Formation of pure NaX zeolite: Effect of ageing and hydrothermal synthesis parameters

Asma' Ahmadon[1], Liyana Salwa Mohd Nazir[1, 2], Yin Fong Yeong[2], Shamsina Sabdin[1]

[1]PETRONAS Research Sdn. Bhd., Lot 3288&3289, Off Jalan Ayer Itam, Kawasan Institusi Bangi, Kajang, 43000, Selangor, Malaysia
[2]Chemical Engineering Department, Faculty of Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610, Perak, Malaysia
liyana_salwa@petronas.com

Abstract. Among the challenges of synthesizing NaX zeolite is the formation of competing phases during the hydrothermal process which results with impurities in the product. The competing phases of NaX zeolite may include NaP zeolite, hydroxylsodalite and NaA zeolite. In this paper, relationships between the preparation parameters and hydrothermal synthesis parameters towards the formation of high purity of NaX zeolite are studied. The studied parameters include ageing duration, hydrothermal synthesis temperature and hydrothermal synthesis duration. Sodium silicate, sodium aluminate, sodium hydroxide and distilled water are used as the main reactant sources at a fixed molar ratio. The morphology, Si/Al ratio and zeolite phase of the resultant particles were characterized using field emission scanning electron microscope (FESEM), energy-dispersive x-ray spectroscopy (EDS) and X-ray diffraction analyser (XRD), respectively. Hydrothermal synthesis temperature of 90˚C and synthesis duration of 16 hours were identified as the optimum synthesis parameters for producing high crystalline, single phase NaX zeolite. In addition, the relationships between synthesis parameters and NaX zeolite produced were also studied. Longer ageing duration and longer hydrothermal synthesis duration results in high crystalline product with potential impurities phases, while higher hydrothermal synthesis temperature produced pure NaX zeolite at shorter hydrothermal synthesis duration.

1. Introduction

Zeolites have superior thermal and chemical stability and good shape-selectivity, which are suitable for various applications, particularly the oil and gas industry. Their polycrystalline structure with well-defined pores allows the permeation of selective gas molecules through molecular sieving and competitive adsorption. The size-exclusion mechanism happens when the zeolite pore size falls between the kinetic diameters of the desired gas molecule with those of the unintended species in the feed [1]. FAU framework zeolites, namely NaX (Si/Al ratio of 1 to 1.5) and NaY (Si/Al ratio larger than 1.5), are being studied for CO_2 and N_2 separation from natural gas. The pore size of these zeolites are 0.74 nm, allowing the permeation of certain molecules in natural gas. The selective permeation through the zeolite pore is determined by the surface diffusion and pore constriction [2].

In comparison with polymeric membranes for gas separation, inorganic membranes have the potential of CO_2 and N_2 removal from natural gas with better performance, such as CO_2/CH_4 selectivity of 200 and N_2/CH_4 selectivity of 10 [3]. The current available membranes reported in literature have yet to be developed for commercial application due to the difficulty in scaling up. Recently, inorganic

membranes with zeolite separation layer have shown significant separation and promising results. One of the challenges in fabrication of NaX zeolite membrane is the formation of impurities phases during hydrothermal synthesis. The growth of impurities, such as NaP zeolite, NaA zeolite and hydroxylsodalite, on the membrane surface hinders the permeation of desired gas through the membrane, thus, reducing the performance of the membrane [4]. This essential factor is among the reasons of the study to develop high purity NaX zeolite. Their nature as metastable materials causes the zeolites to transform into other more stable materials if left in their aluminosilicate gel solution. Interestingly, other factors can also impact zeolite crystallization even when the gel solution is stable, such as hydrothermal synthesis duration and temperature, types of raw materials used, the order of mixing these materials, stirrer method and aging technique [5,6].

In this study, the synthesis of high purity NaX zeolite via hydrothermal method is reported. The ageing duration and hydrothermal synthesis parameters and their effect towards the synthesis of NaX zeolite are investigated.

2. Experimental Section

2.1. Materials and Methods

For the NaX zeolite synthesis, the materials used were as follows: (1) sodium silicate (100% (w/w) Na_2SiO_3; Fisher Chemical, UK); (2) sodium aluminate (100% (w/w) $NaAlO_2$. Fisher Chemical, UK); (3) sodium hydroxide pellets (90-100% (w/w) NaOH; Avantor Performance Materials, USA) and (4) Deionized water. No further purification was performed and the raw materials were used as received. Sodium silicate and sodium aluminate were used as the silica source and alumina source, respectively.

The NaX zeolite synthesis batches were prepared by mixing the silica source solution into the alumina source solution and stirred at 600 rpm until a homogeneous mixture is formed. The gel mixture was stirred with varying durations (4 – 72 hours) at room temperature using a fixed stirrer speed in order to age the mixture. Then, the synthesis gel was filled into an autoclave and hydrothermal synthesis was carried out at temperatures of 80 to 100 °C and from 8 to 24 hours without stirring under autogenous pressure. Upon completion of hydrothermal synthesis, the gel was cooled at room temperature, filtered and washed until the filtrate was at pH 7. The crystals collected was then dried at 90 °C. Throughout the experiment, the final composition of the aluminosilicate gel mixture of NaX zeolite batches was maintained at Al_2O_3:SiO_2:Na_2O:H_2O = 1:4.8:17:975 in a molar composition, according to the method reported by Hasegawa et al [7].

2.2. Characterization

The zeolite powder samples were characterized by using powder X-ray diffraction (XRD; Shimadzu XRD-7000) with Cu-Kα radiation, operated at 40.0 kV and 30.0 mA in order to identify the X-ray diffraction patterns of the crystal structure. The zeolite morphology was observed using field emission scanning electron microscope (FESEM; Hitachi SU8020) while the elemental Si/Al ratios were determined using energy dispersive X-ray spectroscopy (EDS; Horiba EMAX).

3. Results and Discussion

3.1. Effects of Ageing Duration

Figure 1 shows the XRD patterns of NaX zeolite powder samples obtained using synthesis solution aged at room temperature for 24 and 72 hours, respectively. Both samples were synthesized at 80 °C for 24 hours. Referring to Figure 1, a mixture of low crystallinity and amorphous phase can be seen for the sample aged for 24 hours with all the weak peaks corresponding to NaX zeolite, as reported by Treacy and Higgins [8]. Further aging of the synthesis solution of up to 72 hours resulted in a highly crystalline phase, indicated by the sharp and intense XRD peaks and low background radiation line. However, the sample contained both zeolite phases of NaX and NaP.

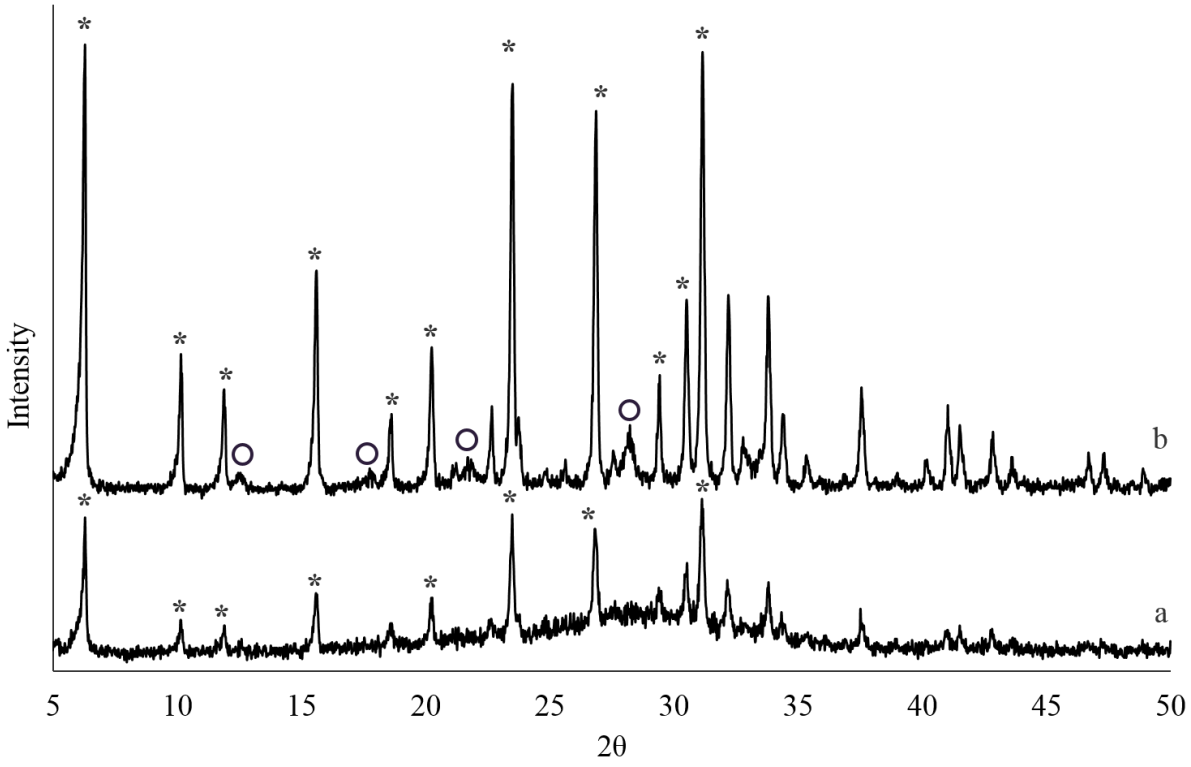

Figure 1. XRD patterns of zeolite samples synthesized from solution aged for: (a) 24 hours and (b) 72 hours. (o: NaP zeolite, *: NaX zeolite).

These results are consistent with previous studies reported by Oyinade et al, which suggest that ageing is a significant factor in the nucleation process of zeolite NaX [9]. The longer the ageing duration, the higher the crystallinity of the sample. The ageing process enables the control of crystal size, acceleration of crystallization and reduction of the formation of impurity phases [10–14]. It was observed that sufficient ageing leads to rapid crystallization of FAU zeolite and to attain this, a shorter hydrothermal synthesis duration is necessary to maintain the purity and avoid the formation of NaP zeolite [13]. During the ageing process, more siliceous species are formed which consequently merges with the aluminosilicate species to form FAU phase precursors. At longer ageing duration, the dissolution of the sodium silicate is accelerated and incorporated into the high Al-rich aluminosilicate gel to form a pure phase of NaX zeolite [15–17]. Ageing encourages the self-generation of structured elements (crystal proto-nuclei) in comparison to gels, which were prepared and immediately heated for hydrothermal synthesis without ageing [11].

The ageing process gradually releases the siliceous species to evolve and transform the secondary building units (SBUs) from zeolites with small membered rings to larger structures [13,14]. Bondareva reported that longer initiation time is needed for the formation of NaP zeolite due to its slow rate of nucleation as compared to NaX zeolite [18]. This explains the formation of NaP zeolite at 72 hours ageing duration.

The FESEM images of the samples are shown in Figure 2. Based on Figure 2, both samples demonstrate crystals in the shape of octahedral, resembling FAU zeolite framework. For the sample synthesized using synthesis solution aged at 24 hours (Figure 2(a)), both amorphous and crystalline phased were observed, where the NaX crystals were between 4.7 to 5.5 μm in size. On the other hand, referring to Figure 2(b), NaP zeolite crystals in the form of spherelutic particles and the NaX crystals with 3.0 – 4.5 μm in size [19] were obtained in the sample synthesized using synthesis solution aged at 72 hours. This finding explains that longer ageing duration produces smaller particle sizes and is in

agreement with the ideas of Ogura et al and Ginter et al [13,16]. The FESEM results are in consistent with the XRD results shown in Figure 1.

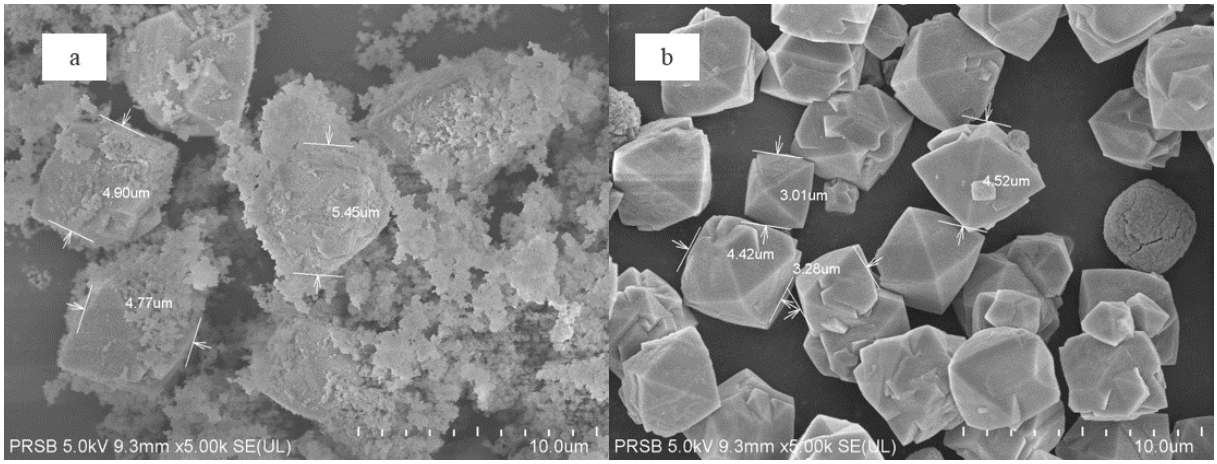

Figure 2. FESEM images of samples synthesized using synthesis solution aged for: (a) 24 hours and (b) 72 hours.

3.2. Effects of Hydrothermal Synthesis Parameters

In order to study the effect of hydrothermal synthesis temperature on the formation of NaX zeolite, the synthesis solution was aged for 4 hours and hydrothermal synthesis duration was fixed at 12 hours. Meanwhile, the hydrothermal synthesis temperatures used were varied from 80 to 100 °C. Referring to Figure 3(a-b), it can be observed that the samples synthesized at 80 and 90 °C for 12 hours exhibit NaX zeolite structure with low crystallinity and presence of amorphous phase. Due to the resulting amorphous phase, further investigation was done where zeolite samples were prepared at 90 °C and 100 °C with longer hydrothermal synthesis duration (24 hours). Figure 3(c) shows that the crystallinity of the sample improving significantly and the XRD peaks show high crystallinity and pure NaX zeolite for 90 °C. Elemental analysis for the sample synthesized at 90 °C for 24 hours was done using EDS. The Si/Al ratio was 1.45, which is within the range of NaX zeolite. Figure 3(d) shows that the samples obtained from hydrothermal synthesis conducted at 100 °C resulted in a mixture with NaX zeolite as the main phase and NaP zeolite as the minor phase.

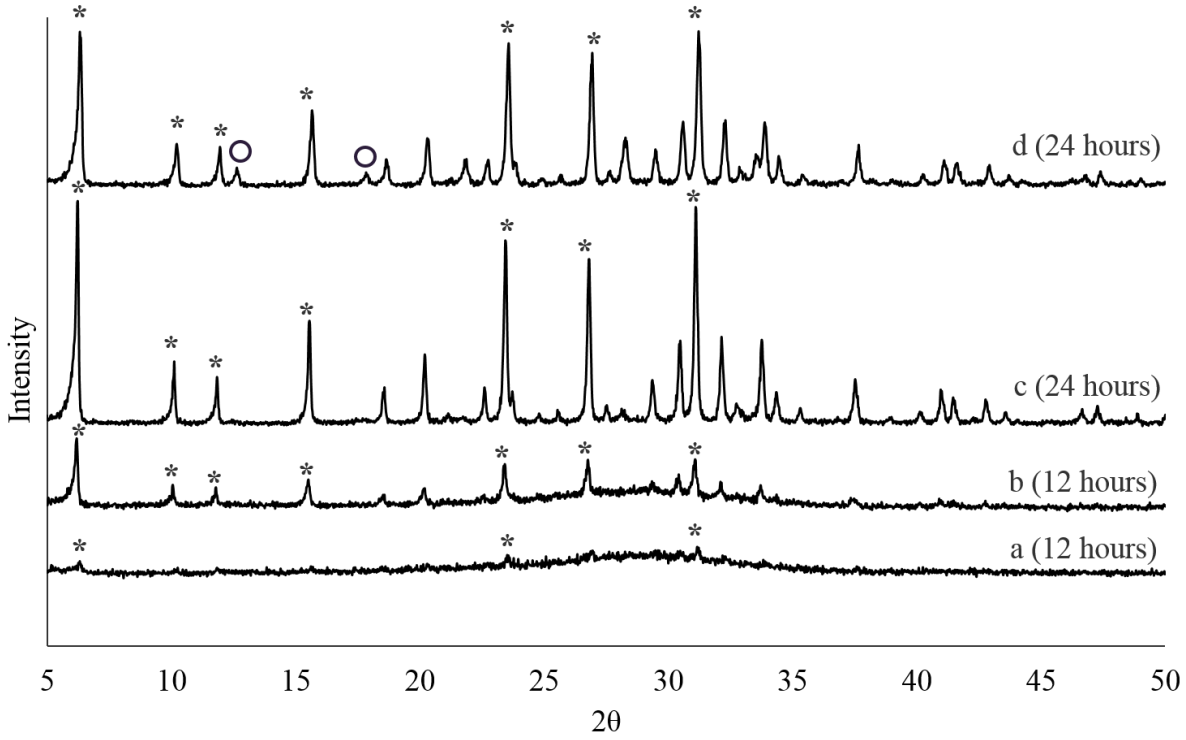

Figure 3. XRD patterns of samples synthesized at different hydrothermal synthesis temperatures of: (a) 80 °C, (b) 90 °C, (c) 90 °C and (d) 100 °C (o: NaP zeolite, *: NaX zeolite).

The effect of hydrothermal synthesis temperature on zeolite formation is observed in this study with the gradual increment in crystallization phase, which agrees with reported literature. The amorphous phase of a zeolite sample signifies that the shorter hydrothermal synthesis duration was insufficient to form full crystalline phases. At higher hydrothermal synthesis temperature, the crystallization rate of NaX zeolite increases and the structure tend to form dense zeolite structures, such as NaP zeolite [1,20]. The hydrothermal synthesis temperature majorly affects the nucleation process and crystallization process of zeolite formation. The energy contained from the high reaction temperature increases the nucleation and crystallization rate, thus shorter hydrothermal synthesis duration is required [21].

To study the effect of hydrothermal synthesis duration, samples were aged at room temperature for 4 hours and treated at 90 °C. The XRD patterns of samples synthesized at 8 to 24 hours are shown in Figure 4. From the patterns, it is apparent that the samples obtained below the synthesis duration of 14 hours demonstrate low crystallinity, which signifies that the hydrothermal synthesis duration to achieve NaX zeolite was insufficient. Hydrothermal synthesis duration of 8 hours produced an amorphous phase zeolite sample. Weak peaks relating to the NaX zeolite structure start to emerge at 12 hours of hydrothermal synthesis. At 14 hours of hydrothermal synthesis durations, the percentage crystallinity of the samples increased and sharp XRD peaks was achieved. Upon longer hydrothermal synthesis duration (20 to 24 hours), the gel crystallized into a mixture of zeolites: NaX and NaP as minor peaks of zeolite NaP are observed. These results are consistent with the results reported by Zhang et al [21].

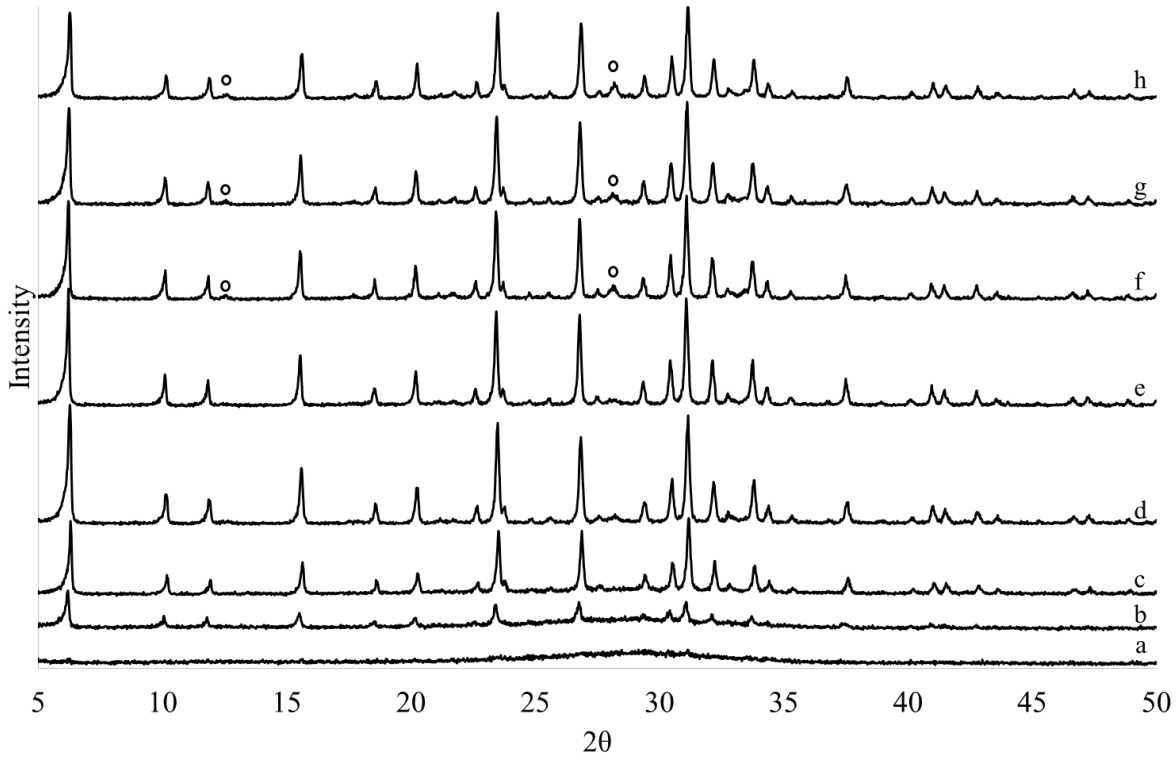

Figure 4. XRD patterns of samples synthesized at different hydrothermal synthesis duration (a) 8 hrs, (b) 12 hrs, (c) 14 hrs, (d) 15 hrs, (e) 16 hrs, (f) 20 hrs, (g) 22 hrs and (h) 24 hrs at synthesis temperature of 90 °C (o: NaP zeolite,)

In this study, the hydrothermal synthesis duration of 16 hours resulted in high purity NaX zeolite. From elemental analysis using EDS, the Si/Al ratio for the samples synthesized at 16 hour hydrothermal synthesis duration was 1.46, confirming the formation of NaX zeolite. Overall, these results indicate that exposing the zeolite samples at longer durations higher than 16 hours resulted in the formation of impurities (NaP zeolite).

The morphology of the zeolite samples synthesized at different durations were further analysed using field emission scanning electron method, and their FESEM images are shown in Figure 5. Referring to Figure 5(a), samples obtained at 14 hours demonstrates loosely packed crystals with the presence of amorphous phase. Formation of octahedral crystals of NaX zeolite was visible for the sample synthesized at 15 and 16 hours, as shown in Figure 5(b) and (c). Further synthesis duration beyond 16 hours ignited the growth of NaP zeolite, which resemble the shape of spherelutic particles (Figures 5(d), (e) and (f)). Beyond the hydrothermal synthesis duration of 16 hours, the zeolite morphology of the samples shows mixture of spherical aggregates and octahedral crystals [19].

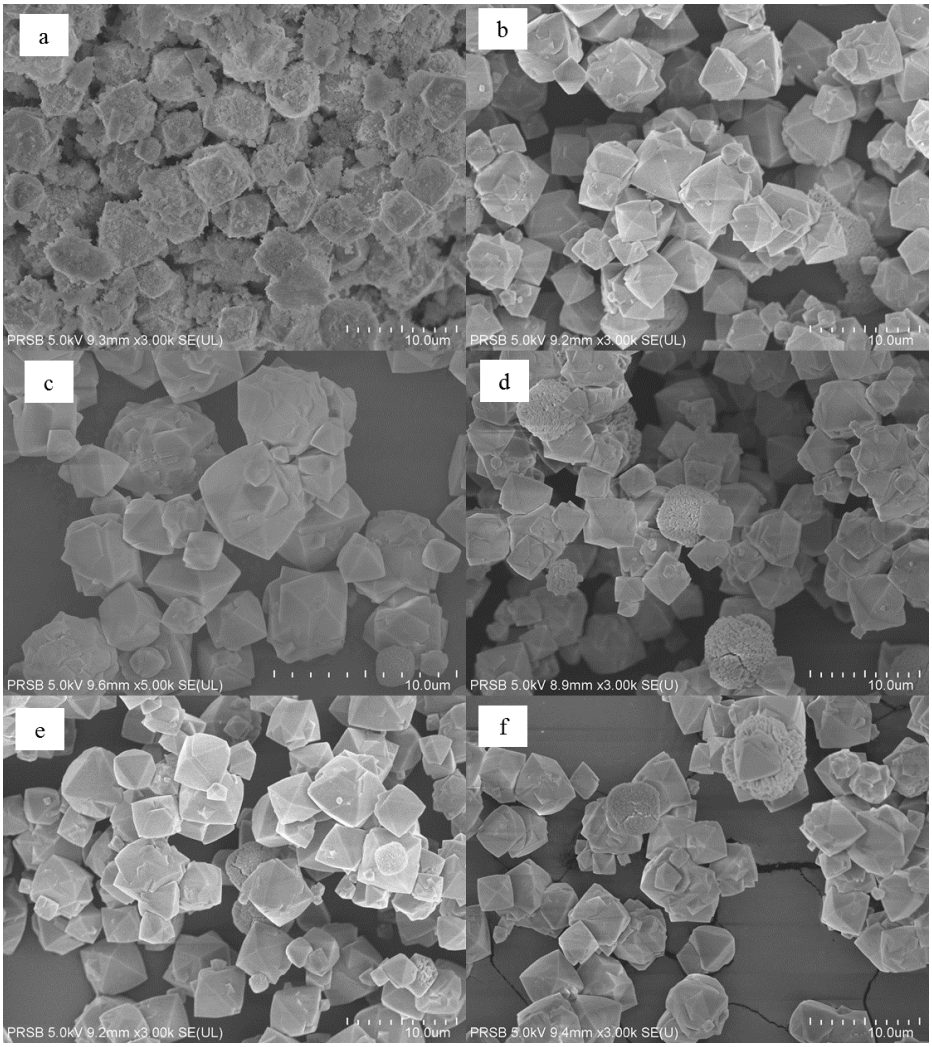

Figure 5. FESEM images of samples obtained at different hydrothermal synthesis durations of: (a) 14 hours, (b) 15 hours, (c) 16 hours, (d) 20 hours, (e) 22 hours and (f) 24 hours at synthesis temperature of 90 °C

4. Conclusions

In this work, pure NaX zeolite can be synthesized using sodium silicate and sodium aluminate by adjusting the ageing and hydrothermal synthesis parameters. Hydrothermal synthesis temperature of 90˚C and synthesis duration of 16 hours were identified as the optimum synthesis parameters for producing high crystalline, single phase NaX zeolite. Longer ageing duration and longer hydrothermal synthesis duration results in high crystalline product with potential impurities phases, while higher hydrothermal synthesis temperature produced pure NaX zeolite at shorter hydrothermal synthesis duration. Further work will be focusing on the growth of zeolite membrane for the separation of CO_2 and N_2 from natural gas using NaX zeolite seed prepared using the optimized parameters in this study.

Acknowledgements

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