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Synthesis of Zeolite NaA Nano-Crystals: Effect of Synthesis Parameters on Crystallinity and Crystal Size

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ABSTRACT

Hydrothermal synthesis of zeolite NaA crystals with a composition of Al_2O_3:aSiO_2:bNa_2O:cH_2O was investigated. Effects of SiO_2/Al_2O_3, Na_2O/Al_2O_3, and H_2O/Al_2O_3 ratios, crystallization temperature, and time on crystallinity and crystal size of zeolite NaA crystals were studied. An attempt was made to understand the interactions between these parameters. The crystal species of zeolite NaA were characterized by XRD and SEM. Considering the interactions between these parameters showed that the effects of increasing SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios simultaneously neutralized each other so that their overall effect was found to be insignificant. On the other hand, the effects of increasing SiO_2/Al_2O_3 and H_2O/Al_2O_3 ratios reinforced each other and significantly affected crystallinity and crystal size. Increasing alkalinity increases crystallization rate and reduces synthesis time. Also, effects of increasing crystallization temperature and time simultaneously reinforced each other. The effect of decreasing alkalinity was moderated with that of increasing Na^+ content in the synthesis gel.

1. Introduction

Zeolites are nanoporous crystalline materials with a uniform pore size distribution on a molecular scale and with high thermal, mechanical, and chemical stability. They have been recently developed for many industrial separation processes, such as adsorption and membrane technologies, due to their molecular sieve properties. Zeolites can be used in many separation processes, e.g., gas separation, pervaporation, and membrane reactors [1].

Zeolite NaA is an important type of zeolites with high hydrophilic properties that has been reported to be a very attractive material as catalysts and adsorbents in several chemical processes [2]. Small and uniform pores of zeolite NaA with a pore diameter of approximately 0.3 nm have received great attention in recent years due to its high selectivity to many components, especially water in dehydration processes [3].

Positive effects of the crystal size reduction on reaction kinetics and mass transfer rates in certain catalytic and separation processes were claimed [1]. The crystal size reduction is probably the simplest way to overcome mass transport limitations and ensure high surface

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accessibility. Furthermore, fine crystals with narrow particle size distributions can be effectively used in chemical sensing and electrochemical analysis. Many applications of zeolite membranes for separation processes in various industries have been reported [4]. As is known, zeolite membranes are composed of two layers: porous support and zeolite effective top layer. The size of zeolite crystals in membranes is a strong function of the primary crystal size, which in turn depends on operating parameters in the synthesis steps. Zeolite membranes with fine selective layers and narrow particle size distributions can be employed in a wide range of separation applications. The objectives of the present study are to investigate the effects of synthesis parameters on crystallinity and crystal size of zeolite NaA crystals. The effects of synthesis parameters containing SiO_2/Al_2O_3, Na_2O/Al_2O_3, and H_2O/Al_2O_3 ratios and crystallization temperature (T) and time (t) were investigated. The synthesized zeolite NaA crystals were characterized using XRD and SEM.

2. Experimental

2.1. Zeolite synthesis

The hydrothermal method was used to prepare zeolite NaA crystals. The materials used to form the aluminosilicate gel include aluminum powder (Al 99.9 % wt, Lobachem), sodium silicate (SiO_2: 27 % + Na_2O: 8 % wt, Merck), sodium hydroxide (NaOH, 98 % wt, Merck), and dionized water. Composition ratios of the gel were Al_2O_3: $aSiO_2$: bNa_2O: cH_2O. In the experimental design, the above coefficients were adjusted as a=1.92-5.0, b=3.16-50.0, and c=128-1000.

The zeolite NaA gel with ratios of Al_2O_3: $1.92SiO_2$: $3.16Na_2O$: $128H_2O$ was prepared as follows (basis on 100 g gel): 4.65 g of NaOH was dissolved and mixed in 84.78 ml of distilled water. The solution was divided into two equal volumes and kept in polypropylene bottles. Aluminate solution was prepared by dissolving 1.98 g aluminum powder into one part of the NaOH solution and was mixed until cleared. Due to the very exothermic reaction, the reactor was cooled vigorously. Silicate solution was prepared by adding 15.78 g sodium silicate to another part of the NaOH solution. These two solutions were stirred for 1 h at 60 °C; then, the silicate solution was poured into the aluminate solution and mixed until a thick homogenized gel was formed. This aging step was prolonged at least for 1 h. After aging, the aqueous gel was carefully poured in a Teflon-lined autoclave. The autoclave was sealed and kept in an oven at 80, 90, and 100 °C for 3, 4, and 5 h to synthesize the NaA zeolite crystals. Then, the autoclave was taken out from the oven to stop the crystallization process. The synthesized crystals were filtered and washed several times with distilled water and, then, dried in a vacuum oven at 100 °C for 2 h.

In this study, the effects of synthesis parameters on the formation of zeolite NaA crystals were investigated, including relative amount of the source materials, such as $a=SiO_2/Al_2O_3$, $b=Na_2O/Al_2O_3$, $c=H_2O/Al_2O_3$, and crystallization conditions, e.g., crystallization temperature and time. These parameters and their related levels are presented in Table 1. Other synthesis conditions were kept constant in all the experiments; Stirring Time (1 h), Stirring Temperature (60 °C), and Drying Temperature (100 °C).

The purpose of these investigations is to estimate the influences of the above five synthesis parameters on crystallinity and crystal size of the synthesized zeolite NaA

crystals.

According to literature [5-8], the common composition of synthesized zeolite NaA crystals and the related crystallization conditions, including temperature and time, are Al_2O_3: $1.92SiO_2$: $3.16Na_2O$: $128H_2O$, 100 °C and 3 h, respectively, that has been investigated by many researchers. Thus, in this research, this composition was selected as the basis of the experimental design. The synthesis experiments were started with the above composition and crystallization conditions. Then, the next synthesis experiments were carried out using different levels of each parameter (e.g., SiO_2/Al_2O_3), while the other parameters were kept constant. This procedure was then repeated for all of the above parameters, separately.

Finally, some complementary experiments were carried out in order to investigate the interactions between the above parameters. The values of synthesis parameters and the related samples are presented in Table 2. According to Table 2, zeolite NaA crystals were synthesized using nine different molar gel compositions, as shown in Table 3.

Table 1
Synthesis parameters of zeolite NaA crystals and their related levels.

No.	Parameter	Level 1	Level 2	Level 3
1	SiO_2/Al_2O_3 (a)	1.92	3.50	5.00
2	Na_2O/Al_2O_3 (b)	3.16	26.50	50.00
3	H_2O/Al_2O_3 (c)	128	300	1000
4	Crystallization temperature, T (°C)	80	90	100
5	Crystallization time, t (h)	3	4	5

Table 2
The values of synthesis parameters and the related samples according to Table 1.

Sample	SiO_2/Al_2O_3	Na_2O/Al_2O_3	H_2O/Al_2O_3	Synthesis temperature (K)	Synthesis time (h)	Aging time (h)
S1	1.92	3.16	128	100	3	3
S2	3.50	3.16	128	100	3	3
S3	5.00	3.16	128	100	3	3
S4	1.92	3.16	1000	100	3	3
S5	1.92	26.50	1000	100	3	3
S6	1.92	50.00	1000	100	3	3
S7	1.92	3.16	300	100	3	3
S8	1.92	3.16	128	100	5	3
S9	1.92	3.16	128	90	3	3
S10	1.92	3.16	128	80	3	3
S11	1.92	3.16	128	100	4	3
S12	5.00	50.00	1000	100	3	3
S13	5.00	3.16	1000	100	3	3
S14	5.00	50.00	1000	90	3	3
S15	5.00	50.00	1000	100	4	3

Table 3
Nine different molar gel compositions of zeolite NaA synthesis.

No.	Gel composition
1	Al_2O_3: 1.92SiO_2: 3.16Na_2O: 128H_2O
2	Al_2O_3: 3.5SiO_2: 3.16Na_2O: 128H_2O
3	Al_2O_3: 5.0SiO_2: 3.16Na_2O: 128H_2O
4	Al_2O_3: 1.92SiO_2: 26.5Na_2O: 1000H_2O
5	Al_2O_3: 1.92SiO_2: 50.0Na_2O: 1000H_2O
6	Al_2O_3: 5.0SiO_2: 50.0Na_2O: 1000H_2O
7	Al_2O_3: 1.92SiO_2: 3.16Na_2O: 300H_2O
8	Al_2O_3: 1.92SiO_2: 3.16Na_2O: 1000H_2O
9	Al_2O_3: 5.02SiO_2: 3.16Na_2O: 1000H_2O

2.2. Zeolite characterization

The zeolite crystals were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (SIEMENS, D5000, 1500 W, 35 kV, 20 mA, λ =1.54056 Å) with Cu radiation. In order to investigate the effects of synthesis parameters on zeolite NaA crystal size, the average crystal size was estimated using standard Debye-Scherrer equation (Cullity, 1956) [9]:

$$D = 0.89\,\lambda / \beta \cos\theta \qquad (1)$$

where D is the average crystal size, λ is the X-ray wavelength (CuKα), β is the broadening of the diffraction line measured at half the line maximum intensity, and θ is the diffraction angle. Since the coherent effect is neglected by this formula, the measured crystal size may be used just as an approximation. Crystallinity of the synthesized powder was measured based on the X-ray diffraction data (intensity of the three highest peaks), compared with the reference patterns [10].

Morphology of the synthesized crystals was examined by Scanning Electron Microscopy (SEM) using a scanning electron microscope (JEM-1200 or JEM-5600LV equipped with an Oxford ISIS-300 X-ray disperse spectroscopy (EDS)).

3. Results and discussion

Figure 1 shows the XRD patterns of zeolite NaA crystals synthesized using compositions and conditions according to Table 2. The results of XRD patterns indicated that the zeolite crystals were formed with many of the compositions and in different conditions, yet with different degrees of crystallinity. As mentioned, crystallinity of the zeolites was measured by using intensity of the three highest peaks of the XRD patterns and by comparing the results with the reference patterns. The three strongest peaks of zeolite NaA are at 2θ = 7.18, 10.17, and 23.99 [10]. The standard XRD pattern of zeolite NaA reported in literature is presented in Figure 2 [10].

Table 4 summarizes the results of crystallinity and crystal size calculated for the synthesized zeolites according to Table 2. Figure 3 shows crystallinity of the synthesized zeolites as functions of the five selected parameters. Figure 4 shows crystal size of the synthesized zeolites as functions of the five selected parameters. Figure 5 shows SEM photographs of the crystals for samples S1, S7, S9, and S11. As observed, the size of

the cubic zeolite NaA crystals is in a relatively narrow range of 0.5 to 3 µm.

Considering Table 4 and Figure 5, it can be concluded that the mean crystallite sizes of samples S1, S7, S9, and S11 obtained using Debye-Scherrer equation are equal to their related values obtained from SEM photographs.

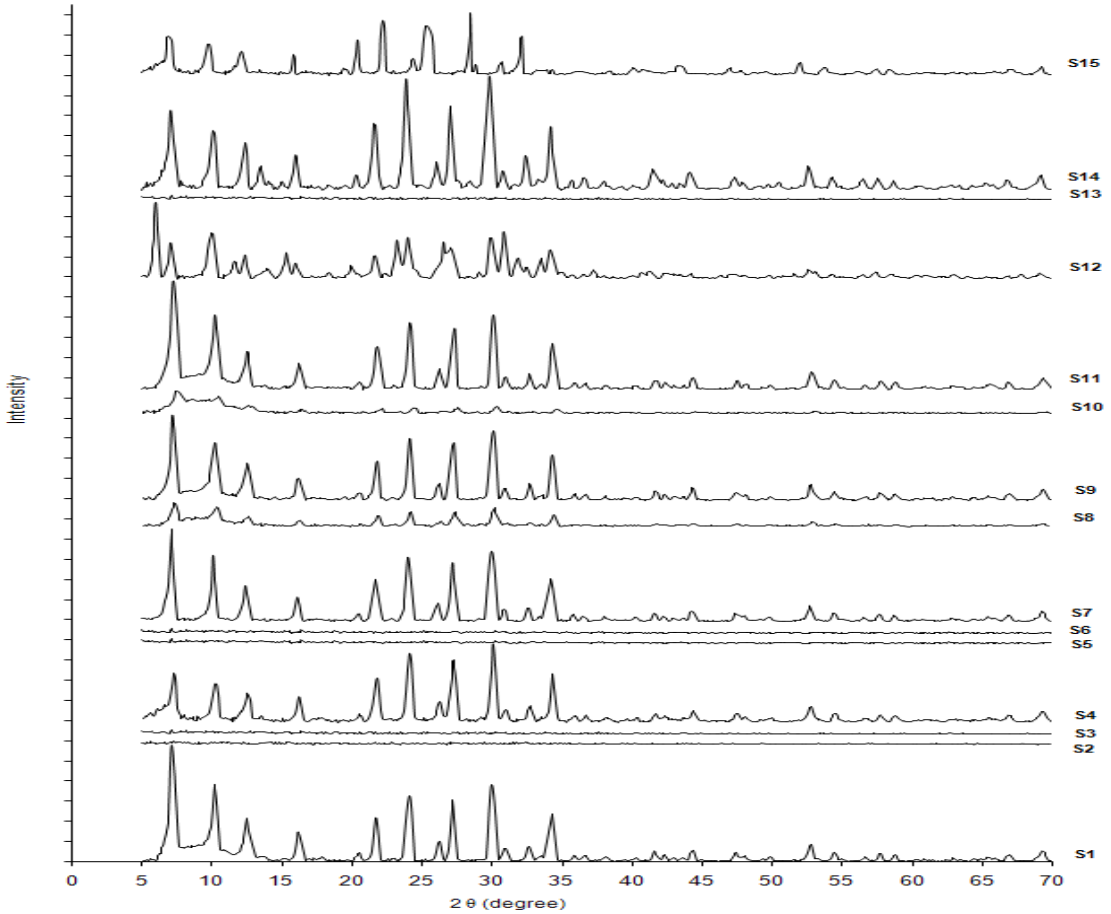

Figure 1. XRD patterns of zeolite NaA crystals synthesized according to Table 2.

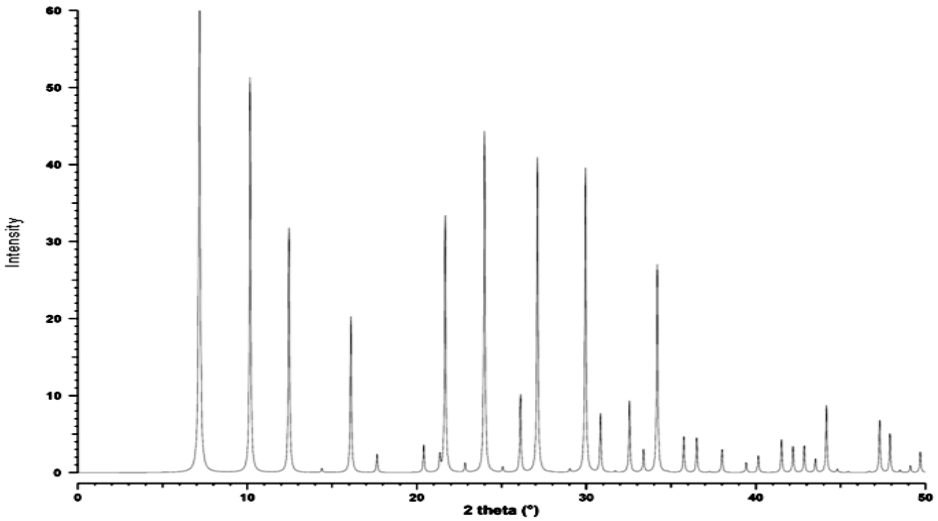

Figure 2. Standard XRD pattern of zeolite NaA.

Table 4
A summary of crystallinity and crystal size calculated for the synthesized zeolites according to Table 2.

Sample	Crystallinity (%)	D (nm)
S1	100	19.89
S2	2.6	-
S3	3.3	-
S4	47.4	14.65
S5	1.9	-
S6	1.1	-
S7	83.2	17.26
S8	21.8	13.38
S9	80.3	12.53
S10	17.0	7.08
S11	96.6	17.55
S12	49.0	14.37
S13	5.7	-
S14	73.5	14.26
S15	39.0	4.31

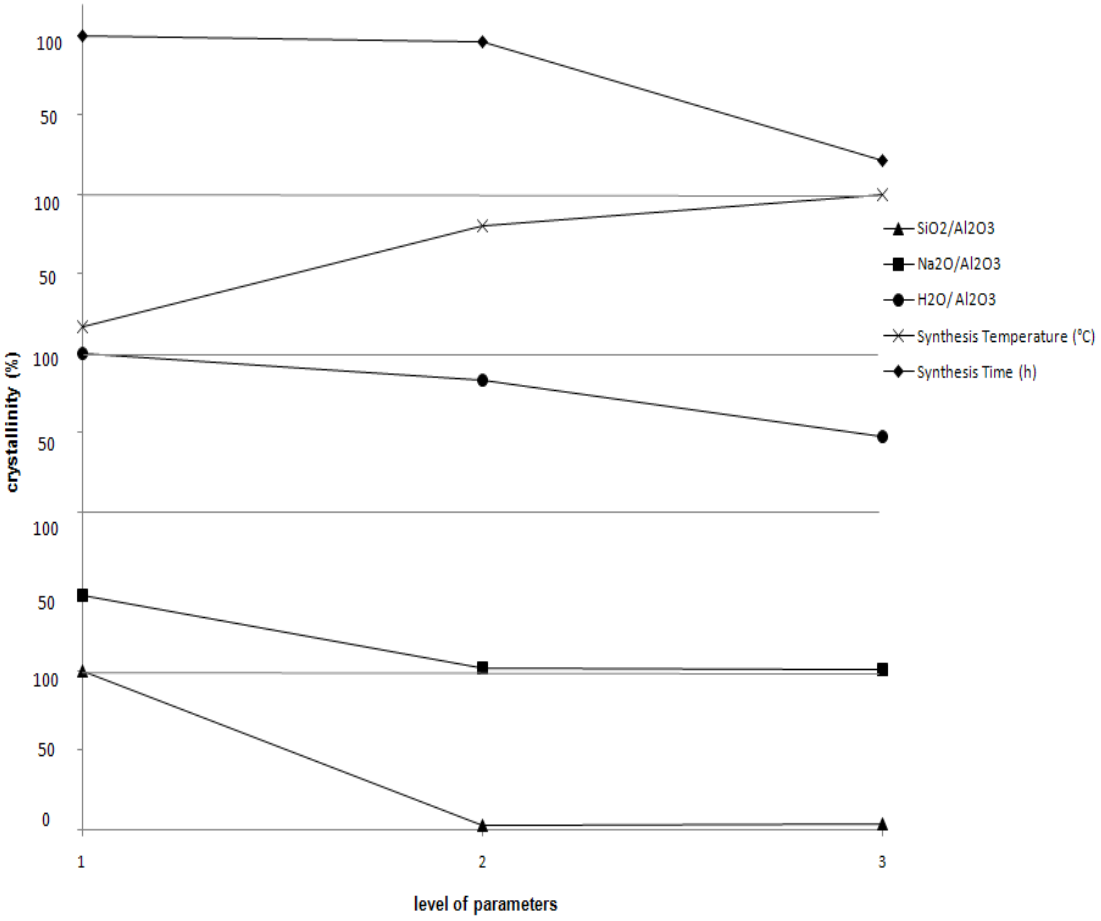

Figure 3. Crystallinity of synthesized zeolites.

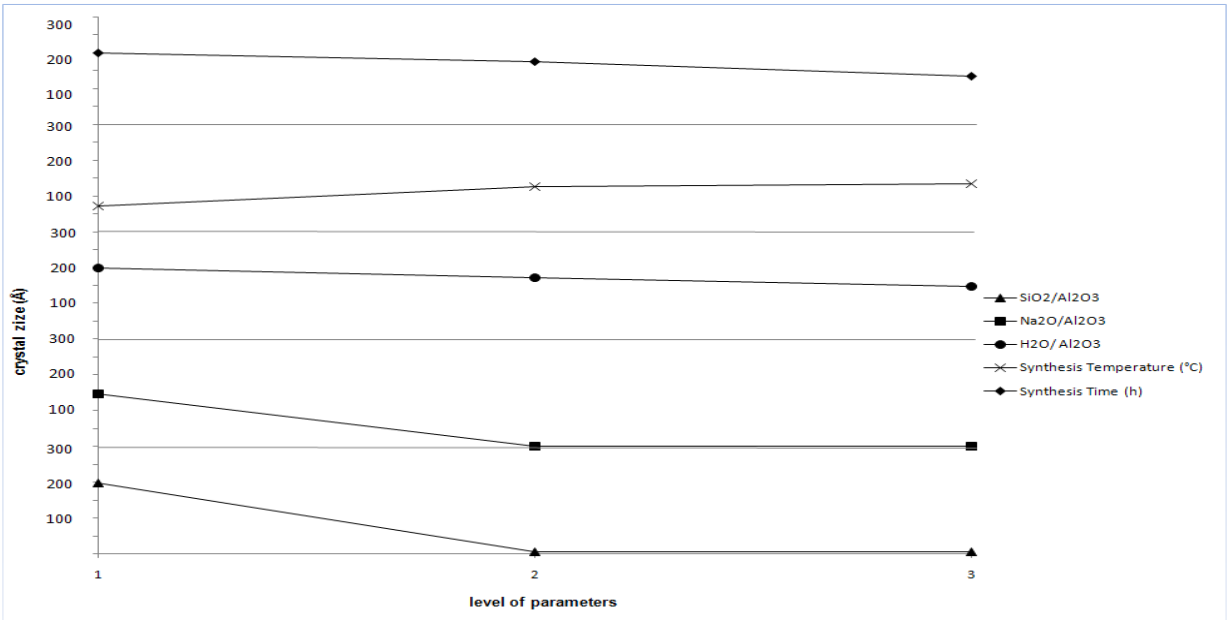

Figure 4. Crystal size of synthesized zeolites.

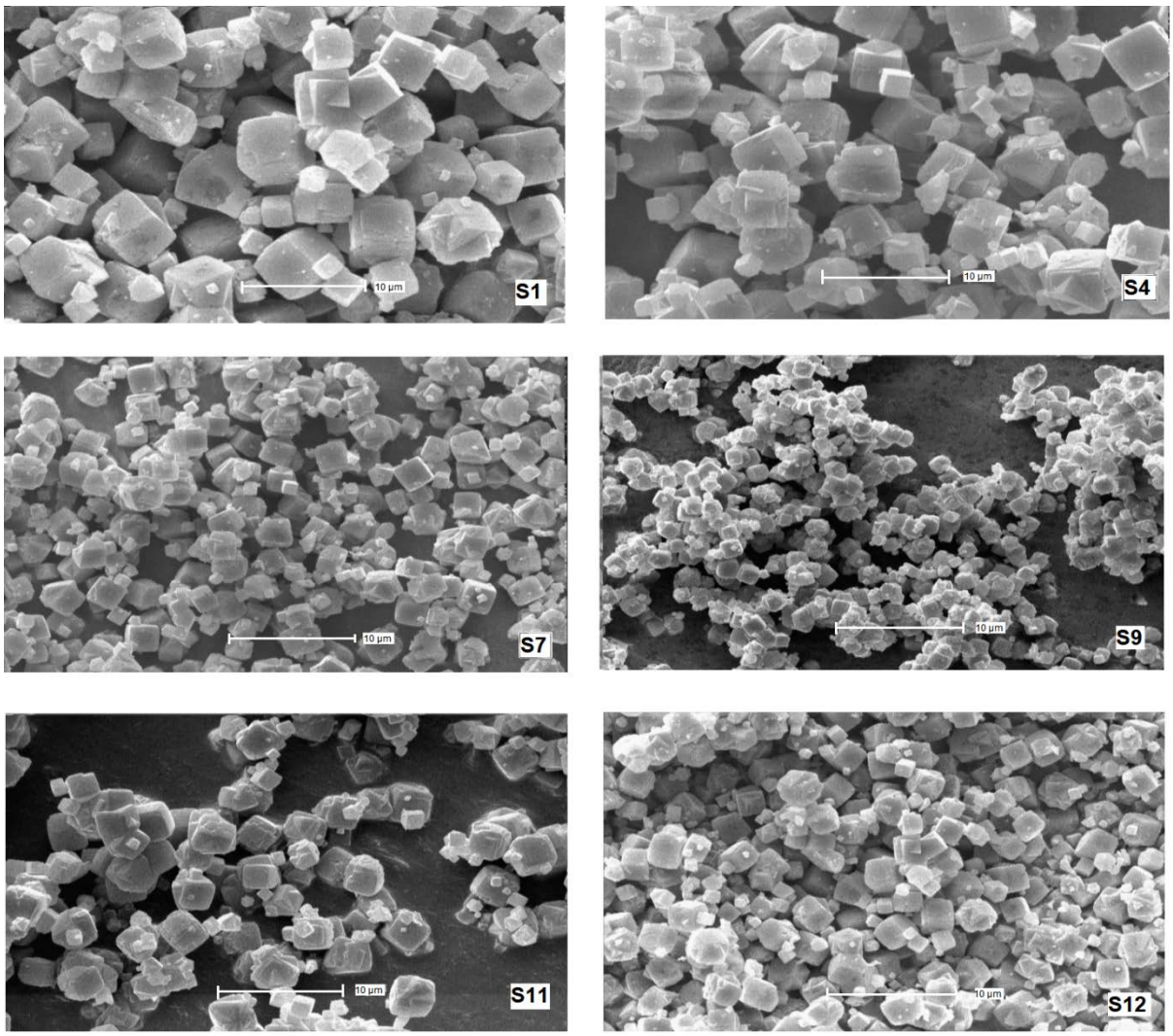

Figure 5. SEM photographs of the crystals for samples S1, S4, S7, S9, S11 and S12.

3.1. Effects of synthesis parameters

3.1.1. SiO_2/Al_2O_3 ratio

SiO_2/Al_2O_3 ratio in the reaction system plays an important role in determining the structure and composition of the synthesized crystals.

In order to investigate effects of SiO_2/Al_2O_3 ratio on crystallinity and crystal size of zeolite NaA crystals, the results of S1, S2, and S3 samples were considered. Figure 6 shows XRD patterns of these samples. As observed in Figures 3 and 4, pure zeolite NaA crystals with the highest crystallinity (100 %) and mean crystal size of 19.89 nm were obtained (sample S1). The results show that slightly increasing SiO_2/Al_2O_3 ratio reduces crystallinity significantly. Thus, it can be concluded that, in these conditions (low alkalinity), zeolite NaA crystals can be only produced if SiO_2/Al_2O_3 ratio is the lowest (1.92). According to the literature [11], direct synthesis of high-silica zeolite LTA has been a challenge for decades. The problem can be solved with increasing alkalinity (Na_2O/H_2O ratio), which is explained later.

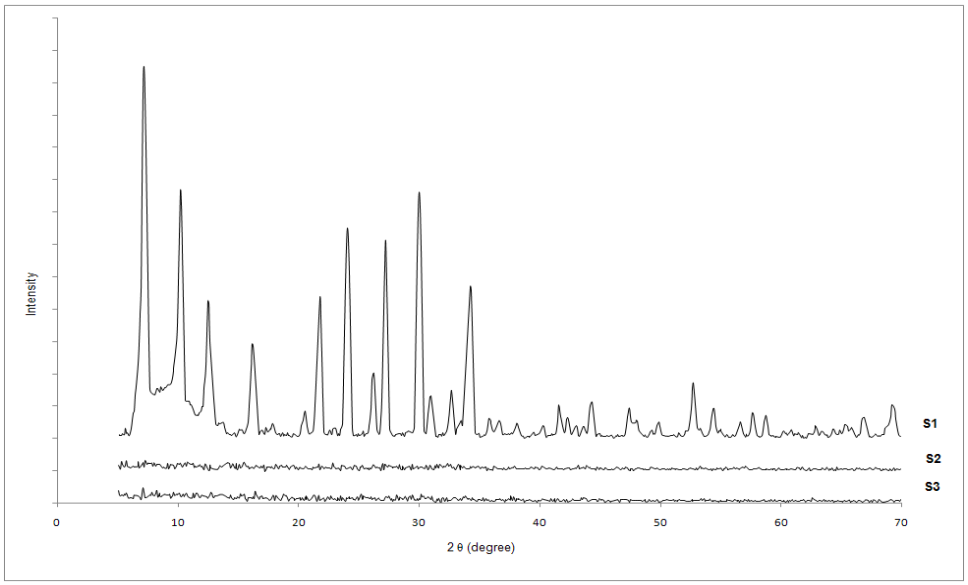

Figure 6. XRD patterns of S1, S2, and S3 samples.

3.1.2. Na_2O/Al_2O_3 ratio

Figure 7 indicates XRD patterns of S4, S5, and S6 samples. As observed in Figures 3 and 4, among these samples, only sample S4 is zeolite NaA with crystallinity of 47.4 % and crystal size of 14.65 nm. The results show that increasing Na_2O/Al_2O_3 ratio terminates the formation of zeolite NaA crystals. Thus, it can be concluded that, in these conditions, zeolite NaA crystals can be only produced with medium crystallinity if alkalinity is the lowest (0.003). Most zeolites are crystallized from the basic Na_2O-Al_2O_3-SiO_2-H_2O systems. For this specific system, alkalinity can be defined as OH^-/Si ratio or Na_2O/H_2O ratio. At higher alkalinity, solubility of Si and Al sources increases, polymerization degree of silicate anions decreases, and polymerization of polysilicate and aluminate anions accelerates. Consequently, increasing alkalinity reduces induction and nucleation periods and speeds up crystallization of zeolites [12]. According to the above descriptions, it can be said that increasing alkalinity reduces nucleation time and accelerates crystal formation. Thus, during experiments in which alkalinity increases within a constant period, crystallinity

increases first; however, the synthesized zeolite crystals are then dissolved again in the alkali mixture, and crystallinity decreases, finally. Thus, it can be concluded that, for increasing crystallinity, at higher alkalinity, synthesis time should be shortened.

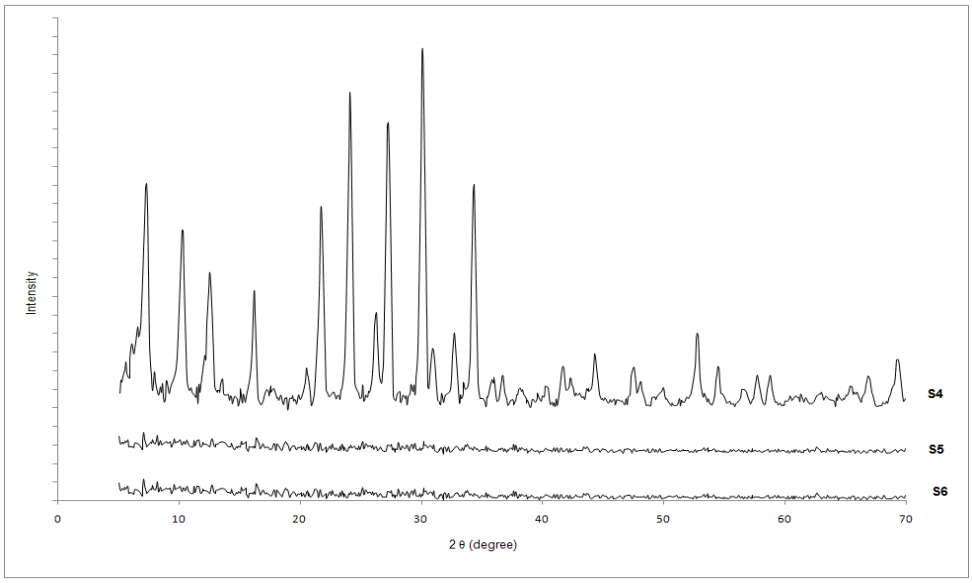

Figure 7. XRD patterns of S4, S5 and S6 samples.

3.1.3. H_2O/Al_2O_3 ratio

The results showed that increasing H_2O content (H_2O/Al_2O_3 ratio) had the weakest effect on crystallinity and crystal size of zeolite NaA. Figure 8 indicates XRD patterns of S1, S7, and S4 samples. As observed in Figures 3 and 4, among these samples, increasing H_2O content in the synthesis gel or reducing concentration of reactants decreased crystallinity and crystal size of zeolite NaA.

It can be explained that an overall dilution of the synthetic mixture causes less supersaturation; as a result, the crystal growth is favored at the expense of nucleation; consequently, large crystals can be obtained. Variation of H_2O content can also change crystallization region of zeolite phases [12].

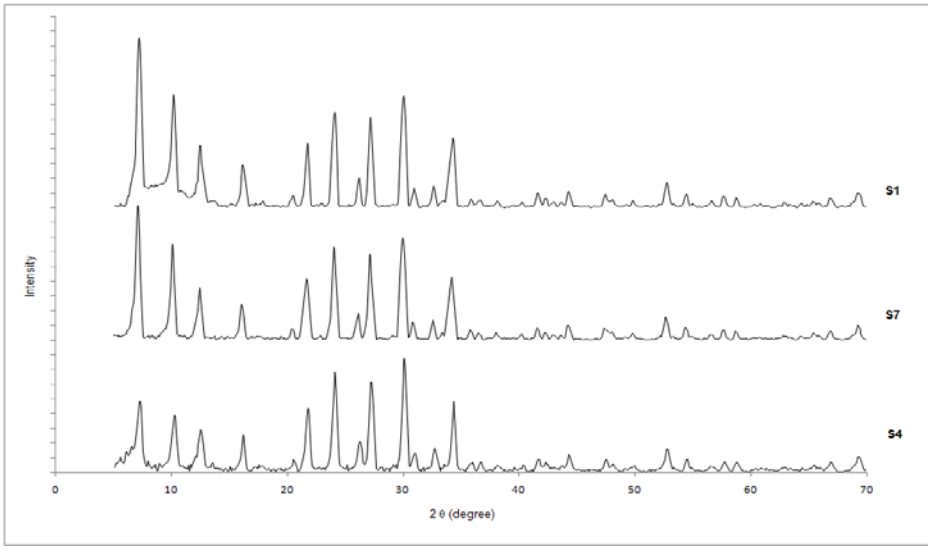

Figure 8. XRD patterns of S1, S7 and S4 samples.

3.1.4. Synthesis temperature

Temperature is an important factor in synthesis of zeolites. All researches have paid a particular attention to crystallization temperature due to its strong effect on formation of zeolites. Desired zeolites can typically be obtained only within specific temperature ranges [13].

In order to investigate the effects of synthesis temperature on crystallinity and crystal size of zeolite NaA crystals, the results of S8, S9, and S10 samples were considered. Figure 9 indicates XRD patterns of these samples. As observed in Figures 3 and 4, increasing synthesis temperature from 80 to 100 °C significantly increases the crystallinity of zeolite NaA. A similar trend can be observed for crystal size that increases with increasing synthesis temperature. Thus, it can be concluded that, in these conditions, larger zeolite NaA crystals can be produced with higher crystallinity at higher crystallization temperatures. According to the literature [14], nucleation and crystal growth are strongly affected by crystallization temperature. Increasing temperature increases both nucleation rate and crystal growth rate. Thus, higher growth rates and larger crystals can be obtained at a higher temperature.

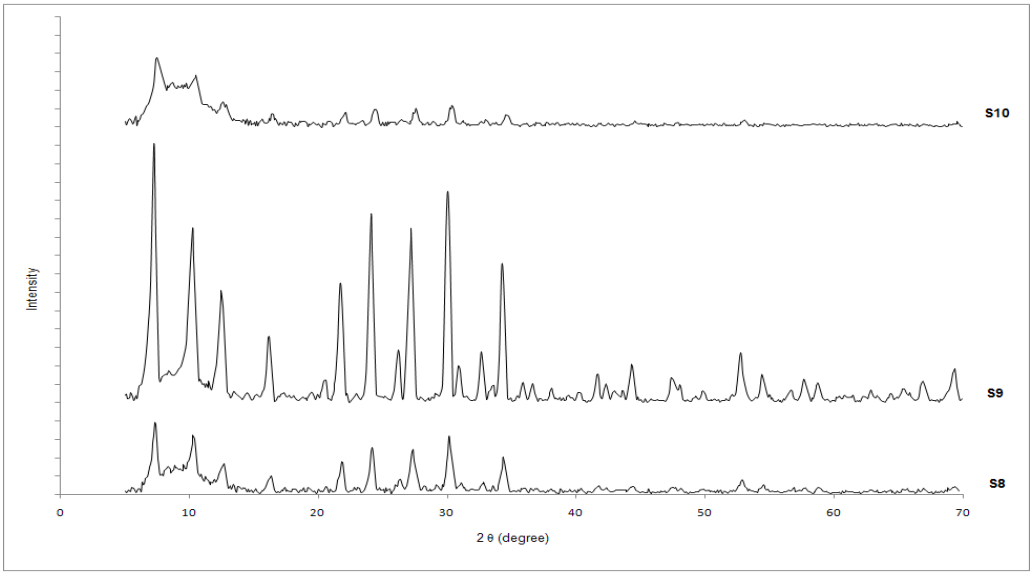

Figure 9. XRD patterns of S10, S9 and S8 samples.

3.1.5. Synthesis time

Figure 10 indicates XRD patterns of S1, S8, and S11 samples. As observed in Figures 3 and 4, among these samples, increasing synthesis time terminates the formation of zeolite NaA crystals. Crystallinity and mean crystal size of zeolite NaA decrease by increasing the synthesis time from 3 to 5 h.

As known, crystallinity increases with time. However, it should be noted that zeolites are thermodynamically metastable phases. In general, Ostwald's law of successive reactions is followed in zeolite synthesis, i.e., a metastable phase appears first and, then, successively more stable phases are replaced with each other. For example, with prolonged crystallization time, zeolite A (LTA) is dissolved to form zeolite sodalite (SOD), when synthesized in an alkaline aluminosilicate gel [15]. Thus, this can be the reason for our observations in this research. In other words, increasing crystallization time

causes dissolution of synthesized zeolites in the alkaline solution and, as a result, decreases crystallinity and crystal size. However, it must be mentioned that the formation of zeolites cannot be rationalized on a thermodynamic basis alone, and kinetics must be considered, too [16].

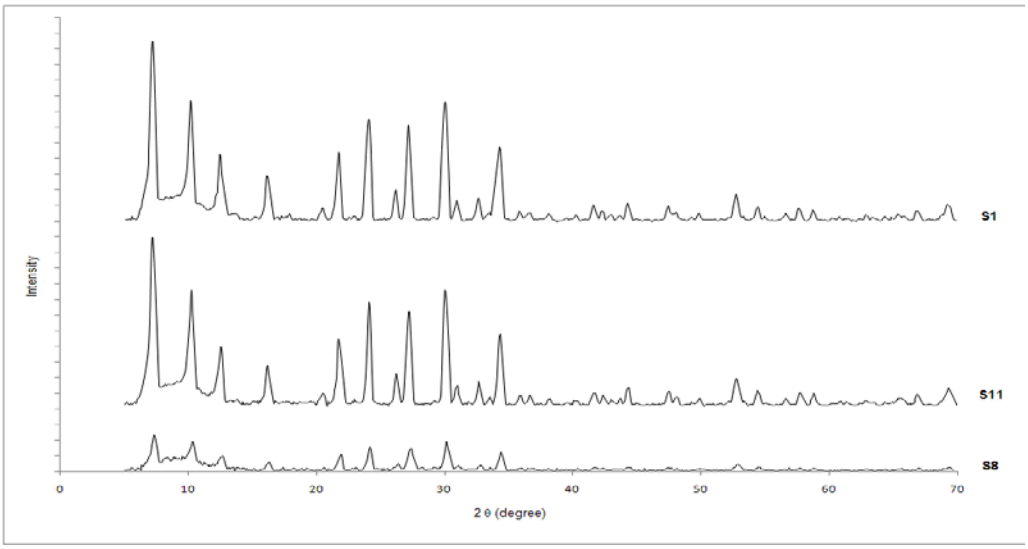

Figure 10. XRD patterns of S1, S11, and S8 samples.

3.2. Interactions of parameters

Table 5 presents the results of interactions between the five mentioned parameters with respect to crystallinty and crystal size of zeolite NaA crystals.

Table 5
Results of interactions between the five investigated parameters on crystallinty and crystal size of zeolite NaA crystals.

Interactions	Sample	Crystallinity (%)	D (nm)
SiO_2/Al_2O_3 + Na_2O/Al_2O_3	S4	47.4	14.65
	S12	49.0	14.37
SiO_2/Al_2O_3 + H_2O/Al_2O_3	S1	100	19.89
	S13	5.7	-
Na_2O/Al_2O_3 + H_2O/Al_2O_3	S1	100	19.89
	S6	1.1	-
T + t	S8	21.8	13.38
	S10	17.0	7.08
SiO_2/Al_2O_3 + Na_2O/Al_2O_3 + H_2O/Al_2O_3	S11	96.6	17.55
	S15	39.0	4.31
	S1	100	19.89
	S12	49.0	14.37

3.2.1. Interactions of SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios

In order to investigate the interactions between SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios, the results of S4 and S12 samples were considered. Figure 11 indicates XRD patterns of these samples. In sample S4, the amounts of SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios were 1.92 and 3.16, respectively. Their values in sample S12 were 5.0 and 50.0.

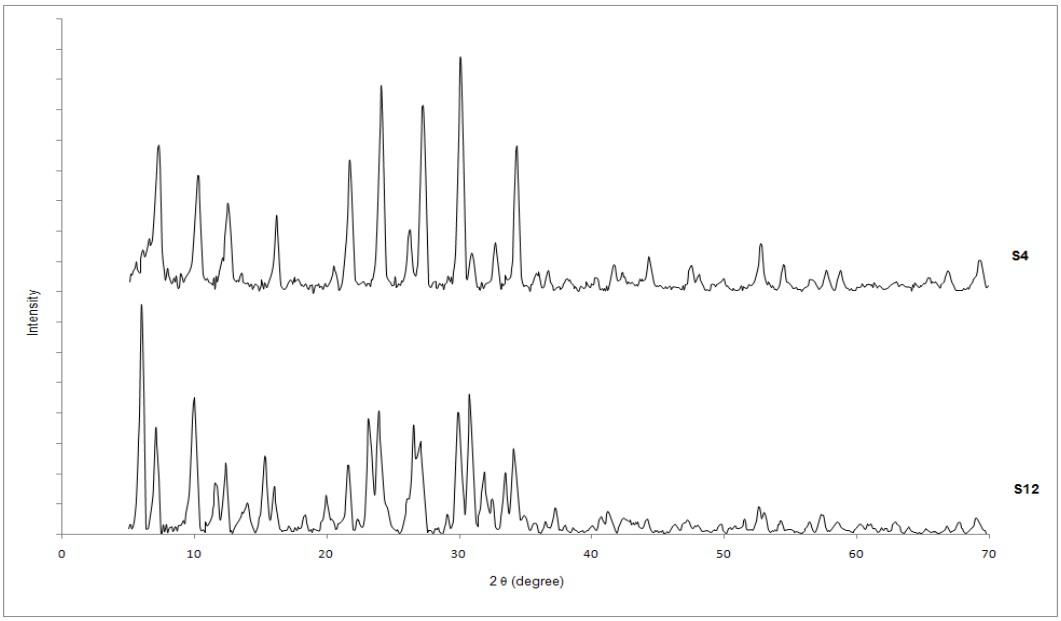

Figure 11. XRD patterns of S4 and S12 samples.

As mentioned, increasing SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios reduces crystallinty and crystal size of zeolite NaA significantly. However, as observed in Table 5, increasing both the ratios simultaneously has no significant effect. In other words, increasing the two ratios neutralizes their individual effects. Thus, it can be concluded that increasing Si and Na contents in zeolite NaA synthesis gel has reciprocal effects, making these two parameters have approximately the same minor effects on crystallinity and crystal size of zeolite NaA.

According to the literature [11], zeolites with a low SiO_2/Al_2O_3 ratio ($Si/Al \leq 5$), for example, zeolites NaA, X (FAU), and hydroxysodalite (SOD), are prepared from reaction mixtures with a low Si/Al ratio and strong alkalinity, whereas high-silica zeolites ($Si/Al \geq 5$), for example, zeolite beta (BEA), ZSM-11 (MEL), and ZSM-5 (MFI), are prepared from a gel with a high Si/Al ratio and weak alkalinity. Thus, it can be concluded that in order to synthesize zeolite NaA with high SiO_2/Al_2O_3 ratio, the gel should be strongly alkaline.

3.2.2. Interactions of SiO_2/Al_2O_3 and H_2O/Al_2O_3 ratios

In order to investigate the interactions between SiO_2/Al_2O_3 and H_2O/Al_2O_3 ratios, the results of S1 and S13 samples were considered. Figure 12 indicates XRD patterns of these samples. In sample S1, the amounts of SiO_2/Al_2O_3 and H_2O/Al_2O_3 ratios were 1.92 and 100, respectively. Their values in sample S13 were 5.0 and 1000.

As mentioned, increasing SiO_2/Al_2O_3 ratio reduces crystallinity and crystal size of zeolite NaA significantly, while increasing H_2O/Al_2O_3 ratio has no significant effect. However, as observed in Table 5, increasing both the ratios simultaneously reduces crystallinity and crystal size of zeolite NaA significantly. Thus, it can be concluded that the effect of SiO_2/Al_2O_3 ratio is more important than that of H_2O/Al_2O_3, and crystallization of zeolite NaA cannot be performed when there is a high-silica content and alkalinity is weak ($Na_2O/Al_2O_3 = 3.16$).

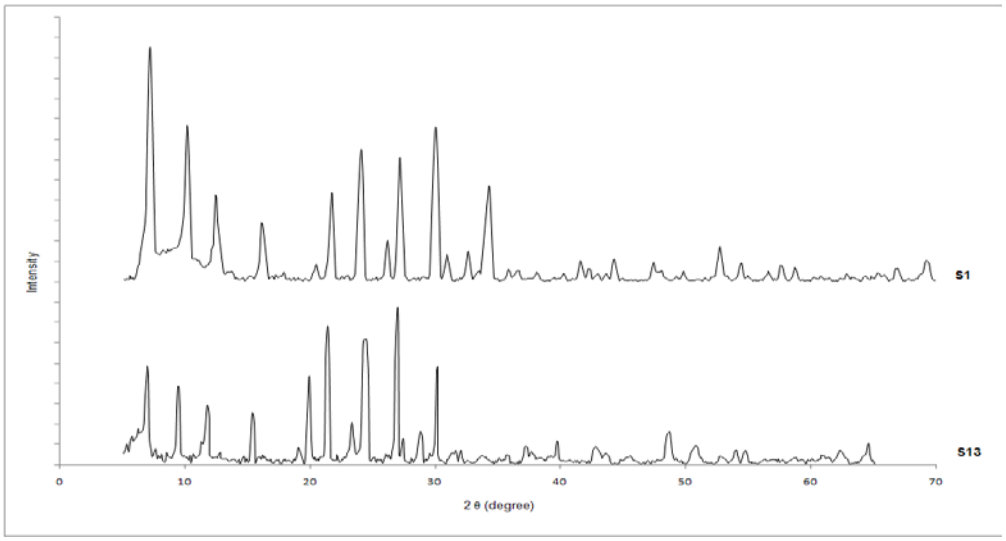

Figure 12. XRD patterns of S1 and S13 samples.

3.2.3. Interactions of Na_2O/Al_2O_3 and H_2O/Al_2O_3 ratios (alkalinity: Na_2O/H_2O)

In order to investigate the effect of alkalinity or interactions between Na_2O/Al_2O_3 and H_2O/Al_2O_3 ratios, the results of S1 and S6 samples were considered. Figure 13 indicates XRD patterns of these samples. In samples S1 and S6, the amounts of alkalinity (Na_2O/H_2O) were 0.024 and 0.050, respectively.

As observed in Table 5, increasing both the ratios simultaneously or, in other words, increasing alkalinity reduces crystallinity and crystal size of zeolite NaA significantly. Thus, it can be concluded that crystallization of zeolite NaA in a mixture with strong alkalinity (0.05) is not performed, while, at weak alkalinity (0.024), crystallinity and crystal size of zeolite NaA increase significantly.

As mentioned, increasing alkalinity increases the solubility of Si and Al sources, shortens the induction and nucleation times, and speeds up crystallization of zeolites.

Alkalinity has also an effect on particle size of zeolites. Increasing alkalinity results in the reduction of particle size and narrowing of particle size distribution [17].

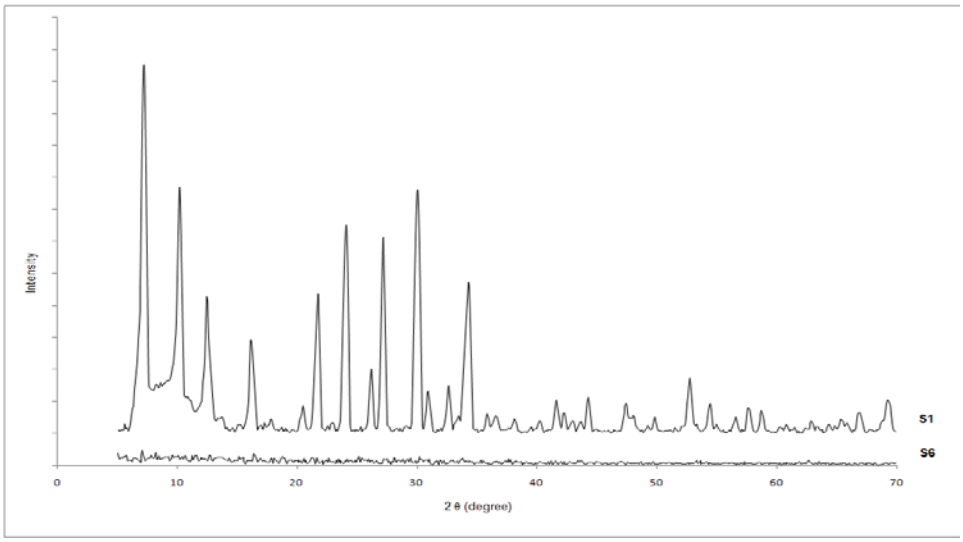

Figure 13. XRD patterns of S1 and S6 samples.

3.2.4. Interactions of synthesis temperature and time

In order to investigate the interactions between synthesis temperature and time on crystallinity and crystal size of zeolite NaA, the results of these samples were considered. Figure 14 indicates XRD patterns of S10 and S8 samples. In sample S10, the values of synthesis temperature and time were 80 °C and 3 h, respectively. Their values in sample S8 were 100 °C for 5 h.

As mentioned, increasing the synthesis temperature from 80 to 100 °C significantly increases crystallinity of zeolite NaA, while increasing the synthesis time from 3 to 5 h decreases crystallinity. However, as observed in Table 5, increasing both temperature and time simultaneously has no significant effect. In other words, increasing the two parameters simultaneously neutralizes the individual effects of each other. Thus, it can be concluded that increasing the synthesis temperature increases the nucleation rate and, thus, crystal size of zeolite NaA. On the other hand, increasing synthesis time causes synthesized crystals to be dissolved in alkaline solution, leading to an a decrease in crystallinity and crystal size. Thus, these two effects are neutrlize each other; therefore, the crystallinity of zeolite NaA does not considerably change.

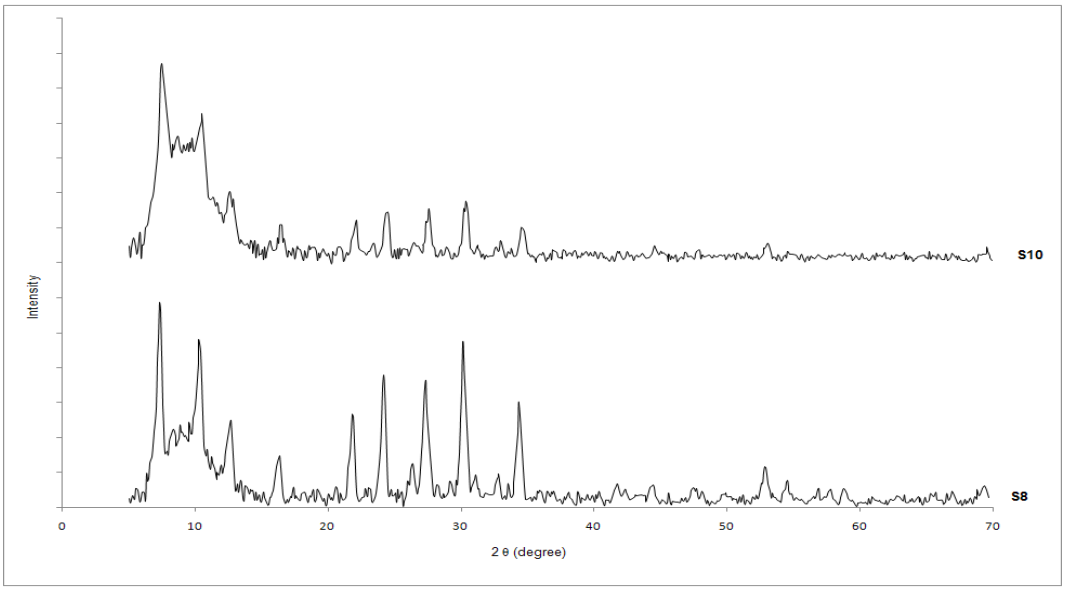

Figure 14. XRD patterns of S10 and S8 samples.

3.2.5. Interactions of SiO_2/Al_2O_3, Na_2O/Al_2O_3 and H_2O/Al_2O_3 ratios

As explained, Na_2O/Al_2O_3 and H_2O/Al_2O_3 ratios are equivalent to alkalinity (Na_2O/H_2O ratio). Thus, interactions of SiO_2/Al_2O_3, Na_2O/Al_2O_3, and H_2O/Al_2O_3 ratios can be summarized as interactions between (Si+Na)/Al ratio and alkalinity.

In order to investigate the interactions between (Si + Na)/Al ratio and alkalinity, the results of two couple samples were considered: (S11, S15) and (S1, S12). In samples S1 and S11, the values of SiO_2/Al_2O_3, Na_2O/Al_2O_3, and H_2O/Al_2O_3 ratios were 1.92, 3.16, and 128, respectively (i.e., (Si+Na)/Al ratio = 7 and alkalinity = 40.5). Their values in samples S12 and S15 were 5.0, 50.0, and 1000 (i.e., (Si+Na)/Al ratio = 60 and alkalinity = 20). Figure 15 indicates XRD patterns of these samples.

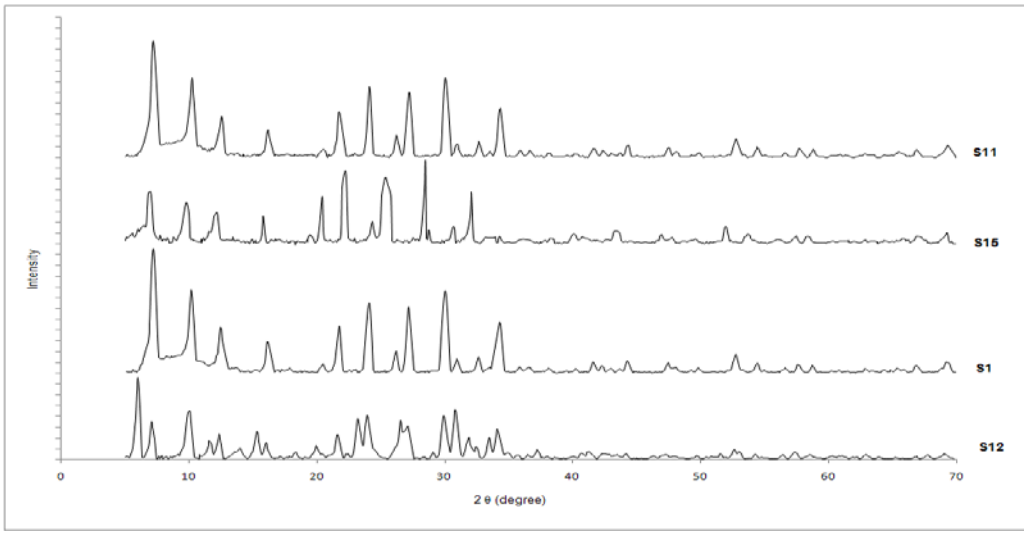

Figure 15. XRD patterns of S11, S15, S1 and S12 samples.

As mentioned, increasing both SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios simultaneously neutralizes effects of each other; thus, crystallinity and crystal size of zeolite NaA do not any change significantly. On the other hand, decreasing alkalinity reduces crystallinity and crystal size of zeolite NaA significantly. However, as observed in Table 5, increasing these three ratios simultaneously reduces crystallinity and crystal size of zeolite NaA significantly. For the both couple samples, the same reduction in crystallinity is observed (S1→S12: 100→49.0, S11→S15: 96.6→39.0).

As observed, a reduction in crystallinity and crystal size is smaller than that observed when decreasing alkalinity. It may be due to the fact that, in this case, the Na/Si ratio is increased. In other words, increasing Na^+ content in the synthesis gel moderates the effects of alkalinity decreasing. In general, a cation is added as a base in the form of MOH, resulting in concentration of hydroxide ions being controlled simultaneously by concentration of the cation. Hydroxide ions affect dissolution and polymerization–depolymerization reactions of silicates and aluminosilicates [11,18]. Thus, it can be concluded that despite the decreasing alkalinity, the increase of Na^+ content and, consequently, OH^- content increases the dissolution of aluminosilicates and, thus, increases crystallinity and crystal size. Therefore, crystallinity and crystal size reduction in this situation is smaller than that observed when decreasing alkalinity.

4. Conclusions

Zeolite NaA crystals were synthesized by the hydrothermal method. Effects of gel composition and synthesis parameters on zeolite NaA crystal formation were investigated. The XRD results indicated that the zeolite crystals synthesized with a composition ratio of $1.92SiO_2$: Al_2O_3: $3.16Na_2O$: $128H_2O$ at 100 °C for 3 h had the highest degree of crystallinity and the smallest crystal size. In order to investigate the effects of synthesis parameters on crystallinity of zeolite NaA, five parameters of SiO_2/Al_2O_3, Na_2O/Al_2O_3, and H_2O/Al_2O_3 ratios and synthesis temperature and time were considered. The results indicated that increasing four parameters of SiO_2/Al_2O_3, Na_2O/Al_2O_3, and H_2O/Al_2O_3 ratios and synthesis time reduces the crystallinity and

crystal size of zeolite NaA, while increasing the synthesis temperature enhances crystallinity and crystal size. Considering the interactions between these parameters showed that effects of increasing SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios simultaneously neutralize each other so that they have overally no significant effect. On the other hand, effects of increasing SiO_2/Al_2O_3 and H_2O/Al_2O_3 ratios reinforce each other and, as a result, significantly affect crystallinity and crystal size. It was found that alkalinity was an important parameter in zeolite NaA synthesis. Increasing alkalinity increases crystallization rate and, thus, reduces synthesis time. As a result, in a mixture with strong alkalinity, synthesis time should be shortened. Otherwise, the synthesized crystals are dissolved again in the alkali mixture. This phenomenon was observed in the experiments performed for longer synthesis time. Thus, effects of increasing crystallization temperature and time simultaneously neutralized each other.

On the other hand, in samples with high Na/Si ratio, even at weak alkalinity, crystallinity and crystal size increased. In other words, increasing Na^+ content in the synthesis gel moderated effects of decreasing alkalinity.

As a final conclusion, it can be said that five considered parameters have different effects with different significance levels on zeolite NaA synthesis. Their significances can be arranged as follows:

- $SiO_2/Al_2O_3 \approx$ Alkalinity $> H_2O/Al_2O_3$
- Synthesis temperature > Synthesis time

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