

Synthesis and Characterization of Zeolite NaP Using Kaolin Waste as a Source of Silicon and Aluminum

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The synthesis of zeolite NaP using kaolin waste, from the Amazon region, as a predominant source of silicon and aluminum has been studied. The zeolitisation process occurred in hydrothermal conditions using static autoclaving and the effects of time, temperature, and the Si/Al ratio were investigated. The starting material and the phases formed as reaction products were characterized by XRD, SEM and FTIR. The results showed that pure zeolite NaP is hydrothermally synthesized, at 100 °C for 20 hours, using metakaolin waste material in alkaline medium in presence of additional silica. The XRD and SEM analyses indicate that the synthesized zeolite presents good crystallinity.

Keywords: *zeolite P, hydrothermal synthesis, kaolin industrial waste, Amazon region*

1. Introduction

Zeolites are porous aluminosilicates with a crystalline structure formed by the combination of silica tetrahedra [SiO₄]⁴⁻ and alumina [AlO₄]⁵⁻, joined by oxygen atoms¹. Traditionally, these microporous materials are commonly produced from hydrogels aluminates and sodium silicates; however, the production of zeolites from alternative sources of silica and alumina such as ash², volcanic glasses³, diatomites⁴ and clays⁵, continue to be investigated. Among the clays, several investigators have studied the preparation of zeolite from kaolin and have been successful in the synthesis of zeolites, mainly NaA⁶, mordenite⁷, faujasites⁸, and zeolite NaP^{9,10}.

According to the International Zeolite Association (IZA)¹¹ zeolite NaP has a GIS (gismondine) structure type showing small pores. Such structure results interesting because of its applications both in industry and in environmental protection^{3,12}. Usually, this type of zeolite synthesis occurs at temperatures ranging from 70 °C to 250 °C during long crystallization times¹³. The standard procedure established by IZA for obtaining zeolite NaP is based on the works by Rees and Chandreskar⁹ that synthesized this zeolitic phase in hydrothermal conditions at 85 °C during 60 days, using Indian kaolin as the source of silicon and aluminum. Recently, Acorsi et al.¹⁰ using Brazilian kaolin from various sources obtained zeolite NaP

at 100 °C in 4 days, using the alkaline fusion procedure. In this context, the efficiency in the synthesis process of this type zeolite requires the appropriate raw materials, time, and crystallization temperature.

Brazil and the U.S. have some of the largest reserves of kaolin in the planet. In Brazil, the state of Pará (Amazon region) stands out for having one of the most important international kaolin deposits for the paper industry¹⁴. During the processing steps for purifying raw kaolin, waste is produced and stored in settling ponds which occupy large area. This situation presents a problem due to the impact on the environment¹⁵.

Kaolin waste is unsuitable for use in paper-making industries; however, this material has the potential of being used in other applications, such as: alumina production¹⁵, refractories¹⁶, pozzolans¹⁷ and synthesis of zeolitic materials¹⁸⁻²⁰.

The utilization of kaolin waste for the production of NaP zeolite may be a good alternative to re-use this material. Thus, economic advantages would be obtained over chemical reagents used in processes to obtain zeolites that are relatively expensive.

Therefore, the main purpose of this study was to synthesize zeolite NaP using kaolin waste from the Amazon region as the main source of silicon and aluminum, improving crystallization time for lower values.

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2. Material and Methods

2.1. Materials

Kaolin wastes (KW) and metakaolin waste material (CKW), obtained from calcined kaolin waste at 700 °C for 2 hours were used in the zeolitization process. These materials were obtained from a paper-coating factory located in Pará. Sodium metasilicate pentahydrate ($\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 5\text{H}_2\text{O}$) and commercial NaOH were used as a secondary source of silicon and as a mineralizing agent, respectively.

2.2. Synthesis

The zeolitic material was obtained by hydrothermal synthesis in a stainless steel autoclave (47.4 mL capacity) internally coated with Teflon. In the initial series of experiments, the hydrothermal reaction was performed at 115 °C for 20 hours, the synthesis gel was prepared, by mixing 2.53 g of kaolin waste, NaOH and sodium metasilicate (Table 1). The batches' composition was calculated stoichiometrically with a reaction mixture of $3\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - x\text{SiO}_2 - \text{H}_2\text{O}$, with values of x in the range of 3.5 to 5.0 mol. In the second series of experiments, the following conditions of synthesis were evaluated: temperature (90, 95, 100 and 115 °C at 20-hour) and time (6, 20, 24 and 48 hours at a 90 °C). The samples were based on molar composition $4\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - 4\text{SiO}_2 - \text{H}_2\text{O}$ using 2.18 g of metakaolin waste material, 1.569g NaOH and 4.157 g of $\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 5\text{H}_2\text{O}$. In none of the experiments was the aging step applied to the gel. The water volume added in the autoclave was 40 mL, and the reactions of zeolitization occurred without agitation. Subsequently, the products of the synthesis formed were washed by filtration, with distilled water up to pH 7-8, and then subjected to drying at 100 °C for 24 hours. The synthesis conditions are summarized in Table 1.

2.3. Materials characterization

The starting material and the synthesized products were analyzed using X-ray diffraction (XRD), scanning electronic microscopy (SEM) and diffuse reflectance spectroscopy in the infrared Fourier transform (DRIFTS). The XRDs were performed on a diffractometer model X'Pert Pro MPD (Panalytical) using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) with Ni K β filter. The scan range was 5° to 90° 2 θ ; 40 kV and 35 mA. To observe the morphology and the size of the crystals, a Philips SEM brand, model XL30, was used and the samples were previously metalized with a thin gold film in "sputter coater" brand BALZERS equipment. The infrared spectroscopy (FTIR) was performed in a Thermo-Nicolet Magna equipment 560 with 400 to 4000 cm^{-1} (mid-infrared) scan and 4 cm^{-1} resolution, using a diffuse reflectance cell.

3. Results and Discussion

3.1. X-ray diffraction (XRD)

Figure 1 shows the XRD patterns of kaolin waste (KW) and synthesized products. This revealed that the kaolin waste was mainly composed of kaolinite. A small amount of quartz was observed by a peak of low intensity at $2\theta = 26.7^\circ$. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is one of the major parameters that guide the formation of the crystalline structure of a zeolite¹. In XRD patterns of the synthesized products obtained after the zeolitisation process using kaolin waste, the formation of zeolite NaP was observed through reflections on $2\theta = 12.4^\circ$, 17.7° , 21.8° , 28.2° and 33.5° , according with data from other studies^{3,12}. For the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio equal to 3.5 mol, the X-ray diffraction analysis shows the presence of faujasite zeolite in the synthesized sample as evidenced from reflections of low intensity near $2\theta = 6.2^\circ$, 15.6° and 30.9° .

Analyzing the change of some peaks observed by XRD patterns of the synthesized products, it is interesting to note that the zeolite NaP formed is of the cubic and tetragonal

Table 1. Synthesis conditions of samples.

Assay	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 5\text{H}_2\text{O}$, g	NaOH, g	Temperature, °C	Time, h
First series					
<i>Effect of initial $\text{SiO}_2/\text{Al}_2\text{O}_3$</i>					
01	3.5	3.117	1.411	115	20
02	4.0	4.157	0.941	115	20
03	4.5	5.196	0.471	115	20
04	4.8	5.819	0.187	115	20
05	5.0	6.235	- - -	115	20
Second series					
<i>Effect of crystallization temperature</i>					
01	4.0	4.157	1.569	90	20
02	4.0	4.157	1.569	95	20
03	4.0	4.157	1.569	100	20
04	4.0	4.157	1.569	115	20
<i>Effect of crystallization time</i>					
01	4.0	4.157	1.569	90	6
02	4.0	4.157	1.569	90	20
03	4.0	4.157	1.569	90	24
04	4.0	4.157	1.569	90	48

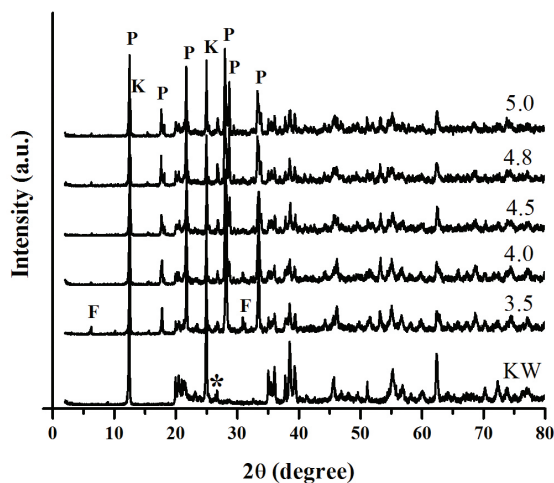


Figure 1. XRD patterns of synthesized products using kaolin waste (KW) to $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from 3.5 to 5.0 mol. P = zeolite NaP, F = faujasite, K = kaolinite, * = quartz.

type. The former, predominating in samples with lower $\text{SiO}_2/\text{Al}_2\text{O}_3$ (3.5 and 4.0 mol), and the latter in the highest ratios. This is justified, for example, by the observation that some simple peaks were divided into twin peaks such as peak (200) at $2\theta = 17.7^\circ$ which dismembers to (200) and (002). According to Breck¹, this phenomena is usually observed when a higher symmetry array turns into a lower symmetry array; in this case, cubic zeolite NaP to tetragonal zeolite NaP. A similar behavior was observed in Huo et al.²¹ in which successive samples of zeolite NaP were synthesized with two different morphologies. XRD results (Figure 1) indicated that in the synthesized products were found as impurities, quartz and kaolinite, originated from the kaolin waste samples. This fact can be verified by the presence of these mineral phases in the XRD patterns.

Figure 2 shows the results of synthesis reactions using metakaolin waste material. At this stage, the crystallization time and temperature were studied. First, a loss of KW crystallinity is observed from the XRD pattern of CKW, indicating effective metakaolinization at 700°C for 2 hours. Metakaolinite is much more reactive and thus a very suitable source for zeolite synthesis²². Figure 2a shows that the formation of zeolite NaP is induced at 95°C and 20 h. At 100°C and 20 h, NaP appears as a single-phase of high crystallinity according to the strong signals in the XRD pattern. Below and above this temperature range, the competitive phases appear as faujasite and chabazite. Literature reports^{1,8}, show that these two types of zeolites can be formed from the same compositional pattern ($\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$), thus competing with zeolite NaP.

Figure 2b shows that at 90°C for a 6-hour reaction time, no zeolitic phase is formed. Only the existence of amorphous material was observed, as well as the presence of a characteristic peak of quartz, which is a constituent of the starting material and, therefore, not a synthesis product. However, by increasing reaction time (up to 20 hours), characteristic reflections of zeolite NaP are observed.

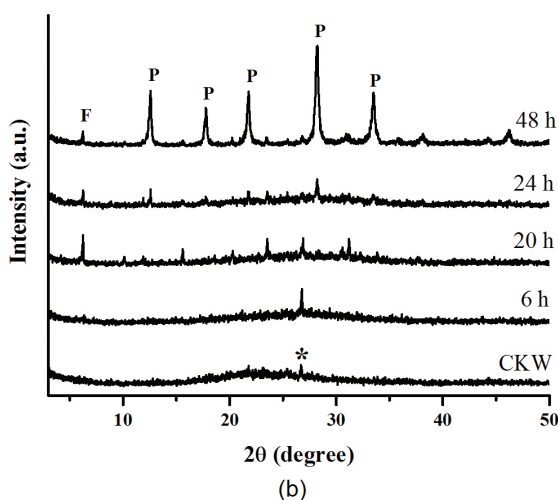
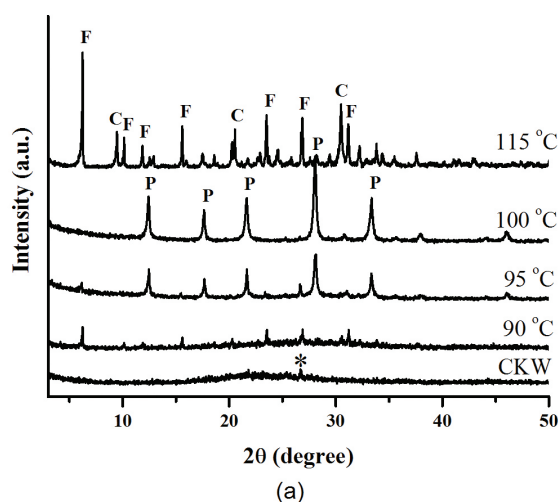


Figure 2. XRD patterns of synthesized products using metakaolin waste material (CKW) at different (a) temperatures for 20 hours; and different (b) times of crystallization at 90°C . P = zeolite NaP, F = faujasite, C = chabazite, * = quartz.

Competing with it, faujasite-type zeolite, a predominance of zeolite NaP occurs after a 48-hour reaction time.

3.2. Scanning electron microscope (SEM)

The progress of zeolitization reactions can be observed through changes in the morphology of the starting material and synthesis products. The SEM images of Figure 3 allow verifying that the kaolin waste (Figure 3a) consists predominantly of agglomerated particles with stacking *booklet* type and pseudo-hexagonal crystals characteristic of kaolinite. In the metakaolin waste material, Figure 3b, the stacking is modified but the form is maintained¹⁸. The morphology of the synthesized samples can be observed in the micrographs of Figures 3c and d; they are similar to those presented by Zubowa et al.¹³, in which zeolite NaP is identified by pseudo-spherical forms constituted by small plates, which form polycrystals with an average size of approximately $7.0\text{-}9.0\ \mu\text{m}$. Similar results were also reported

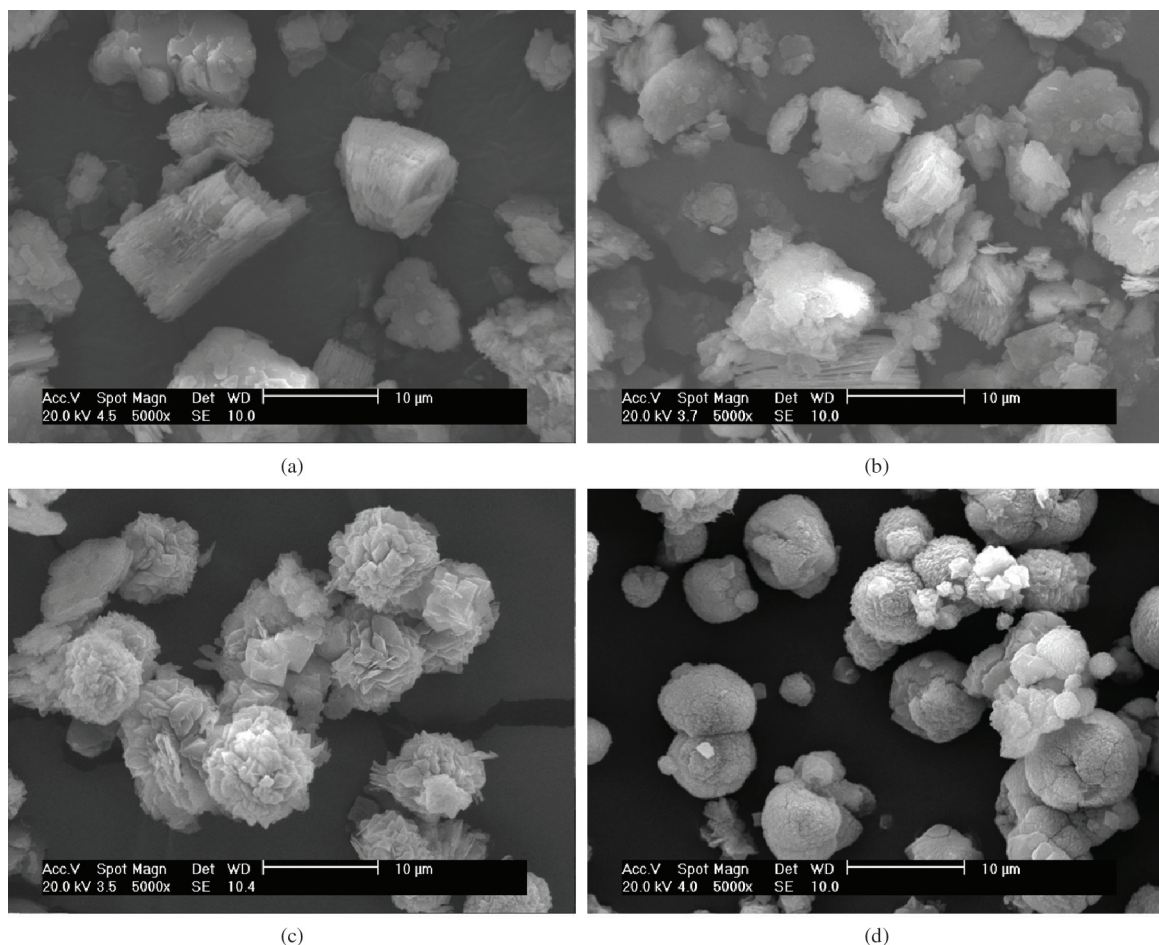


Figure 3. SEM images: (a) kaolin waste, (b) metakaolin waste material; (c) synthesized sample at 115 °C/20 hours using kaolin waste; (d) synthesized sample at 100 °C/20 hours from metakaolin waste material.

by Rees and Chandrasekhar⁹ who obtained zeolite NaP with spherulitic habit, and 10.0 mm in diameter synthesized from Indian kaolinite. Figure 3c also illustrates the coexistence of a certain amount of unreacted kaolinite during the process, which relates with the results from XRD in Figure 1. The better definition in crystal morphology observed in Figure 3d, in relation to those shown in Figure 3c, can be attributed to the increase in the crystallization of the zeolite NaP in the conditions studied.

3.3. IR-spectroscopy (FTIR)

The vibrational spectra of Figure 4 show the changes that occur from the starting material to the synthesis products. In the KW sample (spectrum a in Figure 4), there are stretch bands of OH group at 3697, 3653 and 3621 cm^{-1} , characteristic of kaolinite. Their absence in the CKW sample (spectrum b in Figure 4) demonstrates the conversion of kaolin into metakaolin²³.

For the synthesized products (spectra c and d in Figure 4), the bands with a maximum at 3420 and 1646 cm^{-1} are peculiar of vibrations of functional groups of OH type and are ascribed to water with zeolitic nature. Similar behavior was found by

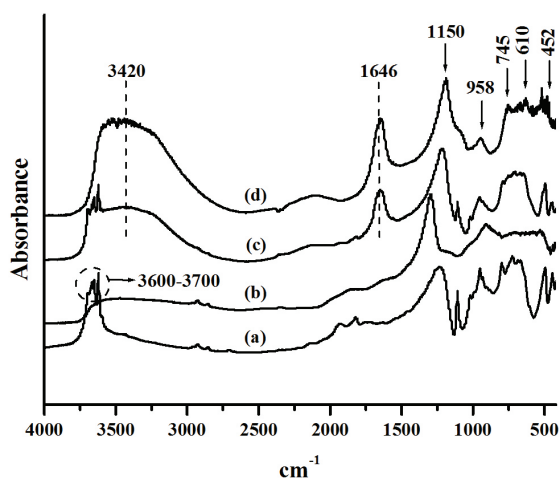


Figure 4. FTIR spectra of the samples (a) kaolin waste; (b) metakaolin waste material; (c) synthesized sample at 115 °C/20 hours from kaolin waste; (d) synthesized sample at 100 °C/20 hours from metakaolin waste material.

Albert et al.²⁴ while obtaining highly crystalline zeolite NaP. According to Huo et al.²¹, frequencies near 1000 cm⁻¹ are ascribed to asymmetric stretching of bonds Si–O or Al–O. Vibrations at 435 cm⁻¹ are related to the deformation mode of the same bonds. The peaks near 680 and 745 cm⁻¹ are assigned to symmetric T–O–T vibrations (T=Si, Al) of zeolite Na P framework structure. The peak at 610 cm⁻¹ indicates the double ring vibration which constitutes the structure of the zeolitic phase²⁵.

4. Conclusions

Kaolin waste from the Amazon region is a promising source of silicon and aluminum for the synthesis

of zeolite NaP. Thus, pure zeolite NaP with good crystallinity was obtained at 100 °C in a 20-hour synthesis, using kaolin waste thermally activated. This demonstrates that the time and temperature of zeolitisation has an important role in the crystallization of the desired phase. The reaction period of 20 hours for the formation of zeolite NaP in the conditions studied, was much shorter than the time established by the standard procedure of IZA (60 days).

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