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Study on the NaOH/metakaolin Ratio and Crystallization Time for Zeolite a Synthesis from Kaolin Using Statistical Design

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The NaOH/metakaolin ratio and crystallization time were studied for the synthesis of zeolite NaA from a sample of kaolin from a Capim mine. The tests were carried out by using statistical design with axial points and replication of the central point. The samples obtained were characterized by X-ray diffraction (DRX), scanning electron microscopy and chemical analysis using a microprobe EPMA. The results showed that there is a relationship between the amount of NaOH added and crystallization time. The tests carried out using the lowest NaOH/metakaolin ratio (0.5) and the shortest time (4 h) produced a non-crystalline material. On the other hand, increasing the NaOH/metakaolin ratio and the crystallization time led to the formation of a NaA phase with a high structural level, but with the presence of a sodalite phase as an impurity.

Keywords: *Zeolite NaA, metakaolin, statistical design*

1. Introduction

Kaolin is a type of clay with various applications such as ceramics, adsorbents, and a source of Si and Al for the synthesis of zeolites. This material is composed mainly of the clay mineral kaolinite, which has a Si/Al ratio close to 1, making it very interesting for the synthesis of zeolite A[1,2,3].

Materials synthesized from clays can be applied in both adsorption and catalysis with results comparable to or even better than some commercial materials. Loiola et al (2012)[4] showed that a NaA type zeolite synthesized from metakaolin (produced from a Brazilian kaolin calcined at 900 °C for 2 h) more efficiently removed Ca^{2+} from water than commercial zeolite A. Magnetization treatments can be carried out on these materials without a great loss in efficiency. Liu et al (2013)[5] synthesized a zeolite with magnetic properties by adding Fe_3O_4 from a metakaolin. It was used in the following conditions: $SiO_2/Al_2O_3 = 2.3$, $Na_2O/SiO_2 = 1.4$, $H_2O/Na_2O = 50$, and crystallization time of 8 h at 95 °C, and an efficiency of over 95% was observed for the removal of lead and copper. Cation exchange with Ca^{+2} in zeolite NaA synthesized from kaolin, with a cation exchange capacity of 183.40 meq/100 g, has produced an adsorbent for arsenic[6].

These materials can also be used as supports in catalysis. Selim and El-Maksoud (2004)[7] have carried out tests with zeolite LTA produced from the hydrothermal treatment of an Egyptian kaolin with Ni, in which they observed that the material studied showed high catalytic activity in the hydrogenation of sunflower oil.

Because of these and other studies that show different potential applications of these materials, the study of the synthesis of zeolites is important because of the variations in the chemical and mineralogical composition of raw materials (kaolin). These natural products are obtained from different regions, and their characteristics influence the synthesis of zeolitic materials. For this reason, different studies have been or are being conducted on the synthesis procedures to adapt and improve methodologies for the use of regional raw materials.

For example, Alkan et al (2005)[8] studied the influence of NaOH concentration and the solid/liquid ratio on the synthesis of zeolite NaA using a metakaolin obtained at 900 °C for 2 h. The synthesis time was fixed at 2 h, with the best concentration of 4 mol/L NaOH used. However, by using a concentration of 6 mol/L, the best solid/liquid ratios obtained for the synthesis were from 1.25 to 5.0 g in 25 mL at 2 h with a synthesis temperature of 105 °C.

Kaolin can be activated mechanically or by calcination. The use of both types of activated kaolin is interesting for the production of zeolite A. Cristóbal et al (2010)[9] have shown that a kaolin composed of 47.76% SiO_2, 39.68% Al_2O_3 and only 5% quartz, treated either by mechanical grinding or

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by calcination, can provide the formation of zeolite A after activation with NaOH 5 mol/L at 90 °C for 3 h with stirring. However, in the same study, a sample with a high quartz content, 89%, and only 7% kaolinite was not suitable for the production of zeolite A due to the higher amount of quartz present.

In addition to hydrothermal methods, the synthesis of zeolite A can be performed by using an alkaline fusion pre-step, as used by Rios et al (2009)[3], in which kaolin was mixed at a proportion of kaolin/NaOH = 1/1.2 by weight. This process used a non-calcined kaolin and produced a zeolite A with a high structural degree. Some studies have had good results regarding the formation of a pure zeolite A phase with microwave synthesis. Chandrasekha and Pramada (2008)[10] studied the optimization of synthesis conditions by using microwaves. The best conditions observed by the authors for synthesis with metakaolin were exposing the reaction mixture to 2 minutes of microwave irradiation, followed by aging at room temperature for 20 h and finally heating the mixture in a microwave for 2 h (85 °C).

The amount of NaOH added in the synthesis will also influence the formation process of the desired structure. According to the standard IZA synthesis, the Na/Al ratio used for the synthesis of zeolite A is 1.78. In the study of Maia et al (2011)[11], the Na/Al ratios of 1.26, 1.36 and 1.45 with a synthesis time of 24 h at 110 °C were studied. It was observed that the Na/Al ratio of 1.36 gave the best results in terms of crystallinity for the zeolite NaA synthesis using a calcined Amazon kaolin. By changing the Na/Al ratio, it is possible to indirectly modify the NaOH/kaolin ratio in the synthesis, and vice versa.

This work aims to study different ratios of NaOH/metakaolin according to crystallization time by using statistical design to define a domain in which these synthesis parameters can be optimized.

2. Experimental

2.1. Materials and methods

The kaolin used in this study comes from the Capim mine located in Pará state, Brazil. The kaolin used in all experiments was calcined at 700 °C for 2 h in a muffle furnace to transform it into the more reactive metakaolin phase.

2.2. Zeolite NaA synthesis

To study the relationship between the parameters of crystallization time and NaOH/metakaolin ratio, a 2^2 statistical design with 3 central points was used. The design matrix with the studied crystallization time ranges and NaOH/metakaolin ratios are presented in Table 1. The samples were named as P***x***ZA***y***H, where ***x*** represents the number of the test and ***y*** represents the crystallization time used.

Table 1: Matrix of the experimental design and crystallization time ranges and NaOH/metakaolin ratio studied for zeolite A synthesis.

Tests	Crystallization time	NaOH/kaolin ratio
P1ZA4H	-1	-1
P2ZA28H	-1	+1
P3ZA4H	+1	-1
P4ZA28H	+1	+1
*P5ZA16H	0	0
*P6ZA16H	0	0
*P7ZA16H	0	0
P8ZA16H	0	- 1.41
P9ZA16H	0	+1.41
P10ZA0H	- 1.41	0
P11ZA33H	+1.41	0
Levels	Crystallization time (h)	NaOH/kaolin ratio
-1.41	0	0.42
-1	4	0.5
0	16	0.7
+1	28	0.9
+1.41	33	0.99

*Central points

The molar composition of the synthesis gel of all procedures performed was set to be: 0.04 SiO_2 : 0.02 Al_2O_3 : 2.4 H_2O: *x* NaOH, with the value of ***x*** equal to 0.046, 0.055, 0.078, 0.1 or 0.11 for procedures in which the NaOH/metakaolin ratio (g/g) varied from 0.42 to 0.5, 0.7, 0 9 and 0.99. Tests 6 and 7 are replicates of test 5. The standard time for synthesis of zeolite A is 4 h. Thus, the minimum time used in these studies was from 0 to 4 h, and the maximum values and the values of the central point were 16, 28 and 33 h. A diagram of the standard zeolite NaA synthesis is presented in Figure 1.

A very small amount of sodium aluminate was added so that the Na/Al ratios reached the following values: 1.65, 1.97, 2.75, 3.54 and 3.89 for the samples with NaOH/metakaolin ratios of 0.42, 0.5, 0.7, 0.9 and 0.99, respectively.

2.3 Characterization

The initial metakaolin sample and all samples obtained from the tests were analyzed by X-ray diffraction in a DIFFRAKTOMETER instrument –D2-PHASER Model (Bruker) with a nickel filter and Cu-Kα radiation (λ = 1.54 Å). The data obtained from this technique were used to calculate the relative crystallinity of the samples. These results were statistically analyzed by using Statistica 6.0 software (Statsoft Inc., Tulsa, USA). The results regarding the chemical composition and morphology of all samples were obtained through scanning electron microscopy and chemical analysis by using a microprobe EPMA, Model 1720H, Shimadzu, with an accelerating voltage of 15 kV and a BC ranging from 50

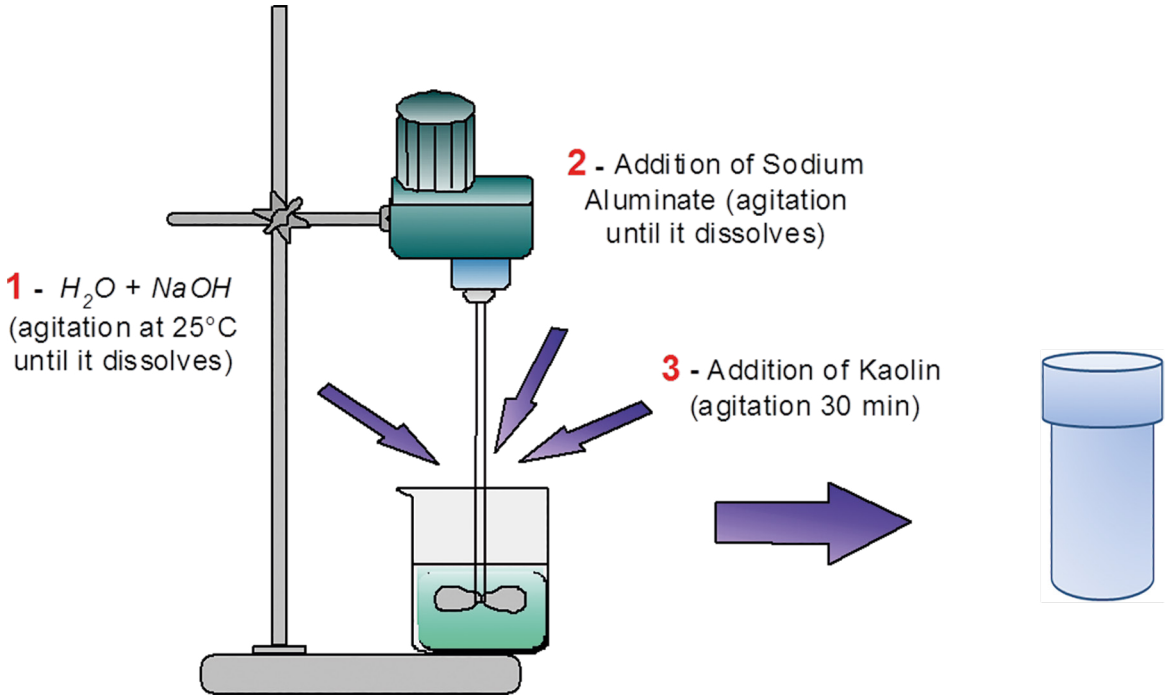

Figure 1: Synthesis diagram for zeolite NaA.

nA to 0.01 nA. For this analysis, the samples were mounted with carbon tape and metallized with gold.

3. Results and Discussion

The non-calcined kaolin showed characteristic reflections indicating the presence of kaolinite (Figure 2a). After the calcination process, the diffractogram shown in Figure 2b is characteristic of an amorphous material.

The micrograph images show that the calcined kaolin has an irregular morphology resembling disorganized plates. Calcination promotes the dehydroxylation of kaolinite and thus a change in the environment around the aluminum atoms, which begin to acquire coordination numbers 4 and 5[12]. Thus, the octahedral aluminum starts to become tetrahedral, making the material amorphous and more reactive. According to the results of chemical analysis, the kaolin is composed of aluminum (16.27%), silicon (15.75%), titanium (0.27%) and iron (0.5%). The microprobe analysis is semi-quantitative, and the results are in accordance with those expected for kaolin samples.

In Figure 3, the diffractograms of the samples obtained from the statistical design show that the synthesized materials are all characterized by the presence of the zeolite A phase.

The diffractograms in Figure 3 show the characteristic reflections of zeolite NaA, with the peaks identified from a comparison with a standard (8664 to zeolite A) from the "Inorganic Crystal Structure Database" (ICSD), except for the samples P1ZA4H and P10ZA0H. These samples show the characteristic diffractogram of an amorphous material. At 2θ between 20 and 35°, there is an elevation of the "background signal", especially for samples P3ZA4H, P2ZA28H and P8ZA16H. This indicates that a portion of the metakaolin was not completely converted into zeolite. In the samples P4ZA28H, P9ZA16H and P11ZA33H, this elevation is lower, indicating a more efficient synthesis.

The relative crystallinity values were calculated for each synthesized sample from the sum of the areas under the peaks at 2θ equal to 7.2°, 12.5°, 16.1°, 21.7°, 30°, and 34.2°. A sample of zeolite A synthesized by the IZA method was used as the standard. The equation used to calculate the relative crystallinity is shown below.

$$\%\ relative\ crystallinity = \frac{\sum peaks\ area\ of\ synthesized\ sample}{\sum peaks\ area\ of\ s\tan dard\ sample}$$

The relative crystallinity values of all the samples synthesized by using the experimental design are presented in Table 2.

The samples P4ZA28H, P9ZA16H and P11ZA33H are the most crystalline compared to the other synthesized samples. Table 3 shows the molar ratios of Na/Al and H_2O/NaO_2 for each of the NaOH/metakaolin ratios used.

For the most crystalline samples (P4ZA28H and P9ZA16H), the NaOH/metakaolin ratio was the highest at 0.9 and 0.99, which led to Na/Al ratios of 3.54 and 3.89. For the P11ZA33H synthesis, the NaOH/metakaolin ratio was 0.7, but this sample had the longest synthesis time, 33 h, which led to the formation of a material with a high

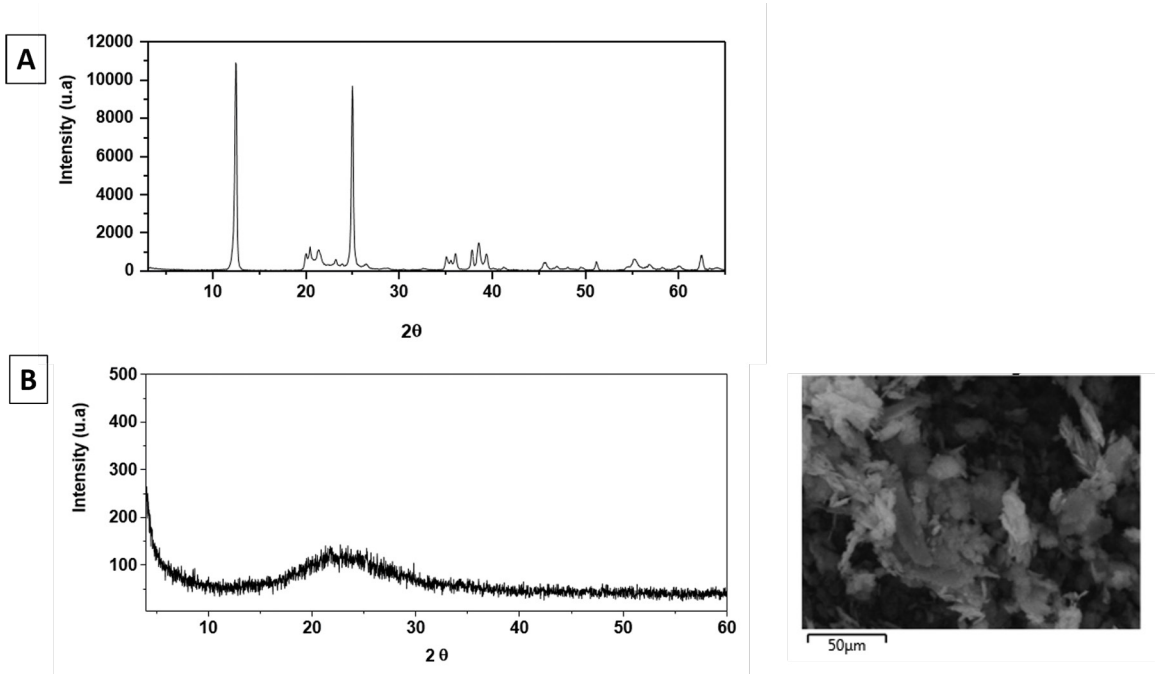

Figure 2: Diffractogram and micrographs of samples of natural kaolin (A) and kaolin calcined at 700 °C for 2 h (B).

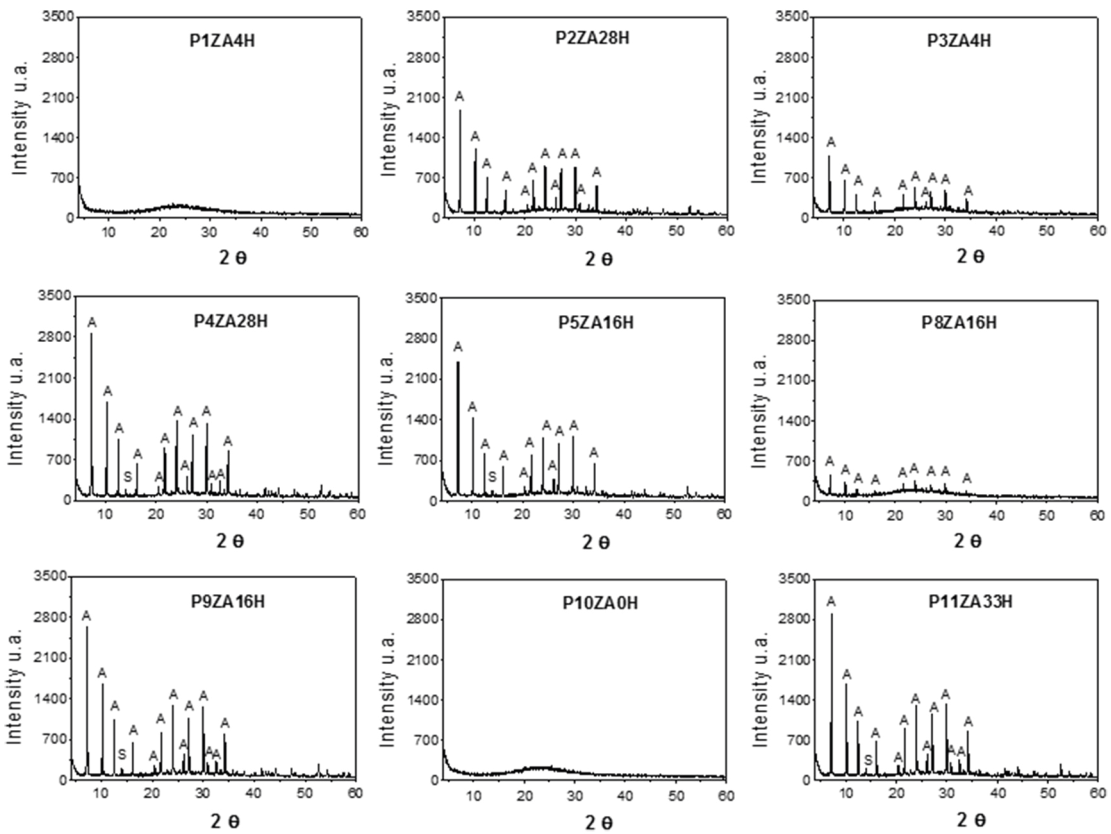

Figure 3: Diffractograms of the samples obtained from the 2^2 statistical design with 3 central points for zeolite A from calcined kaolin (A = zeolite NaA and S = sodalite).

Table 2: Percentage of relative crystallinity of the samples synthesized using a 2^2 statistical design with 3 central points.

Samples	Crystallinity Percentage
P1ZA4H	0
P2ZA28H	49.7
P3ZA4H	31.3
P4ZA28H	66.4
P5ZA16H	60.2
P6ZA16H	59.5
P7ZA16H	58.8
P8ZA16H	18.5
P9ZA16H	62.4
P10ZA0H	0
P11ZA33H	65.4

Table 3: H_2O/Na_2O ratios for the syntheses carried out.

NaOH/metakaolin mass ratio	H_2O/Na_2O molar ratio	Na/Al molar ratio
0.42	104	1.65
0.5	96	1.97
0.7	60	2.75
0.9	48	3.54
0.99	44	3.89

structural degree. In the synthesis of zeolites, the charge compensating cation (in this case Na^+) can also function as a structural driver[13], which may be one of the factors that led to a more crystalline material. In the zeolite synthesis, there are domains in which the interaction between the synthesis parameters can define the type of structure formed. In this case, the increased amount of NaOH, coupled with a longer crystallization time, led to the formation of a more crystalline NaA phase. The interaction of these two parameters on the yield of the synthesis is best represented by the Pareto chart shown in Figure 4.

The reaction time and the NaOH/metakaolin ratio each have a strong influence, both linear as well as in the quadratic form, on the synthesis regarding obtaining a product with a high structural degree. However, the diffractograms show that the increase in crystallinity of the NaA phase is accompanied by the increased presence of sodalite. The P2ZA28H sample showed the best values of crystallinity with a pure NaA phase. Wang et al (2008)[14], by using coal ash for the synthesis of zeolite A, found that increasing the concentration of NaOH leads to a reduction of the crystallization time. This is expected because the dissolution rate of the raw material in that study increases with increasing amount of NaOH, as also seen with kaolin. However, the formation of more stable phases, such as sodalite (which has a more condensed structure), is also observed, but reducing the amount of NaOH may lead to the formation of amorphous material.

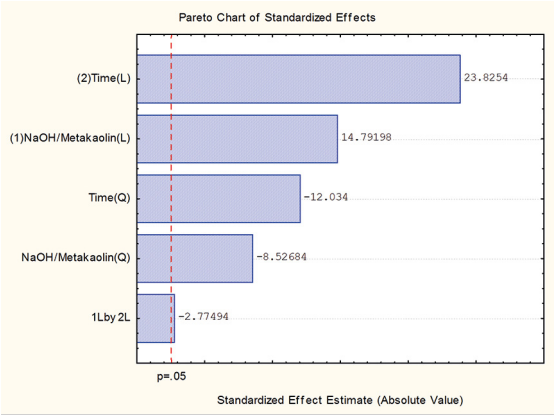

Figure 4: Pareto chart for the synthesis of zeolite A from calcined kaolin.

In Table 4, the proposed model and the analysis of variance for this study are presented. Although this model was not sufficiently robust for these experimental conditions, it is still possible to evaluate the influence of the parameters of crystallization time and NaOH/metakaolin ratio.

In Figure 5, which is a response surface graph, the area where the best results are obtained for the zeolite A crystallinity is in the region of higher temperature and longer crystallization times.

Alkan et al (2005)[8] also observed that increasing the amount of NaOH and decreasing the liquid phase was associated with an increase in the formation of the sodalite phase. When the metakaolin/H_2O ratio was fixed at 0.3, the material produced was all sodalite, while in the range from 0.05 to 0.2, they obtained a mixture of zeolite A and sodalite phases. In this study the metakaolin/H_2O ratio was fixed at 0.1 for all experiments to minimize the effect of the liquid phase on the appearance of the sodalite phase. Changing the NaOH/metakaolin ratio also indirectly changes the H_2O/Na_2O in the synthesis gels because a decrease in H_2O leads to an increase in NaOH concentration. The H_2O/Na_2O ratios are also listed for each completed synthesis in Table 3.

Liu, X. et al (2013)[15], by using tetraethyl orthosilicate with aluminum chloride as a source of aluminum, noted that a decrease in the H_2O/Na_2O ratio led to the formation of a zeolite NaA and NaX mixture, but when this ratio was increased from 20 to 30 or 40, only the pure NaA phase was obtained. In our study, the pure zeolite A phase was synthesized by using a NaOH/metakaolin ratio of 0.5 and a H_2O/Na_2O ratio of 96. However, higher crystallinity was obtained when this ratio was decreased to 48 in the synthesis P4ZA28H. This indicates that with H_2O/Na_2O ratios from 48 to 96, zeolite NaA may be obtained by using metakaolin with high and pure crystallinity. Thus, the use of different sources of Si and Al should be studied to discover the best conditions for the synthesis of these materials.

The micrographs of samples P2ZA28H, P3ZA4H, P4ZA28H and P6ZA16H are presented in Figure 6. The

Table 4: Empirical models that predict the synthesis of zeolite NaA as a function of crystallization time and NaOH/metakaolin ratio and analysis of variance for the model presented. (NaOH/metakaolin = N and crystallization time = T).

Coded model	$59.5 + 6.89.N - 4.74.N^2 + 11.10.T - 6.69.T^2 - 3.65.N.T$			
	Sum of squares	Degrees of freedom	Mean of squares	F calculated
Regression	6,688.8	5	1,337.7	193.3
Residues	34,6	5	6.9	
Total	6,723.4	10		

Listed F5;5;0.95 = 5,05

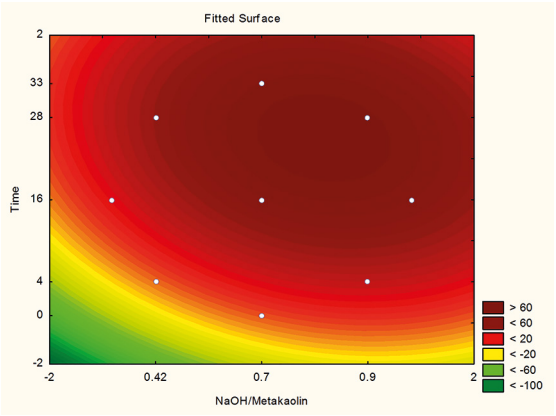

Figure 5: Response surface for the completed tests.

P1ZA4H sample is not presented because it is an amorphous material.

All synthesized samples show crystals with characteristic morphology for zeolite NaA (i.e., cubic crystals). It can be observed using samples P3ZA4H and P6ZA16H that crystal growth occurs over clusters of calcined kaolin, and in all samples, the zeolite A phase exhibits intra-crystalline growth. The sodalite phase identified by DRX appears as spherical clusters on the surface of the zeolite NaA crystals, and the size of these sodalite clusters increased in samples P2ZA4H and P4ZA28H.

4. Conclusion

The increase in the NaOH/metakaolin ratio leads to the formation of a more crystalline zeolite NaA phase, but it also leads to an increase in the sodalite phase. The crystallization time also has a positive influence on the increase of crystallinity. However, working with a low NaOH/metakaolin ratio, the increased time is favorable for the formation of zeolite A without the presence of the sodalite phase, with a relative crystallinity value of 49.7%. The use of statistical design proved to be a good tool to evaluate different synthesis conditions, determining domains in which the parameters of crystallization time and NaOH/metakaolin ratio can be optimized to obtain a pure NaA phase.

5. Acknowledgments

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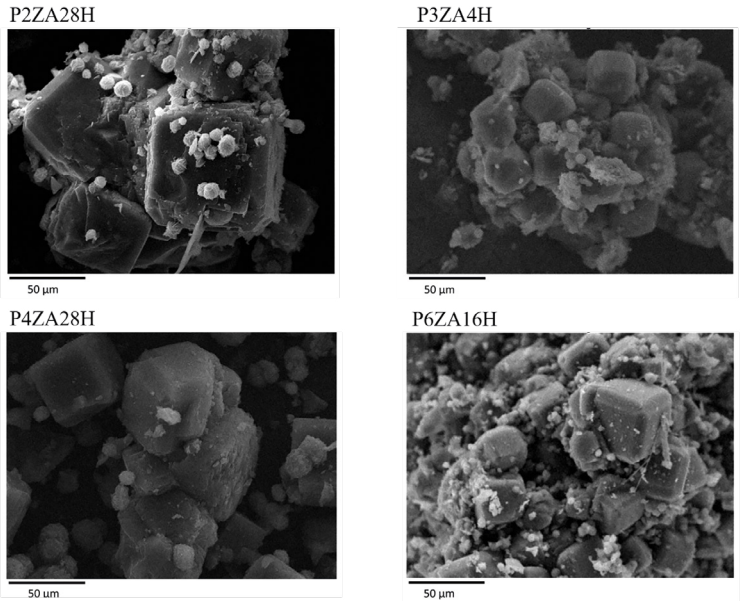

Figure 6: Micrographs of the synthesized samples from the statistical design.

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