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Study of the Thermal Stability of Faujasite Zeolite Synthesized from Kaolin Waste from the Amazon

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The waste from the processing of kaolin in the Amazonian region of Brazil was subjected to a calcination process at 700°C for 2 h to obtain metakaolin, which, together with sodium hydroxide and sodium silicate, formed the reaction mixture. This mixture was subjected to an aging step (24 h at 60 rpm), and a subsequent hydrothermal process at 110°C for 10 h. By means of X-ray diffraction (XRD), differential thermal and thermogravimetric analysis (DTA/TG) and scanning electron microscopy (SEM) techniques, the crystallization of a single phase, faujasite (FAU) zeolite, was observed. In the postsynthesis process, it was verified by means of XRD that the thermal stability of this structure persists up to a temperature of 600°C. At 800°C, the structure of FAU collapses. Beginning at 850°C, new nepheline phases are formed, and at 1000°C, nepheline and mullite phases are formed.

Keywords: *Kaolin waste, metakaolin, faujasite zeolite, thermal stability.*

1. Introduction

Transformations in the environment have been frequently occurring since the Industrial Revolution, and in recent decades, they have presented damage and environmental changes, causing risks and raising warnings about the quality of life of future generations[1]. Although the mineral sector greatly contributes to the country's economy, the industry brings significant socioenvironmental impacts resulting from its processing stages. In the kaolin processing industry, for example, large areas, such as sedimentary basins, are used for the massive storage of waste. This is a great factor to be taken into consideration, even though this waste consists basically of kaolinite, which is a clay mineral and is classified as non-hazardous by the ABNT-NBR standard because the material is generated from a nonmetallic mineral[2].

A number of studies have been presented as means to minimize the impacts generated by the kaolin processing industry by using the wastes to produce new materials, such as ceramics and especially zeolites[3-14].

Zeolites have their structure formed for frameworks of aluminosilicates that are based on an infinite three-dimensional network of tetrahedrons of $(AlO_4)^{5-}$ and $(SiO_4)^{4-}$, connected to each other by oxygen atoms, forming channels and interconnections of voids, where cations and water molecules are found[15]. Thus, due to this structure, zeolites, natural or synthesized in laboratories, are capable of optimizing chemical processes, for example, gas purification, ion exchange in detergents, and the treatment of domestic and industrial effluents, as well as in animal nutrition, in medicine, and in agriculture, among others. In particular, the zeolite of the faujasite (FAU) type (X and Y) is used in the processes of catalytic cracking and adsorption by the petroleum industry[16].

The first experimental works related to FAU were made by A. A. Damour in 1848. The following year (1949), Barrer and Milton synthesized zeolite-type NaX, with a Si/Al ratio between 1.0 and 1.5, to be applied mainly in the adsorbent industry. The zeolite type Y was synthesized by Breck in 1954 and possesses a structure similar to that of X but with a higher Si/Al ratio (1.5 to 3.0)[17]. In addition to contributing to the development of processes based on hydrocarbon transformations through zeolite Y. The reduction in Al content results in a structure with high thermal and acid stabilities[18].

The study of the thermal stability of zeolites aims to verify their resistance and to evaluate up to what temperature it is possible to use this material in their various applications. Rabo found that the thermal stability of zeolites can be considered when their heating is beyond the point of dehydration and does not significantly affect the degree of structural order, in which the geometry of the crystal lattice is the greatest factor in stability[19].

Zeolite thermal analysis graphs show an endothermic peak near 200ºC, which is caused by the elimination of water, and two exothermic peaks, both found at high temperatures - the first being associated with the collapse of the crystalline structure to an amorphous phase, and the second peak indicating the recrystallization to a new phase[19]. In the case of the low-silica zeolite A, two exothermic peaks are located at 900 and 950°C, and the X-ray diffractograms of zeolite A samples heated at these temperatures show the formation of other crystalline phases[8]. Thus, in the case of zeolite A, the two exothermic peaks indicate the formation of new crystalline phases.

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In this way, the present work aims to study the thermal stability of a FAU zeolite synthesized from a kaolin waste to ascertain its structural resistance at high temperatures and enable its use in different industrial chemical processes.

2. Materials and Methods

2.1 Materials

For the synthesis of the FAU-type zeolite and subsequent study of its thermal stability, the kaolinite waste supplied by an industrial kaolin processing plant, located in the municipality of Barcarena, in the Capim Region, was used as the source of Si and Al. In addition, sodium hydroxide (NaOH) was used as a source of sodium, and sodium silicate (Na_2SiO_3) was used as the secondary source of silicon.

2.2 Methods

2.2.1 Waste treatment

The kaolinite waste was initially submitted to a drying process at a temperature of 100°C for 4 h in an oven, and soon after, it was subjected to a treatment for the reduction of its granulometry by spraying in a mortar to obtain a material with particles of the ideal size for the zeolite synthesis process.

According to Maia et al.[3], Hildebrando et al.[20], Maia et al.[10], Rocha Junior et al.[14] and Maia et al.[12], to obtain a material with high reactivity, a heat treatment of the kaolin waste at 700°C for 2 h in a muffle furnace was required.

2.2.2 Synthesis process

The preparation of the reaction mixture was carried out in a Teflon cup (part of the reactor used for synthesis) with a capacity of 200 mL, to which, after being weighed, the starting materials (metakaolin, sodium silicate and sodium hydroxide) were transferred, in addition to water. In the order cited above, the starting materials mass to obtain the reaction mixture was as follows: 8.72g metakaolin, 16.628 g sodium silicate, 6.276 g sodium hydroxide

Based on the work done by Valtchev et al.[21], Cundy and Cox[22] and Maia et al.[12], to accelerate the synthesis time, the reaction mixture passed through an aging step, which occurred in an orbital-type agitator for 24 h at room temperature and at a rotation of 60 rpm.

After the aging step, the hydrothermal process was started in an autoclave, whereby the Teflon cup and the aged reaction mixture were inserted into a stainless-steel reactor, which in turn was placed in an oven at a temperature of 110°C for 10 h.

At the end of the hydrothermal process, the reactor was removed from the oven and subjected to sudden cooling in a running-water bath at room temperature for between 15 and 30 min. Then, the washing and filtration step of the synthesis products was carried out until achieving neutral pH (pH between 7.0 - 8.0). Subsequently, the drying of the synthesis products occurred at 100°C for 4 h.

It is worth mentioning that the tests were performed in duplicate to maximize the reliability of the result.

Samples of kaolin, metakaolin and the synthesis product were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential thermal and thermogravimetric analysis (DTA/TG). X-ray powder diffraction (XRD) analyses were carried out with a PANalytical X' Pert Pro MPD (PW3040/60) diffractometer using a high-speed solid-state linear detector (X'Celerator). X-ray powder patterns were collected on randomly powdered samples in y/y scanning mode using Cu-Ka radiation with a Ni Kb filter. The scan range was 5º to 75º 2Θ, with the following instrumental conditions: 1/8º divergent slit, 1/4º anti-scatter slit, 0.02º 2Θ step size and 20 s per step. Thermal analysis thermogravimetry (TGA) and differential thermal analysis (DTA) were simultaneously carried out on a PL Thermal Science thermoanalyser (N_2 atmosphere, heating rate 20ºC/min). Scanning electron microscopy (SEM) analyses were carried out on a Zeiss LEO 1430 microscope. The samples were previously sputtered with gold using Emitech K 550 equipment. The chemical composition of the kaolin residue was verified by different methods to determine the contents of the following oxides: SiO_2 and Loss on Ignition (LOI) by gravimetry; Al_2O_3 by titrimetry; Fe_2O_3 and TiO_2 by spectroscopy (colorimetric method); Na_2O, K_2O, CaO, MgO by atomic absorption spectrometry

2.2.3 Post-synthesis: thermal stability study of the FAU zeolite

After obtaining the FAU zeolite by means of the hydrothermal synthesis, the thermal stability of this zeolite was studied to determine the maximum temperature where its structure remains intact, as well as the exothermic peaks (phase change indicator) identified at 800 and 880°C in the works of Breck and Rocha Junior et al., respectively[15,14]. For this, 1 g of FAU zeolite was weighed on an analytical balance and placed in a porcelain crucible for a heat treatment at 200°C for 2 h. The tests were repeated in the same manner at different temperatures (400°C, 600°C, 800°C and 1000°C), and the samples were later characterized by XRD and SEM. The zeolite was additionally heated at two other temperatures, 850 and 880°C, using the same procedure described above.

3. Results and Discussions

3.1 Characterization of the starting material

By means of XRD, it was verified that the kaolin waste used in the FAU zeolite synthesis is basically constituted of kaolinite (K), which presents a high degree of structural order, and the kaolinite can be observed by the intensity of the peaks of the clay mineral, according to Figure 1.

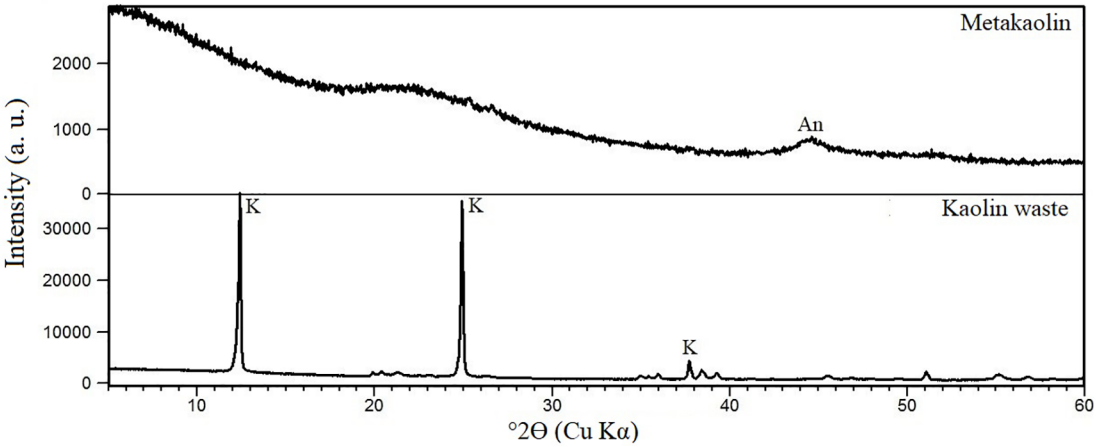

Figure 1. Diffractograms of the kaolin waste and metakaolin.

In the calcination process to obtain metakaolin, the time of 2 h at 700°C was sufficient to cause the total loss of crystallinity in kaolinite (Figure 1) a process that occurs by the elimination of kaolinite's water molecules, resulting in a change in the environment of the aluminum atoms, which generates a suitably reactive amorphous material. In Figure 1, in addition to the kaolinite, it is possible to visualize anatase (An) peaks, which next to the quartz (Q), according to Maia et al., are mineralogical impurities found in the kaolin of the Capim region[3,9].

Figure 2 shows the DTA/TG of the kaolin waste used in the synthesis process, where the endothermic peak characteristic of dehydroxylation is in the region between 430°C and 620°C. In Figure 2, it is also possible to observe by means of the thermogravimetric analysis the theoretical mass loss of kaolinite (approximately 6.3%).

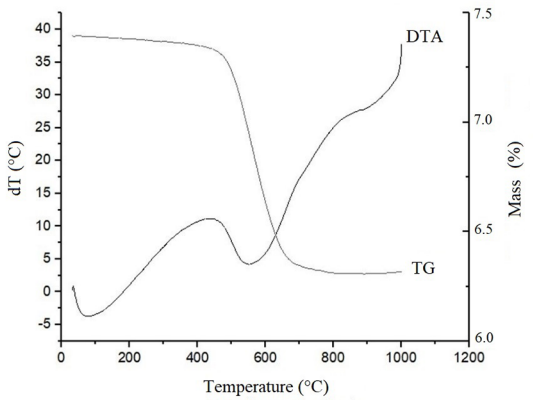

Figure 2. DTA and TGA of the kaolin waste.

From Figure 3, it is possible to observe the morphologies of the kaolin waste and metakaolin by means of SEM images. The kaolin waste consists predominantly of clustered particles with the booklet stacking of crystals of a pseudohexagonal morphology. According to Maia et al., who found the same result, this morphology is characteristic of kaolinite, confirming the presence of this clay mineral in the starting material used in the FAU zeolite synthesis[3].

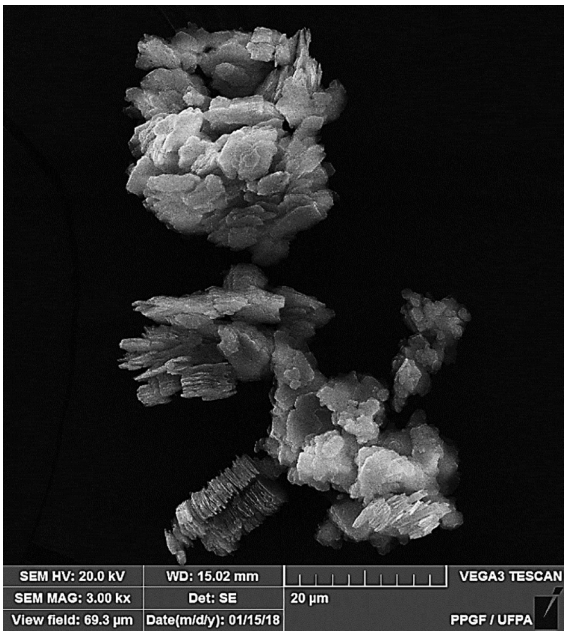

Figure 3. SEM image of kaolin waste.

In Figure 4, the metakaolin resulting from the calcination process at 700°C for 2 h retained its pseudohexagonal shape, but the stacking was altered by means of the reduction of the packed sheets, observed as well in the works of Maia et al.[3], Hildebrando et al.[20], Rodrigues et al.[13], and Rocha Junior et al.[14], among others.

According to the chemical analysis of the kaolin waste used in this synthesis, as well as the value of the loss on ignition (LI), there are high contents of silicon oxide (SiO_2) and alumina (Al_2O_3) similar to those found in the analysis performed by Maia et al.[12]. When considering the theoretical composition of kaolinite as 46.54% (SiO_2), 39.50% (Al_2O_3) and 13.96% (H_2O)[23], it follows that the sample of kaolin

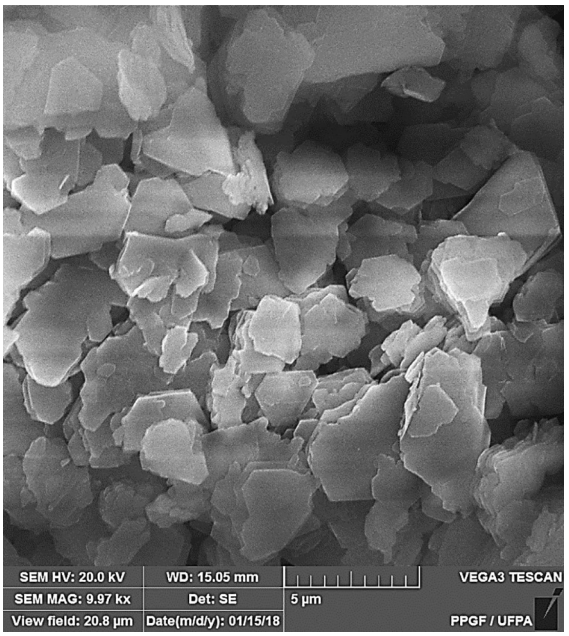

Figure 4. SEM imagens of metakaolin.

waste is essentially formed by kaolinite, since the values were similar. Thus, this chemical analysis confirms that the waste consisted mainly of the clay mineral kaolinite, as shown by XRD and SEM. The amount of SiO_2 present in the kaolin is directly related to the kaolinite and quartz. Furthermore, other oxides, found in the kaolin waste can be denoted as mineralogical impurities, among them, TiO_2 (which is related to anatase)[12].

3.2 Synthesis and post-synthesis process

From Figure 5, it is possible to observe the XRD results of the synthesized product (ZEO) at 110°C for 10 h, in which the FAU-type zeolite was obtained as the predominant phase, with the following corresponding peaks found in the samples: 6.2°/14.16 Å, 15.6°/5.69 Å, 23.5°/3.79 Å and 31.1°/2.87 Å. According to Breck (1974), these are standard values for the zeolite NaY[15]. Thus, the FAU phase formed was probably Y.

Hildebrando et al. obtained the same product, but without stirring, at temperature of 90°C after a period of 20 h[20]. Maia et al., by varying the aging time, synthesized the FAU zeolite after 6 h at 90°C. Additionally, between 8 and 10 h of aging, in addition to FAU, the authors obtained the formation of a zeolite of the phillipsite type as a product[12].

Figure 6 shows the thermal analysis of the obtained zeolitic product, where it is possible to observe the elimination of the adsorbed water in the temperature range of approximately 50 to 200°C, as evidenced by the presence of the endothermic peak in the differential curve (DTA). Additionally, an exothermic peak presented near 750 to 800°C was due to structural collapse leading to the formation of an amorphous material.

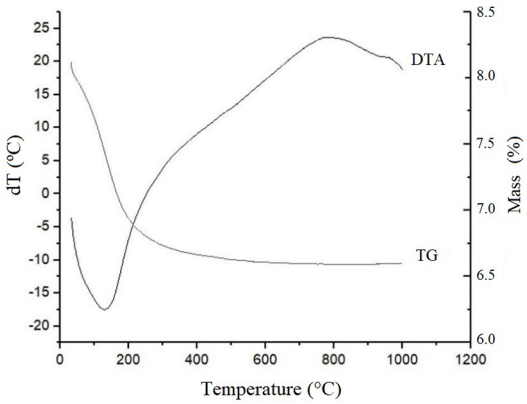

Figure 6. DTA and TGA of the product.

In the thermogravimetric analysis of Figure 7, the mass loss is approximately 6.5%, which was a result of the gradual increase in dehydration.

For the study of the thermal stability, according to Figure 5, the XRD characterization shows that up to 600°C the FAU's crystalline structure remains stable. Thus, the diffractograms of samples heated at 200, 400 and 600°C indicate that the characteristic peaks of the FAU zeolite remain unchanged,

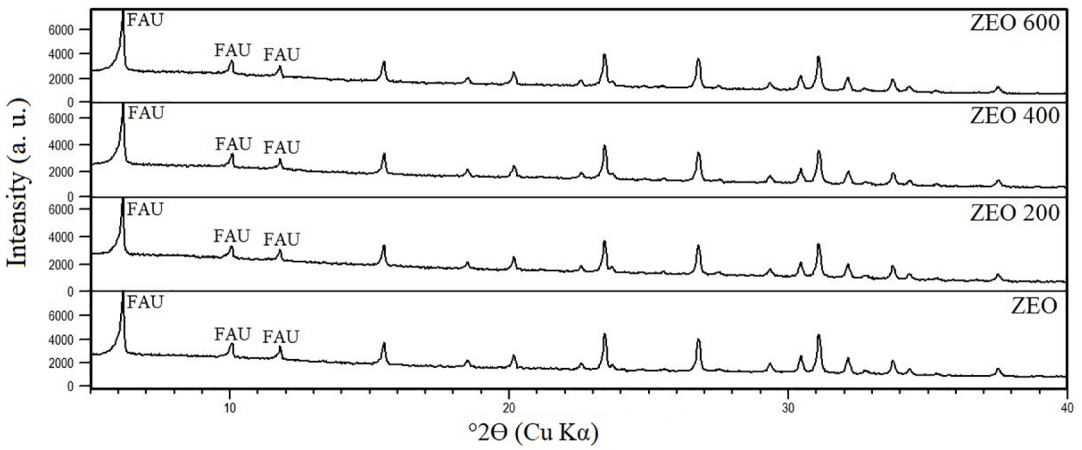

Figure 5. Diffractograms of the product synthetized at 100°C, and thermal stability tests performed at 200, 400 and 600°C.

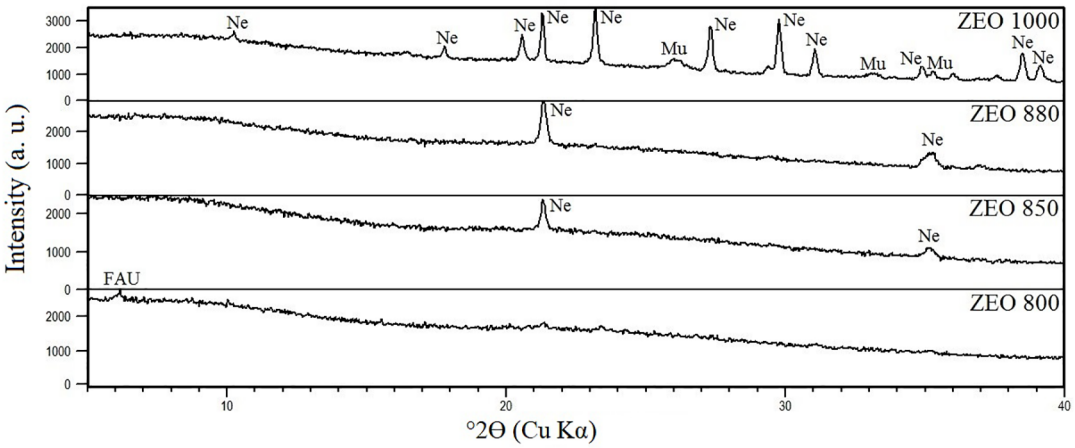

Figure 7. Diffractograms of thermal stability tests at 800, 850, 880 and 1000°C.a

making it possible to use them in chemical processes such as catalysts, for example, at these temperatures.

Figure 7 shows the results of the XRD analysis for high temperatures, in which a collapse of the FAU structure (ZEO 800) occurred at 800°C, presenting only a low intensity peak of this zeolite and a prominent background elevation, indicating the presence of an amorphous material. At temperatures of 850 and 880°C (ZEO 850 and ZEO 880), nepheline formation begins. At 1000°C (ZEO 1000), in addition to the characteristic peaks of nepheline, mullite peaks are also observed.

According to the DTA performed by Rocha Junior et al., the structural collapse of FAU-type Y occurred close to 880°C[14]. In the present work, at that temperature, as mentioned above, the formation of another crystalline phase occurs. According to Breck, the higher the silica content in the zeolite is, the higher its structural thermal stability[15]. However, Maia et al., in a study on the stability of zeolite A (considered as low silica), identified the phase change beginning at 900°C, and at 1000°C, the nepheline and mullite phases were obtained[8]. The zeolite A in question was shown to be stable up to 800°C. In turn, the results of this study show that FAU zeolite, which exhibits a high Si/Al ratio, is stable up to 600°C.

With the results of this research and those of previous ones, it is possible to verify that zeolites with a high Si/Al ratio will not always be the most stable, and this probably will not depend only on this parameter but also on other characteristics of its structure, such as structural order degree (crystallinity) of the zeolites, which in turn depend on the synthesis conditions. The main factors of the synthesis process, which affect the crystal size, are the synthesis time and temperature.[24]

The morphology of the sample synthesized at 110°C for 10 h is shown in Figure 8. It is possible to verify through SEM the predominant presence of bipyramidal crystals characteristic of FAU, according to Hildebrando et al.[20], Rocha Junior et al.[14] and Maia et al.[12], proving the analysis indicated by XRD.

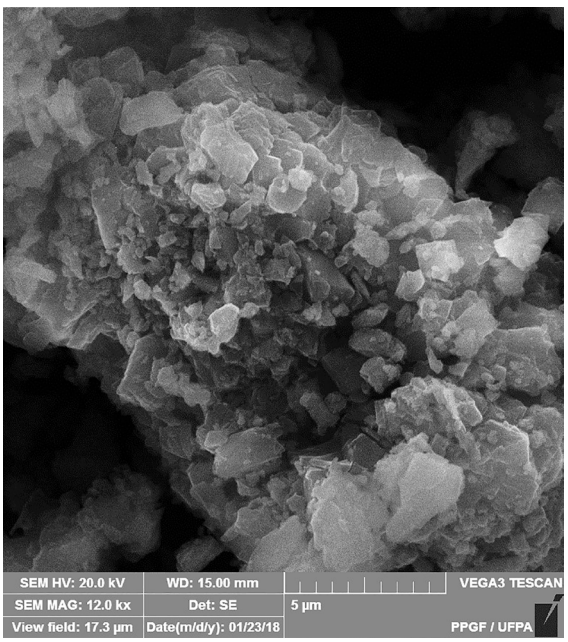

Figure 8. SEM image of the product synthetized at 100° for 10h.

Figure 9 shows the morphology of the FAU zeolite subjected to a temperature of 600°C, where it is possible to observe by SEM that the characteristic morphology of the obtained product remains unchanged, congruent with the XRD analysis, where it was verified that the structure of the FAU was not changed.

From Figure 10, it is possible to observe a change in the FAU morphology when subjected to a temperature of 800°C. This result confirms, as observed in the XRD analysis, the collapse of the FAU structure.

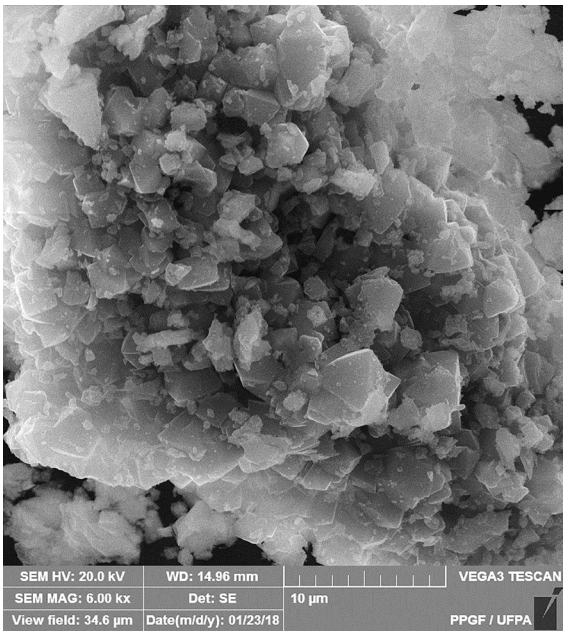

Figure 9. SEM image of zeolite FAU subjected to 600°C.

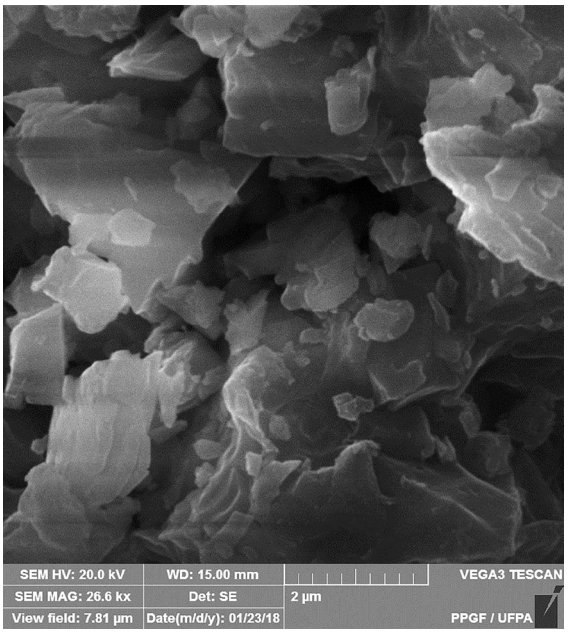

Figure 10. SEM image of zeolite FAU subjected to 800°C.

4. Conclusions

An FAU zeolite was synthesized from kaolin waste by an aging process with stirring at 60 rpm for 24 h and crystallization in an autoclave at 110°C for 10 h.

With respect to thermal stability up to 600°C, the crystalline structure remains unchanged; while from 800°C, early nepheline phases are obtained, and they are predominant at 1000°C but with the presence of mullite.

Most likely, the high or low thermal stability of zeolites is not only related to the Si/Al content but also to other characteristics of the structure.

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