experimental

The used reagents were: (($Al(NO_3)3.9H_2O$; 980g aluminium nitrate/1 L water), ammonium hydroxide (NH_4OH) water solution (14wt% and 28wt%) 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. Thereafter the product of filtration was dried at 70^o C for 24 hours in air. The parameters used in the reactions are showed in Table 1 and the full factorial experimental design is showed in Table 2.
The irradiated samples were submitted to the irradiation with electron beam, from electrons accelerator of the DYNAMITRON, with energy of the order of 1.5MeV and tax of dose of 11.3kGy/s, in the dose of 200kGy.

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

Table 2. Matrix of the full factorial experimental design.

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

Thermal analyses: The thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were performed in a Netzsch-STA409C equipment; heating from room temperature to 1300º C, with 20º C min^{-1} heating rate and 50cm^3/min N_2 and synthetic air flow.
X-rays powder diffraction: For the irradiated sample calcined at 1100º 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 = 0.5º, reception slit = 0.3 mm and step time 6 s. The Rietveld analysis was performed with the Rietveld refinement program GSAS [9]. The profile function used was the Thompson-Cox-Hasting pseudo-Voigt.
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 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.

Results and discussion

During the pseudoboehmite synthesis it was observed that the experiments prepared using low temperature and low ammonium hydroxide concentration (14 wt%) promoted aggregation among the particles during the precipitation. Irradiated samples are yellow and non-irradiated samples are white.
DSC, TG analysis and Specific surface area: A typical DSC curve shows an endothermic curve at 100ºC, due to the water vaporization, and an exothermic curve around 300ºC due to beginning of PVA decomposition. The decomposition of PVA 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 1200ºC 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 (Figure 1). For the irradiated samples, the exothermic peak of α-alumina nucleation was observed at 1211.6º C (average of 4 samples) in nitrogen and 1205.7 º C in air. The same exothermic peak was observed at 1191.1 º C and 1189.5 º C in nitrogen and air respectively, for the non-irradiated samples. The differences are probably due to the difference in the specific surface area. The irradiated samples have a lower specific surface area (175.2m^2/g average) than the non-irradiated samples (262.3m^2/g average). Table 3 shows the data of the specific surface area for the 8 samples.Using the statistical software Minitab (http://www.minitab.com/), for the response variable specific surface area, the data of Table 4 was obtained.
By the analysis of the effects of the variables in the specific surface area (Table 4) it is observed that the irradiation of the samples decreased the specific surface area of the samples calcined at 500º C. This means that the irradiated samples present a smaller specific surface area than the non-irradiated samples and this is the principal effect of the analyzed variables. Figure 2 shows the Pareto chart of the effects for alpha equal 0.21. In this graphic it is possible to see that the effect “radiation dose” (Term C) is the principal effect for the response variable specific surface area.

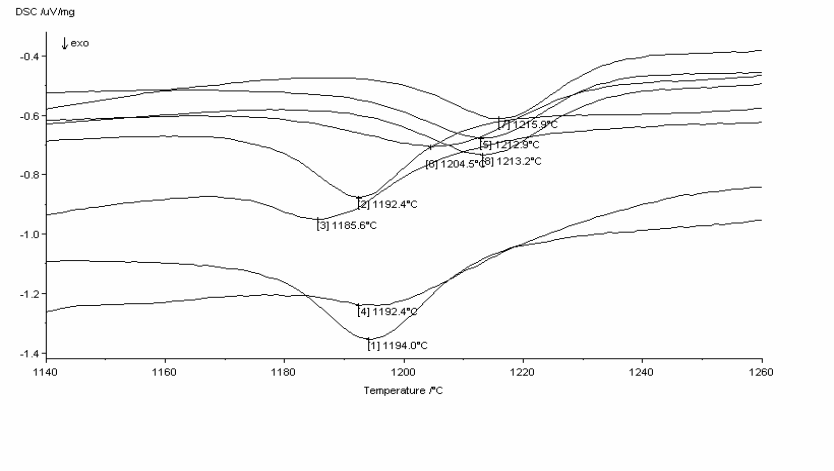

Figure 1. DSC of the irradiated samples (5-8) and the not irradiated samples (1-4) in nitrogen.

Table 3. Specific surface area of the 8 samples.

Sample	Specific surface area(m^2/g)	Sample	Specific surface area(m^2/g)
1	265.8	5	107.3
2	259.5	6	177.9
3	260.7	7	170.8
4	263.2	8	244.7

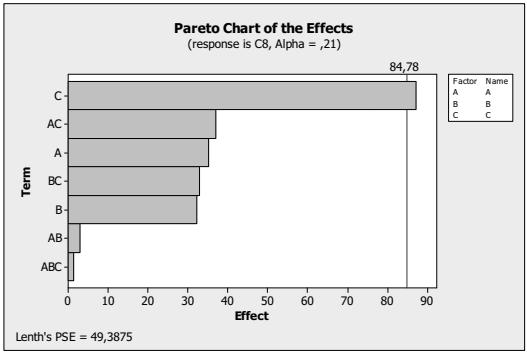

Figure 2. The Pareto chart of the effects obtained using the software Minitab 14.

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 4 shows a comparison between the crystallites of an irradiated and a non-irradiated sample, where it is observed that the irradiated one present a higher amount of

very small particles randomly distributed on the surface of the crystallite. The small surface area of the irradiated samples probably is due to the pore structure.

Table 4. 2^3 experimental factorial designs – Estimated effects and coefficients for the data of table 3

Term	**Effect**	**Coefficient**
Constant		218,7
A-synthesis temperature	35.2	17.6
B– concentration of NH_4OH solution	32.2	16.1
C – radiation dose	-87.1	-43.6
2-way Interactions AB	3	1.5
AC	37.1	18.5
BC	32.9	16.5
3-way interactions - ABC	-1.4	-0.7

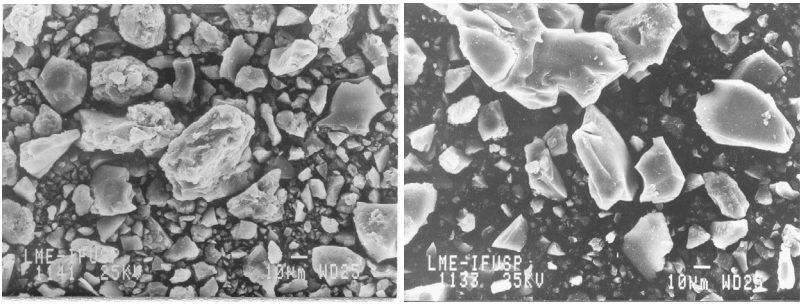

Figure 3. Micrograph of sample 7(left) and 3 (right), magnification of 600X.

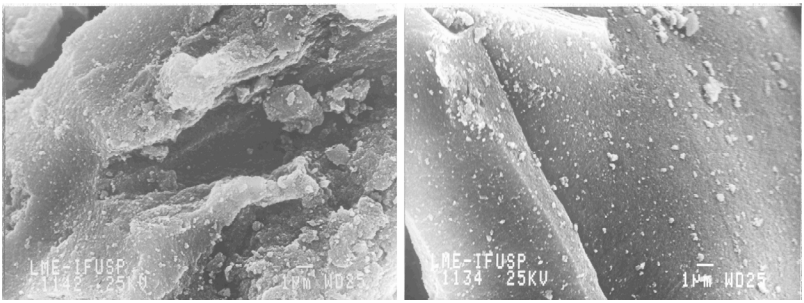

Figure 4. Micrographs of sample 7 (left) and 3 (right), magnification of 6000X.

X-ray powder diffraction: A first comparative overview of powder diffraction data from all samples show that those calcined at 1100°C present the α-Al_2O_3 structure (ICDD 10-173). The samples are pure, i.e. no observable impurities were detected. 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 5).

Table 5. Refinement results and discordance factors for irradiated α-Al_2O_3.

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

The refinement results and discordance factors for a irradiated sample using the Rietveld method are resumed in Table 6.

Table 6. Refinement results and discordance factors for irradiated α-Al_2O_3.

Atomic positions	Al	0	0	0.35223(4)	
x, y, z	O	0.3069(1)	0	1/4	
Thermal U_{iso} (Å^2)	Al	0.01148(14)			a = 4.76035(4), c = 12.9960(2) Å
	O	0.01816(26)			R_{wp}=0.10, R_p=0.072, χ^2=3.47, R_{Bragg}=0.027

Conclusions

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 and no significant microstrain broadening. From the full factorial experimental design, we conclude that: the radiation 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 electrons irradiation promoted the decrease of the specific surface. Due to this, 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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