

SYNTHESIS OF PURE ZEOLITE-X IN A FLOWSYNTH CIRCULATING BATCH MICROWAVE REACTOR FROM CLEAR SOLUTION EXTRACTED FROM COAL FLY ASH

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ABSTRACT

The present work shows that the pure phase of Na-X zeolite can be successfully synthesized via a microwave-assisted system in a flow process from a clear solution extracted from alkaline-treated coal fly ash (CFA). The FlowSynth microwave reactor supplies continuous microwave irradiation for the circulating batch manufacturing of nanomaterials. The effect of crystallization time and temperature of the circulating batch microwave reactor on the yield and crystallinity of the produced zeolite was investigated. The synthesized crystalline zeolite Na-X was thoroughly characterized by XRF, XRD, SEM, EDX, and BET. The maximum crystallinity (99.13%) was achieved at an operating temperature of 85 °C, 124 W, and 4 h. A circular batch-flow microwave reactor enhances and accelerates the crystal growth of zeolite. The produced crystalline zeolite had a high purity.

Keywords: Coal fly ash; synthesis; microwave irradiation; bench scale; zeolite X; extracted solution

INTRODUCTION

Coal fly ash (CFA), a waste by-product of coal-fired power plants, has serious and harmful effects on the environment [1]. To overcome this issue, investigations have been conducted on the zeolitization of CFA as a raw source of silica (SiO₂) and alumina (Al₂O₃). Different types of zeolites have been synthesized, such as Na-A [2, 3], Na-P [4, 5], ZSM-5 [6, 7], Na-X [8, 9, 10], and faujasite-Y [11, 12]. One of the most interesting zeolites is Na-X because of its high cation exchange and adsorption capacity [13]. It is also used for removing and adsorbing gaseous emissions and refining oil as a fluid-catalytic cracking catalyst [14, 15].

Successful conversion of coal fly ash (CFA) to Na-X zeolite was carried out utilizing different approaches [8, 9]. Hussar et al. [16] synthesized zeolite Na-A hydrothermally by using sodium silicate (Na₂SiO₄), sodium aluminate (Na₂AlO₃), and the by-product of an aluminum etching process. They found that high crystallinity of synthesized zeolite could be achieved under high reaction time and temperature. Also, ultrasound has been utilized to produce Na-X from CFA. According to Hums et al., the pure phase of zeolites Na-X, Na-A, and sodalite (SOD) was synthesized via ultrasound-

assisted before the crystallization step from the clear solution extracted from fused coal fly ash [17]. Moreover, microwave irradiation has been studied widely in batch mode to convert CFA into Na-X. Ansari et al. produced pure zeolite Na-X or a mixture of zeolites Na-A and Na-X by utilizing microwave-assisted hydrothermal heating in one step by controlling the reaction temperature and time [9].

Querol et al. [18] used a 10,000 L reactor to synthesize zeolite Na-P by conventional heating at ~150 °C, 0.35 MPa, with a solid/liquid ratio of 0.60 kg/L using a 2.4 M alkaline solution. In addition, Moriyama et al. [19] converted CFA hydrothermally into zeolite P in a 0.6 L reactor at a temperature of 153 °C, a solid/liquid ratio of 0.91 kg/L, 0.48 MPa, and a 3 M alkaline solution. Although these approaches were used for the zeolitization of CFA, some economic and technical issues still exist at the industrial scale. The remaining impurities (heavy and toxic metals) inside the produced zeolitic powder and the expensive cost of processing are the most common issues at large scale [20]. To overcome these problems, extraction of SiO₂ and Al₂O₃ from coal fly ash followed by nucleation of zeolite in the clear phase could be considered as a potential solution. Under certain conditions of reaction time and temperature, additional sodium aluminate or sodium silicate must be added to adjust the Si/Al ratio. This approach shows a significant and remarkable result in producing a pure zeolite compared to the product produced via the hydrothermal process from the CFA slurry. However, the yield from the extracted solution is much lower than the hydrothermal process [17]. Although conventional synthesis techniques have been conducted successfully on a large scale, a quick, cheap, economically viable, and environmentally friendly process is desired for the conversion of CFA to zeolite. Microwave-assisted synthesis of zeolite from a CFA slurry was used [21] with a short reaction time [2, 4, 5]. The scale-up limitations related to applying microwave irradiation to a large volume could be alleviated in a flow process. Circulating batch flow microwave-assisted synthesis is attractive as a potential technique for the production of zeolite from CFA. To our knowledge, microwave-assisted zeolite synthesis from a clear solution in a bench FlowSynth circulating batch Microwave Reactor with a volume of 0.5 L has not been reported.

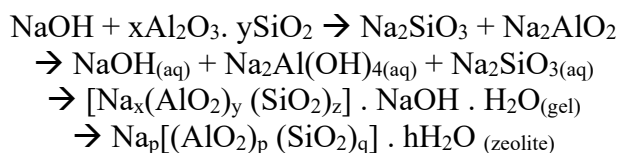
MATERIALS AND METHOD

Materials

Raw coal fly ash (Class C) was obtained from a coal-fired power plant (OPG, Nanticoke) located in Ontario, Canada, and stored in a sealed container before use. According to the American Society for Testing and Materials, ashes from bituminous coal combustion are known as class F with SiO₂+Al₂O₃ +Fe₂O₂ > 70 %, while ashes from lignite coals are known as class C with SiO₂ + Al₂O₃ + Fe₂O₂ in the range 50 – 70 % [22,23]. Analytical grade NaOH (Alphachem, Canada), Na₂AlO₃ anhydrous (Sigma-Aldrich, USA), and Na₂SiO₄ (Sigma-Aldrich, USA), were used as received. Deionized water was used for the preparation of the solutions and washing.

Method

The general reaction scheme for the alkaline treatment and zeolitization of CFA is given by [24]:



Extraction of silica (SiO₂) and alumina (Al₂O₃) from coal fly ash

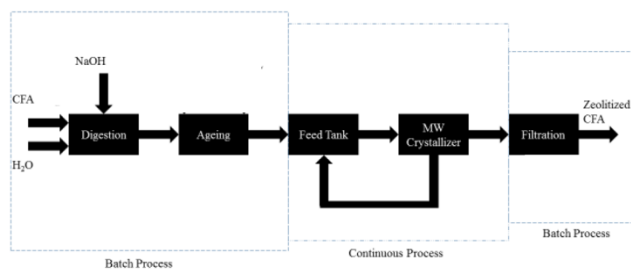
A mixture of 14.0 g of raw CFA and 5.6 g of sodium hydroxide granules was dissolved in 140 mL of deionized water to form an alkaline solution of 1 M. The alkaline hydrothermal process was applied to break down the fly ash crystalline phases and release the SiO₂ and Al₂O₃ content. Therefore, the mixture was subjected to conventional heating under atmospheric pressure at 90 °C for 4 h using a heater stirrer (Thermo Scientific, China). After hydrothermal treatment for 4 h in a 1000 mL glass flask reactor, SiO₂ and Al₂O₃ were dissolved into the liquid, and extra deionized water was added while stirring the mixture at 200 rpm for 18 h. The mixture was filtered, and the supernatant was collected as an aluminosilicate gel.

Circulating Batch Microwave Experiments (Crystallization stage)

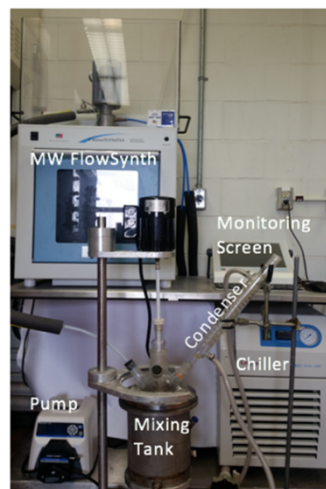
An appropriate amount of filtrate solution was mixed with Na₂SiO₄ and Na₂AlO₃ to render a molar ratio of the sample: 3.0 Na₂SiO₄: 0.5 Na₂AlO₃: 192 H₂O. The resulting solution was left in an aging feed tank for 6 h at 85 °C. The aging feed tank was equipped with a heating jacket and a condenser for controlling reaction temperature. For the crystallization step, the mixture was then pumped into the microwave FlowSynth reactor for crystal growth at different temperatures; 78 °C, 85 °C, and 95 °C for 270 min. The reaction time was 4 h, and the mixture flow rate was 5 mL/min. The system was kept at atmospheric pressure and temperature of 85 °C using a reflux condenser and a recycle stream.

The solution was pumped into the FlowSynth MW reactor via a peristaltic pump (Masterflex L/S, Cole Parmer) with tubing (L/S 15, Tygon Chemical) with an inner diameter of 4.8 mm and recirculated at a constant flow rate of 5 mL/min. The system took about 10 min to reach a steady state. After reaching the steady state, 5 mL samples were withdrawn from the mixing/feed tank every hour. A mechanical mixer was used to control the level of mixing during the experiment. The goal of mixing is to either prevent or reduce temperature or concentration gradient or to ensure good dispersion of multiple phases. Good mixing is preferable for several reasons, such as improving mass transfer in multi-phase systems, side reactions or by-product formation, or ensuring fast heat transfer [25]. Less than 1000 mL of the mixture, 850 mL, from the Flow Synth MW reactor, was recovered (Figure 1(a)). Approximately 150 mL was lost because (1) the liquid content inside the Flow Synth MW reactor could not be completely removed, and (2) the liquid remained in the zeolitized CFA.

The microwave power was constant at 125 W during the experiments. Subsequently, the filtrate solid products were washed and dried overnight at room temperature. The experimental setup of the bench scale reactor, the Milestone FlowSynth circulating batch MW reactor (Milestone, Italy), with 1 L capacity is shown in Figure 1(b) [21].



(a)



(b)

Figure 1. (a) The diagram [21] and (b) experimental setup of the microwave-assisted synthesis utilizing FlowSynth reactor

X-ray fluorescence spectroscopy (XRF) was used to determine the chemical composition of the raw CFA by using PANalytical PW2400 Wavelength Dispersive, as shown in Table 1. To collect XRD data of the synthesized samples, Rigaku-MiniFlex powder diffractometer (Japan) was used; utilizing $\text{CuK}\alpha$ ($\lambda = 1.54059 \text{ \AA}$ over the range of $5^\circ < 2\theta < 40^\circ$ with a step width of 0.02°). The XRD patterns of the synthesized zeolite samples were compared with the characteristic peaks of the standard Na-X from reference [26]. The specific characteristic peak intensity of the synthesized zeolite X was determined by the "peak fitting" algorithm in the MDI-Jade v7.5 software. The characteristic peaks for the Na-X main peaks were found at 2θ of 6.12° , 10.0° , 15.34° , 23.31° and 30.94° . The crystallinity of the sample was determined from the characteristic peak areas of 111 (6.12°) by dividing the peak intensity of the product at $2\theta = 6.12^\circ$ by the peak intensity of the standard sample run for 48 h using conventional hydrothermal synthesis.

The crystallinity was calculated using:

$$\text{Crystallinity (\%)} = \frac{\text{The peak intensity of the sample at } 2\theta = 6.10^\circ}{\text{The peak intensity of the standard sample at } 2\theta = 6.10^\circ} \times 100 \quad (1)$$

The average crystal dimension was calculated using Scherrer's equation [27]:

$$d = \frac{B\lambda}{\beta \cos \theta}, \quad (2)$$

where d is the average crystal size (nm), B is the Scherrer's constant, λ is the wavelength of the X-ray (nm), and θ is the Bragg's angle (the angle of the maximum peak). β is the full width at half-maximum (FWHM) of the broad peak after correction for intrinsic instrumental line broadening and must be in radians [9].

The morphology of the produced zeolite was studied by scanning electron microscope (SEM) using a JSM 600F (Joel, Japan) operating at 10 keV of acceleration voltage. To measure the specific surface area, pore size and pore volume of selected Na-X, Burnauer-Emmett-Teller (BET) technique was used using a Micrometrics Accelerated Surface Area and Porosimetry (ASAP 2010) surface area analyzer (Micrometrics, USA).

Synthesized Na-X samples were degassed for 6 to 8 h at 150 °C, before the analysis. The percentage yield of synthesized zeolite Na-X was calculated by dividing the weight of the sample by the weight of the Na₂AlO₃, and Na₂SiO₄ using the equation below:

$$\text{Yield (\%)} = \frac{\text{Weight of synthesized Na - X}}{\text{Weight of (Na}_2\text{AlO}_3 + \text{Na}_2\text{SiO}_4)} \times 100 \quad (\text{eq. 3})$$

RESULTS AND DISCUSSION

The chemical and mineral compositions of the raw CFA which was used as the main source of SiO₂ and Al₂O₃ are given in Table 1. The SiO₂/Al₂O₃ ratio was found to be 2.13, which is unsuitable for synthesis of zeolite Na-X under the medium concentration of NaOH solution. Therefore, extra aluminate or silicate precursors for adjusting the SiO₂/Al₂O₃ ratio were added [27].

Figure 2 presents the X-ray pattern of synthesis of zeolite Na-X by a) microwave-assisted process from the extracted solution of alkaline treated CFA in the circulating batch flow reactor, b) hydrothermally-synthesized at 75 °C for 48 h, and c) raw CFA. It can be noticed that hydrothermal and MW-assisted methods result in similar XRD patterns. Microwave-assisted synthesis zeolite Na-X had a very high crystallinity and purity with very sharp peaks. Also, the microwave-assisted synthesis reduced the reaction time compared to the conventional conversion, which required 48 h at 75 °C [17]. Moreover, the purity and crystallinity of the synthesized zeolite X increased, although the yield was lower, as will be discussed later [17].

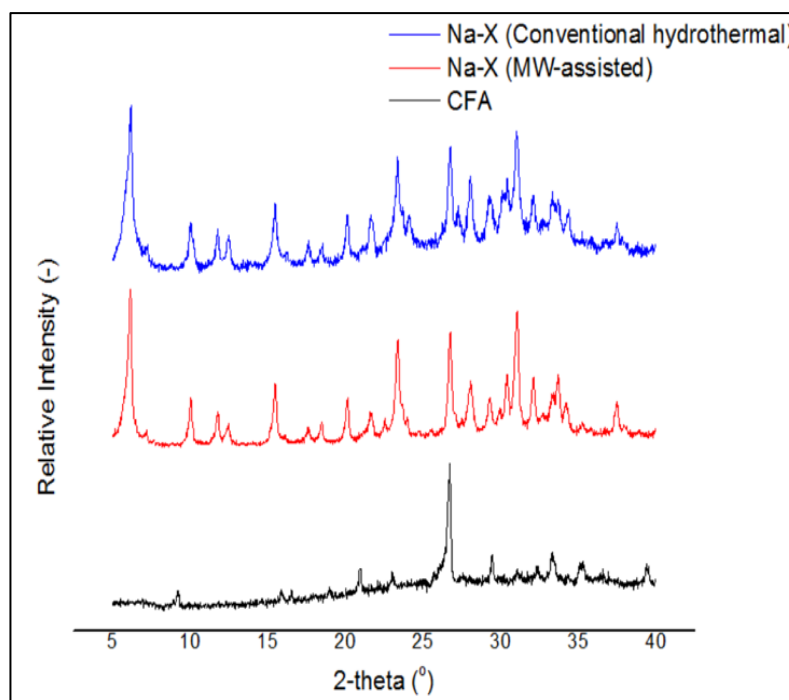


Figure 2. The XRD patterns of Na-X zeolite synthesized by MW-assisted in the circulating batch reactor, hydrothermally-synthesized, and raw CFA

The aging process before the crystallization process for zeolitization of coal fly ash is a very important step. Figure 3 shows the XRD results of the sample with and without

the aging process. There are no characteristic peaks in the XRD results of the sample without the aging step, which means no zeolite Na-X was formed. In addition, a big and strong hump appears, which suggests the powder is still amorphous. However, XRD results of the sample with an aging step before the crystallization step show characteristic peaks at 2θ of 6.12° , 10.0° , 15.34° , 23.31° and 30.94° as shown in Figure 2. For zeolite synthesis, there are three main steps: forming the building units, formation of zeolite nuclei during the aging step, and crystal growth by disposing of the building units on the crystal's surface [28].

In the present experiment to produce zeolites, the effect of different independent variables on the crystallinity, such as NaOH concentration, MW irradiation power, and time, were studied. Although the mixing rate is considered one of the factors that has a strong effect on the quality of synthesized zeolite, it was not considered as an independent variable in the present work. However, Mainganye (2012) successfully synthesized zeolite P1 hydrothermally. He studied the effect of impeller design and agitation rates during the aging step of the synthesis process. His experimental results proved that the phase purity of zeolite Na-P1 was strongly affected by agitation and the type of impeller used during the aging step of the synthesis process [29].

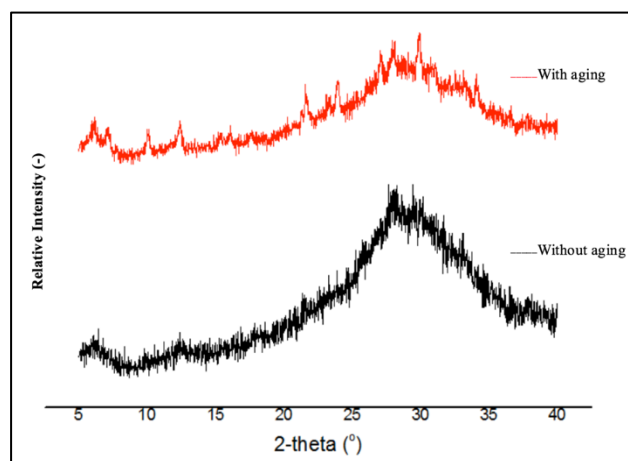


Figure 3. XRD patterns of the mixture after aging and without aging

Adding extra Na_2SiO_4 and Na_2AlO_3 to the mixture is necessary to adjust the desired silica-to-alumina ratio. Na-X could not be formed without adding proper amounts of Na_2SiO_4 and Na_2AlO_3 to the extracted solution of CFA [4, 30].

The effects of crystallization temperature and time were investigated. Crystallization experiments were conducted at different crystallization temperatures: 75°C , 85°C , and 95°C . After 4 h of continuous microwave irradiation in the FlowSynth circulating batch flow microwave reactor, stable phases of zeolite Na-A, Na-X and Na-P with sharp and clear peaks, as seen in Figure 4 were produced. According to Sang et al. [11], zeolite Y was transformed into zeolite P with increasing synthesis temperature. Also, the transformation of zeolite A into zeolite X occurs by increasing reaction temperature. Building units of zeolite X, double 6-ring (D6R), and Sodalite (SOD), were formed with increasing synthesis temperature [31-33]. Figure 5 shows that up to 1 h, no peaks appeared; however, after 2 h of crystallization, the characteristic peaks of zeolite Na-X started to appear. With increasing the crystallization time, the characteristic peak intensities increased and became sharper. Increasing crystallization time enhances the crystallinity of zeolite Na-X, which agrees with the reference [9].

SEM microphotographs of samples of zeolite at different crystallization temperatures; 85 and 95 °C, are presented in Figure 6. Figure 7 displays the Energy Dispersive X-ray spectroscopy (EDX) of chemical analysis. Observations were done at magnifications between 2.5 and 50,000. Figure 6(a) displays SEM micrographs of synthesized Na-X from the extracted solution of CFA. The product contains less impurities and heavy metals compared to the raw CFA, which has impurities as can be seen from the elemental composition analysis in Figure 7 and Table 1 [5, 19]. Moreover, Figure 6(b) shows the results of increasing synthesis temperature, which produced zeolite Na-X with impurity of zeolite Na-P. This confirms the XRD results that were mentioned in previous paragraphs. Also, Figures 7(a) and 7(b) show the EDX results of the amount of impurities such as Ti, Mg, Fe, and Ca, in the final synthesized product. It is noted that the impurities in zeolite Na-X are significantly reduced compared to the starting raw CFA.

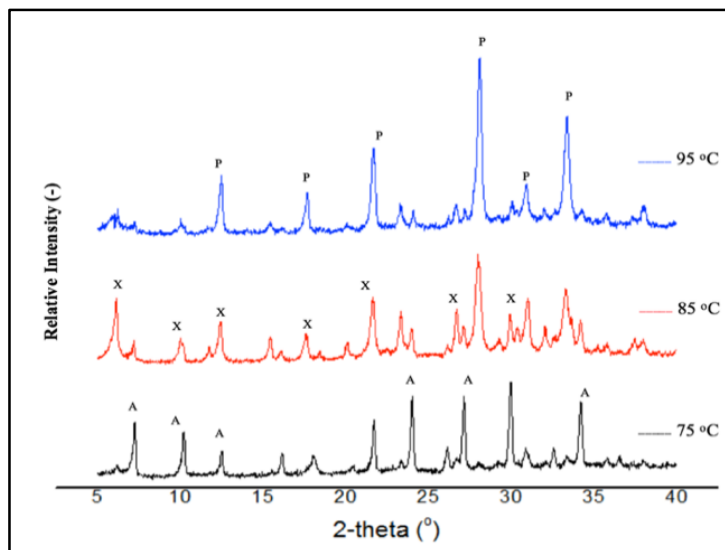


Figure 4. Zeolites produced after 4 h at (a) 75 °C, (b) 85 °C and (c) 95 °C

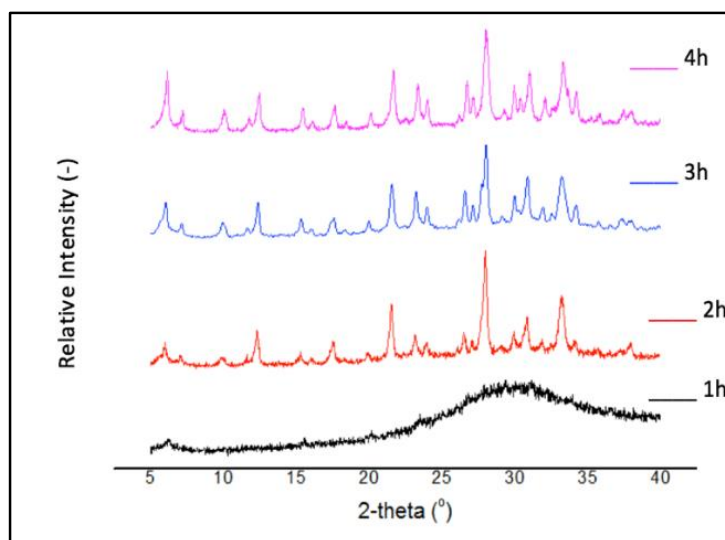


Figure 5. XRD patterns of Na-X zeolites synthesized by the microwave heating at 85 °C after 1 h, 2 h, 3 h and 4 h crystallization time

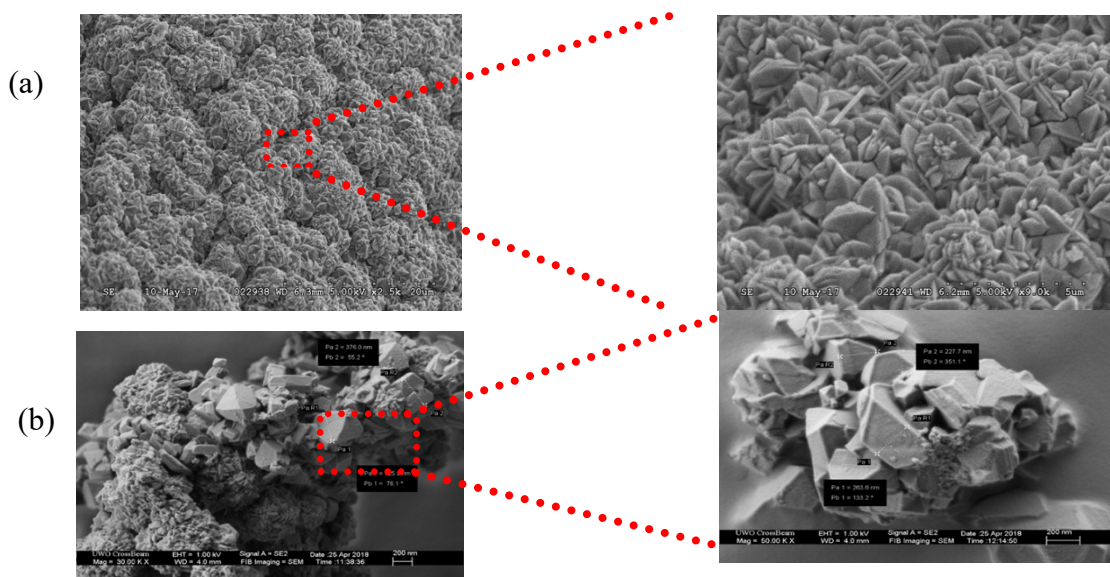


Figure 6. SEM images of the (a) CFA and (b) zeolite

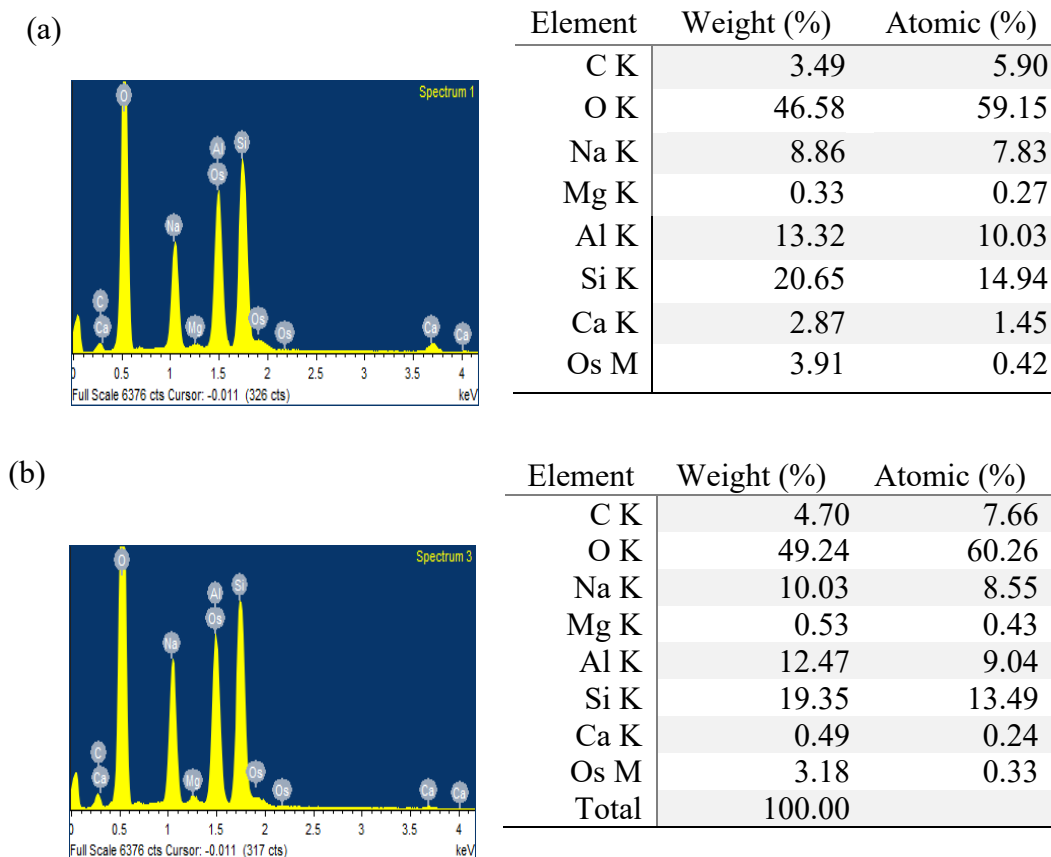


Figure 7. EDAX images and elemental composition of synthesized zeolite Na-X by MW-assisted synthesis (a) 4 and (b) 2 h of crystallization time

Table 1 lists the BET surface area of the raw CFA, the Na-X zeolite synthesized hydrothermally and by the microwave-assisted method. The proposed technique produced zeolite Na-X with surface area ($110.565 \text{ m}^2/\text{g}$), almost three times higher than that synthesized hydrothermally ($42.006 \text{ m}^2/\text{g}$). Nitrogen adsorption/desorption isotherms of the synthesized Na-X product are shown in Figure 8 and represent a type II isotherm. A type II isotherm is known for the nonporous aluminosilicate according to the Applied Chemistry (IUPAC) isotherm classification and the International Union of Pure and Applied Chemistry [34, 35]. Usually, the adsorption isotherm of type II is related to monolayer–multilayer adsorption on an open and stable external surface of a powder, which could be non-porous, macroporous, or, to a limited extent, microporous. The desorption isotherm is a distinct H_3 -type hysteresis loop indicating mesoporous aluminosilicate [34]. The limited adsorption of N_2 inside the pores could be attributed to the amorphous aluminosilicate that will block the outside pores of the zeolite crystals.

The average crystal size of the prepared zeolites at different synthesis times was calculated using Scherrer's from the peak at 2θ of 6.1° . The full width at half-maximum of the broad peak (FWHM), was calculated by the "peak fitting" algorithm in the MDI-Jade v 7.5 software and the results are listed in Table 2. As can be seen in Table 2, there is a proportional relationship between the average crystal size and synthesis time of synthesized Na-X. Increasing the average crystal size could be assigned to the increasing crystallization time that enhances the crystal growth and results in larger particles via agglomeration [9]. Also, the crystallinity of the synthesized product increases with increasing the synthesis time, and this result agrees with the reference [9]. In addition, the yield increases slightly with increasing synthesis time. As mentioned earlier, the yield of the proposed method is less than that of the conventional hydrothermal method. However, optimizing the extraction condition could improve the extracted amounts of SiO_2 and Al_2O_3 from CFA and subsequently increase the yield of synthesized zeolite [17].

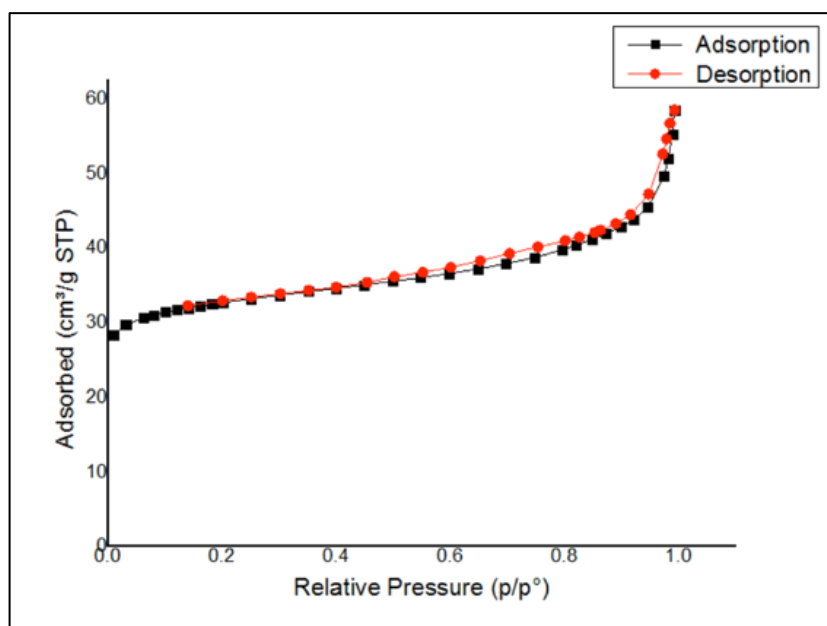


Figure 8. Isothermal plot of synthesized zeolite Na-X

Table 1. BET surface area of CFA and synthesized Na-X

	CFA	Zeolite Na-X	
		<i>Hydrothermally*</i>	<i>MW-assisted</i>
BET surface area (m ² /g)	15.47	42.006	110.565
Micropore volume (cm ³ /g)	3.3765	0.1110	0.0379

*[34]

Table 2. Yield, crystallinity and crystal size of synthesized Na-X

<i>Synthesis Time (h)</i>	<i>Yield (%)</i>	<i>Crystallinity (%)</i>	<i>Crystal size (nm)</i>
2	14.77	63.12	54.27
3	22.19	85.49	227.73
4	35.41	99.13	325.91

The mechanism for the formation of zeolite and the microwave-assisted crystallization process is understood to a certain degree but not completely. However, it is known to provide volumetric heating, rather than conventional heating, which heats by conduction and convection through a surface, leading to a temperature profile within the reacting mixture.

A theory for zeolite synthesis from ash has been provided by Murayama et al. [34]. Their theory was based on the formation of amorphous aluminosilicate gel on the solid particles under high alkaline conditions, followed by crystallization of zeolite due to the reaction between the gel and the alkali or dissolved species in the mother liquor solution. This theory advocated using the hydrothermal method for the zeolite synthesis process; it was based on the type of zeolite produced as a function of time and by following the growth trend as observed in SEM images.

The general assumption is that the crystallization of zeolites proceeds via two steps: (1) nucleation of discrete particles of the new phase and (2) growth of zeolite crystals. During the nucleation stage of zeolites, the smallest entities, "crystal nuclei," with the identity of the new crystalline phase, are formed. The crystal growth process of zeolites is classically described with typical S-shaped crystallization curves (Figure 9) [36].

Even when the reaction mixture is stable, a large number of variables can impact zeolite crystallization. Among these variables, synthesis temperature and crystallization time used are the most influential due to the metastable nature of zeolites [37, 38]. However, the type of raw materials (purities, reactivity), order of mixing, agitation, and aging each have a significant effect, too. It is common that the initial mixtures become gels with high viscosity due to the formation of amorphous aluminosilicate gel particles suspended in the basic medium.

In other words, zeolite crystals form on the CFA's surface via the precipitation method as a result of the fast homogenous heating of particles. Using microwave heating after the hydrothermal treatment at higher solid/liquid ratios increases the rate of crystal growth due to the surface activation characteristic of MW irradiation, which leads to a strong aggregation between zeolite particles and nuclei formed during the conventional heating step [39].

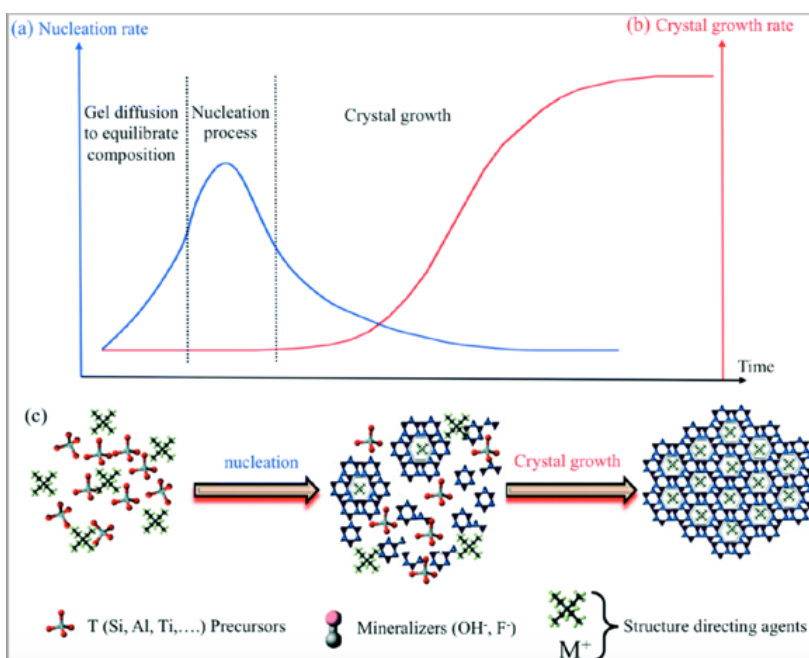


Figure 9. Schematic representation of the (a) nucleation rate and (b) crystal growth rate of zeolites described with a typical S-shaped curve and (c) related rearrangements from amorphous particles into crystalline zeolite during the synthesis [36]

CONCLUSIONS

Pure zeolite Na-X was successfully synthesized from a clear solution containing SiO_2 and Al_2O_3 extracted from CFA, utilizing a FlowSynth circulating batch flow microwave reactor. The effects of crystallization time and temperature on the characteristics of the synthesized zeolite were investigated. Results of XRD data and SEM images showed that the highest percentage of crystallinity of the synthesized product was achieved after 4 h of continuous microwave irradiation at 85 °C in a circulating batch flow microwave reactor. The yield of zeolites obtained was lower than the conventional hydrothermal treatment, but the synthesis time was substantially reduced using microwave technology in the presented technique. The produced zeolite using the microwave-assisted circulating batch process was significantly more pure compared to the conventional hydrothermal. In conclusion, pure zeolite-X could be synthesized in a much shorter time using the circulating batch microwave heating method by controlling the crystallization temperature and time.

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