Proceedings of the World Congress on Recent Advances in Nanotechnology (RAN'16)
Prague, Czech Republic – April 1 – 2, 2016
Paper No. ICNNFC 113
DOI: 10.11159/icnnfc16.113

Effects of Synthesis Parameters on the Characteristics of Naa Type Zeolite Nanoparticles

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Abstract - Hydrothermal synthesis of zeolite-NaA nanocrystals 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 and crystallization temperature and time were studied on crystallinity and crystal size of zeolite-NaA crystals. It was tried to understand the interactions between these parameters. The nanocrystal species of zeolite-NaA were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

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 their overall effect is not significant. On the other hand, the effects of increasing SiO_2/Al_2O_3 and H_2O/Al_2O_3 ratios reinforce each other and significantly affect crystallinity and crystal size. Increasing alkalinity increases crystallization rate and reduces synthesis time. Also, effects of increasing crystallization temperature and time simultaneously reinforce each other. The effect of decreasing alkalinity is moderated with that of increasing Na+ content in the synthesis gel.

Keywords: Crystallinity, Nanocrystal size, Crystallization conditions, Gel-composition, Zeolite-NaA.

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 for example 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 very attractive material as catalysts and adsorbents in several chemical processes [2]. Small and uniform nanopores of zeolite-NaA with pore-diameter of approximately 0.3 nm has 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 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 it 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 wide ranges of separation applications.

The objectives of present study were 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 nanocrystals. The materials used to form the aluminosilicate-gel were aluminum powder (Al 99.9% wt., Lobachem), sodium silicate (SiO_2: 27% + Na_2O: 8% wt., Merck), sodium hydroxide (NaOH, 98% wt., Merck) and deionized 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 it 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 and 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 zeolite-NaA 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 formation of zeolite-NaA nanocrystals were investigated, including relative amount of the source materials 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 (Table 1). Other synthesis conditions were kept constant in all the experiments; Stirring Time = 1h; Stirring Temperature = 60 °C and Drying Temperature = 100 °C.

Table 1: Synthesis parameters and the related levels for zeolite-A crystals.

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

The purpose of these investigations was to estimate the influences of the above five synthesis parameters on crystallinity and crystal size of the synthesized zeolite-NaA nanocrystals. According to literature [5-8], the common composition of synthesized zeolite-NaA nanocrystals 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. Thereupon, zeolite-NaA crystals were synthesized using nine different molar gel-compositions (Table 3).

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 A) 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:

$$D = 0.89\,\lambda / \beta \cos\theta \qquad [9] \qquad (1)$$

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 determined from quantitative X-ray analysis (XRD) (Treacy and Higgins, 2001) [10, 16].

Morphology of the synthesized crystals were 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)).

Table 2: Values of synthesis parameters and the related samples for zeolite-A crystals.

Sample	SiO_2/Al_2O_3	Na_2O/Al_2O_3	H_2O/ Al_2O_3	Synthesis Temp. (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: Synthesis molar gel-compositions for zeolite-A crystals.

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

3. Result and Discussion

The XRD patterns of zeolite-NaA crystals synthesized using compositions and conditions according to Table 2 indicated that the zeolite crystals are formed with many of the compositions and at different conditions but with different degrees of crystallinity. As mentioned, crystallinity of the zeolites was determined from quantitative X-ray analysis (XRD) and comparing the results with the reference patterns. 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 3a shows crystallinity of the synthesized zeolites as functions of the five selected parameters. Figure 3b shows crystal size of the synthesized zeolites as functions of the five selected parameters. Figure 4 shows SEM photographs of the crystals for samples S1, S7, S9 and S11. As observed, size of the cubic zeolite-NaA crystals is in relatively narrow range of 0.5 to 3 μm. With attention to Table 4 and Figure 4, it can be concluded that mean crystallite size of samples S1, S7, S9 and S11 obtained using Debye-Scherrer equation are equal to their related values obtained from SEM photographs.

Table 4: Results of crystallinities and crystal sizes calculated for synthesis samples 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

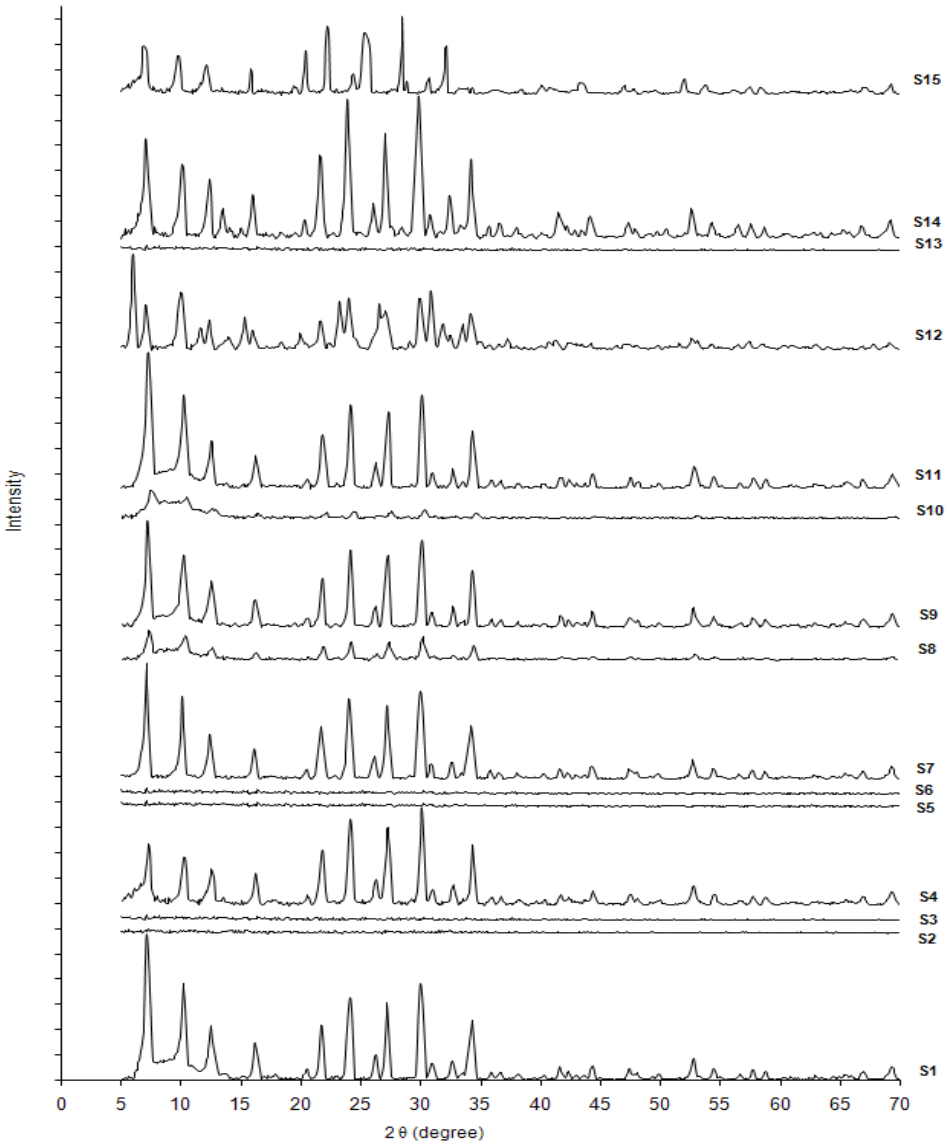

Fig. 1: XRD patterns of zeolite-NaA crystals synthesized according to Table 2.

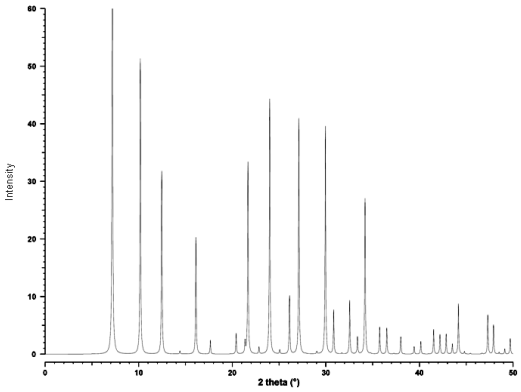

Fig. 2: Standard XRD pattern of zeolite-NaA.

3.1. Effects of synthesis parameters

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 5a indicates XRD patterns of these samples. Pure zeolite-NaA crystals with the highest crystallinity (100%) and mean crystal size of 19.89 nm were obtained (sample S1) (Figures 3a and 3b). The results show that slightly increasing SiO_2/Al_2O_3 ratio reduces crystallinity significantly. Thus, it can be concluded that at 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 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) and this is explained later.

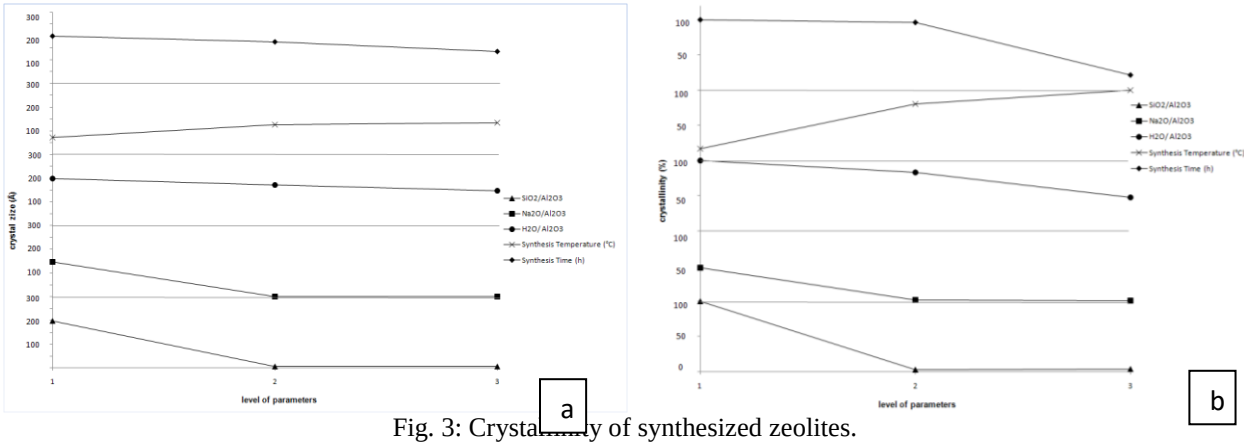

Fig. 3: Crystallinity of synthesized zeolites.

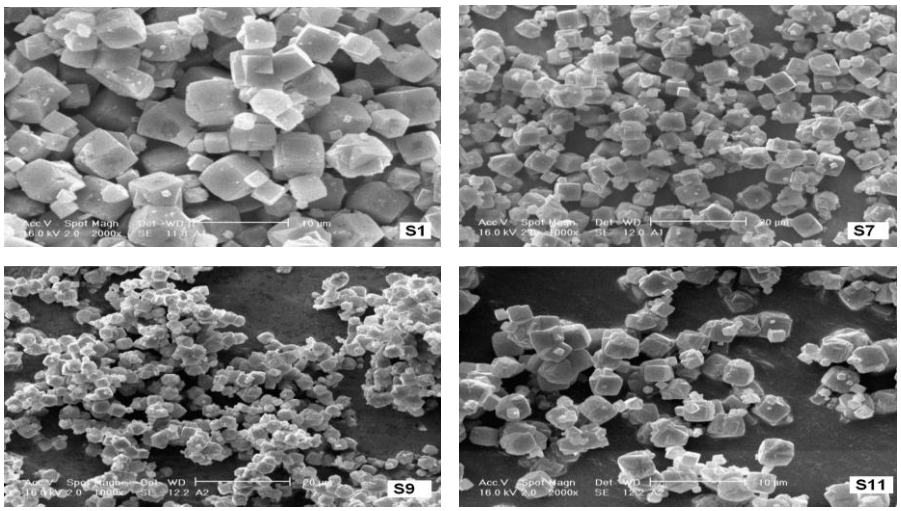

Fig. 4: SEM photographs of the crystals for samples S1, S7, S9 and S11.

Na_2O/Al_2O_3 ratio; Figure 5b indicates XRD patterns of S4, S5 and S6 samples. Among these samples, only sample S4 is zeolite-NaA with crystallinity of 47.4 % and crystal size of 14.65 nm (Figures 3a and b). The results show that increasing Na_2O/Al_2O_3 ratio terminates formation of zeolite-NaA crystals. Thus, it can be concluded that at 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 increase, 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.

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 dissolve again in the alkali mixture and crystallinity finally decreases. Thus, it can be concluded that for increasing crystallinity, at higher alkalinity, synthesis time should be shortened.

H_2O/Al_2O_3 ratio; The results showed that increasing H_2O content (H_2O/Al_2O_3 ratio) has the weakest effect on crystallinity and crystal size of zeolite-NaA. Figure 5c indicates XRD patterns of S1, S7 and S4 samples. Among these samples, increasing H_2O content in the synthesis gel or reduces concentration of reactants, decreased crystallinity and crystal size of zeolite-NaA (Figures 3a and 3b). It can be explained that, an overall dilution of the synthetic mixture causes less supersaturation, and as a result, crystal growth is favored at expense of nucleation, and consequently, large crystals can be obtained. Variation of H_2O content can also change crystallization region of zeolite phases [12].

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 [1]. 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 5d indicates XRD patterns of these samples. Increasing synthesis temperature from 80 to 100 °C, significantly increases crystallinity of zeolite-NaA (Figures 3a and 3b). A similar trend can be observed for crystal size that increases with increasing synthesis temperature. Thus, it can be concluded that at these conditions, larger zeolite-NaA crystals can be produced with higher crystallinity at higher crystallization temperature. According to literature [13], 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 higher temperature.

Synthesis time; Figure 6a indicates XRD patterns of S1, S8 and S11 samples. Among these samples, increasing synthesis time terminates formation of zeolite-NaA crystals (Figures 3a and 3b). Crystallinity and mean crystal size of zeolite-NaA decreases with increasing 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 [14]. Thus, this can be the reason for our observations in this research. In other words, increasing crystallization time causes dissolving of synthesized zeolites in the alkaline solution and as a result decreases crystallinity and crystal size. However, it must be mentioned that formation of zeolites cannot be rationalized on a thermodynamic basis alone and kinetics must be considered as well [15].

5. Conclusion

The Effects of gel-composition and synthesis parameters on formation of zeolite-NaA crystals in hydrothermal method were investigated. The characterization methods indicated that the zeolite crystals synthesized with composition ratios 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 lowest crystal size.

In the next step, the effects of five synthesis parameters of SiO_2/Al_2O_3, Na_2O/Al_2O_3, H_2O/Al_2O_3, synthesis temperature and synthesis time on crystallinity of zeolite-NaA were evaluated. The results indicated that increasing each parameters of SiO_2/Al_2O_3, Na_2O/Al_2O_3, H_2O/Al_2O_3 and synthesis time alone while the other parameters remained at constant levels, reduced the crystallinity and crystal size of zeolite-NaA. For synthesis temperature the opposite effect was observed which both the crystallinity and crystal size increased with increasing temperature.

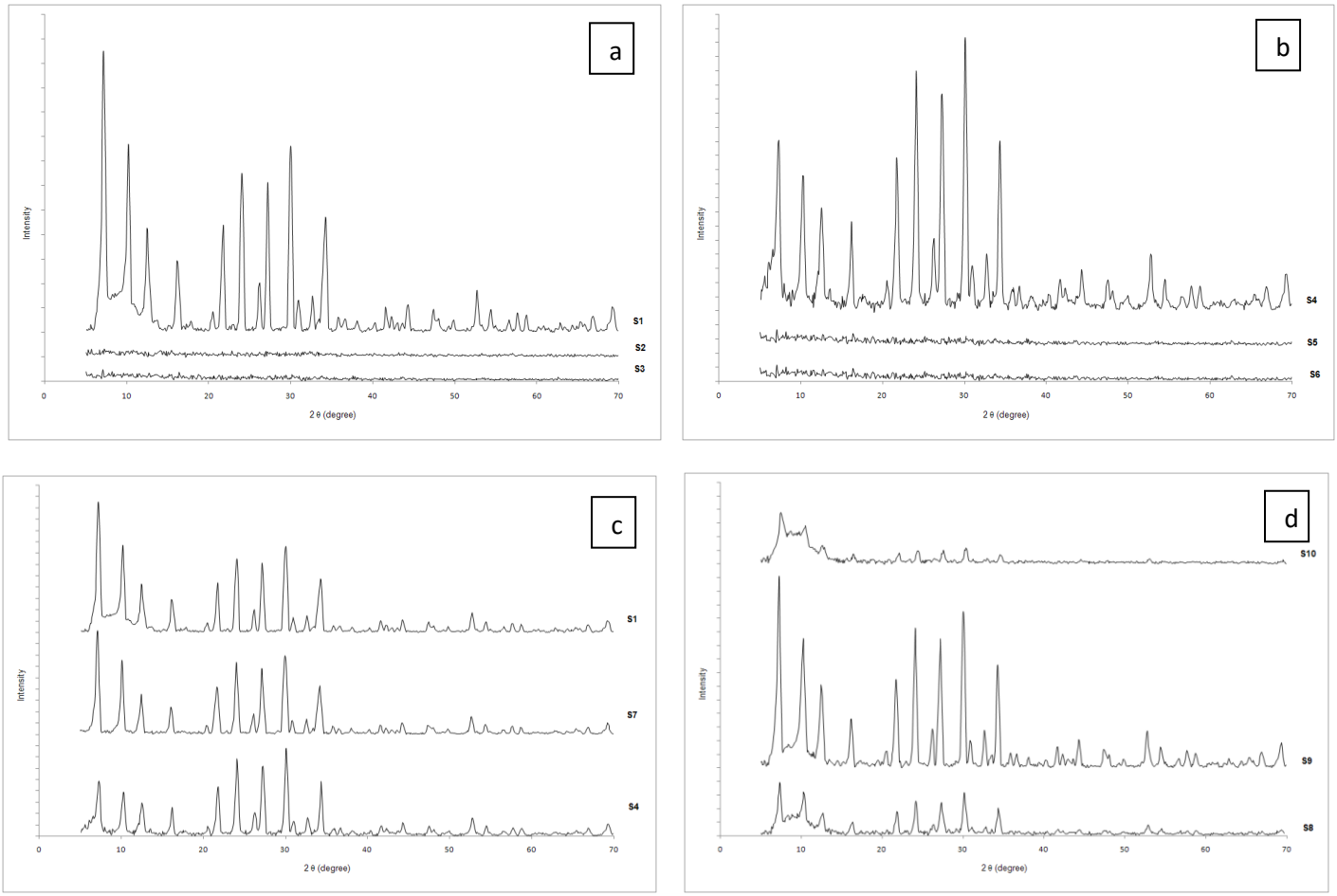

Fig. 5: XRD patterns of S1, S2 and S3 samples (a), XRD patterns of S4, S5 and S6 samples (b), XRD patterns of S1, S7 and S4 samples (c) and XRD patterns of S10, S9 and S8 samples (d).

The evaluation of interactions between these parameters indicated completely different results. For example increasing both SiO_2/Al_2O_3 and Na_2O/Al_2O_3 simultaneously neutralized the above explained effects for each one singly and approximately kept the crystallinity constant. In other words, the high silica zeolite-NaA could be synthesized only in case of increasing alkalinity of reaction mixture. In other case, the effects of increasing SiO_2/Al_2O_3 and H_2O/Al_2O_3 simultaneously reinforced above explained effects for each other and significantly affected crystallinity and crystal size. It was found that alkalinity is the most important parameter in zeolite-NaA synthesis so that increasing alkalinity accelerates the crystallization rate and as a result shortened the required synthesis time. In cases which the synthesis time remain at initial level, the synthesized crystal grains are dissolved again in the alkali mixture and reduce crystallinity again.

The investigation of effects of Na/Si ratio on zeolite-NaA synthesis indicated that in samples with high Na/Si ratio, both crystallinity and crystal size increased even at low alkalinity. It could be explained that increasing Na^+ cations content in the reaction mixture, compensate the effects of decreasing alkalinity and keep the crystallinity constant.

As a final conclusion, it can be said that the five considered synthesis parameters have different effects on zeolite-NaA synthesis. The signification of these parameters in order of influences on crystallinity and crystal size of zeolite-NaA 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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