CHAPTER IV

EFFECT OF SYNTHESIS PARAMETERS ON THE FORMATION OF UNIFORM AND SMALL NaA ZEOLITE CRYSTALS BY MICROWAVE TECHNIQUE

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4.1 Introduction

Zeolite are microporous crystalline materials, mostly used as catalyst, ion-exchanges and adsorbents. They are known as "Molecular sieve" due to their pore structure, excluding the entrance of larger molecule and allowing only the passage of smaller ones[1]. Zeolite NaA, LTA, is an aluminosilicate having a small pore size of 4 °A and containing aluminium in the framework, resulting in a requirement of charge balancing cation. Thus, the hydrophilic characteristic of LTA is nowadays applied for separation membrane. To obtain a reasonable flux, the zeolite membrane must be thin, and the size of zeolite crystals is a significant factor that affects the performance. Thin zeolite films applied for membrane separation can be prepared by using the synthesis condition allowing the formation of small and uniform crystals to obtain faster diffusion and high surfacearea[2]. The crystal size of zeolite is determined by two competing phenomena occuring during synthesis, nucleation and crystal growth. The higher the nucleation rate, the smaller the crystal obtained[3]. Several parameters involved in setting up the relative rates of nucleation and crystal growth, significant parameters, such as, using seeding technique, time, temperature, aging the reaction mixture, etc.,may effect of nucleation and crystal growth[4]. The focus of the work is therefore to study the effect of synthesis parameters on the formation of small and uniform crystals of NaA zeolite.

4.2 Experimental

In this work, NaA zeolte was prepared using seeding technique. Two different methods were used to synthesize the seed. The first method is a direct reaction of

fumed silica and aluminum hydroxide. The second one called indirect method was developed by Wongkasemjit's *et al.*[5], using silatrane to react with alumatrane, synthesized via the OOPS (One Pot Oxide Synthesis) process, via sol-gel process and microwave technique. Both methods used the formula composition SiO_2:Al_2O_3:Na_2O :H_2O =1:1:3:z. These media were aged for 1 day. Effects of parameters, viz. water quality, microwave heating temperature and time, amount of seed crytstal, as well as different sources of seed crystal from the direct method compared with the indirect method, on homogeneity and particle size of NaA zeolite were studied. The crystal structure and morphology of the obtained products were characterized by XRD and SEM.

4.3 Results and Discussion

4.3.1 Effect of Water Quantity

According to the previous study[5] without seeding technique, the stoichiometry of SiO_2:Al_2O_3:Na_2O:H_2O = 1:1:3:410, using silatrane and alumatrane as precursor, gives uniform particle size of NaA zeolite. To study the NaA formation from direct method, the amount of water, z, were fix at 200, 300, 410 and 110°C microwave heating temperature for 3 h. As can be seen in Figure 4.1, without adding crystal seed the SEM results show that the higher water quality, implying the lower alkali concentration, lead to the the bigger and more irregular size. This is probably due to the higher pressure of the hydrothermal system when increasing the amount of water, resulting in the faster accelerated reaction of crystallization process, which leads to less time to reach the thermodynamically favored lattice position resulting in irregular particle size and shapes[5]. At the water amount 410, 110°C microwave heating for 3 h, it was found that mostly amorphous material with a small amount of NaA crystal was generated.

4.3.2 Effect of Seed Crystal

Although the indirect method can generate uniform NaA crystals, the smallest size obtained was 1 μm[5]. Our attempt is to synthesized crystals of NaA at

nano-scale size by using seeding technique. Amount and source of crystal seed are investigated.

4.3.2.1 Amount of Seed Crystals

Ya *et al.* studied the effect of seeding crystals on the NaA zeolite formation and found that the seed crystals reduced the induction time and increased the rate of crystallization[6]. Additionally, the higher amount of seed crystal, the faster is the rate of crystallization due to the accumulative seed crystal surface area needed to assimilate materials from solution. In this work, NaA cystals obtained from the indirect method are used as the seed for NaA zeolite preparation using both the direct and indirect methods.

As the direct method, amount of seed crystals was varied from 1-3 wt% using the SiO_2:Al_2O_3:$3Na_2O$:$410H_2O$ ratio at microwave heating temperature 80°C for 6 h. The results from SEM study shown that the smaller crystal size were obtained with higher seed amount. 4 wt% zeolite crystal seed gives NaA having particle size in range of 400-500 nm. With the indirect method, using the same type of crystal seed, only 1-2 wt% crystal seed could produce crystals as small as 400-500 nm.

4.3.2.2 Different Sources of Crystal Seed

Preparation of NaA zeolite by the direct method was carried out using different sources of crystal seeds preparation from direct and indirect methods. The results indicate the different crystal characteristics. NaA zeolite, using the crystal seed prepared from the direct method, has non-uniform crystal sizes, while the one obtained using the crystal seed from indirect method shows small and uniform crystal size, as clearly seen in Figure 4.3 and 4.4.

4.3.3 Effect of Microwave Reaction Temperature

Temperature strongly influences on the formation of NaA zeolite. The optimal temperature range depends on the Si/Al ratio[5]. From the SEM results, the composition SiO_2:Al_2O_3:$3Na_2O$:$410H_2O$ at 90°C for 5 h mostly give amorphous

material. However, when the temperature is increased to 100°C for 5 h, zeolite with uniform and small crystal size is observed.

4.3.4 Effect of Microwave Heating Time

Many studies in zeolite synthesis reported crystal formation as function of time[8,9]. At constant temperature and mixture composition, the transformation proceeds from amorphous to metastable to more metastable phases. Time, as a parameter, can be optimized in the synthesis process. In the system that produces one zeolite phase, optimizing maximum crystallization over short period of time is important.[7] Thus a rise in temperature can be applied to minimize the crystallization time, as shown in Fig. 4.6. It can be seen that using the direct method to prepare NaA zeolite and with crystal seeds obtained by indirect method, the time to form NaA zeolite decreases by increasing the temperature. However the higher reaction temperature results in the bigger crystal size.

4.4 Conclusions

NaA zeolite can be successfully synthesized by microwave technique. The composition of SiO_2:Al_2O_3:3Na_2O: 410H_2O with 3-4 wt% of seed crystals obtained using the indirect method at the temperature ranging from 60 to 100°C provides uni form and narrow size distribution (0.1-0.2 μm) of NaA zeolite crystals. Although the direct method is a simpler route, the obtaining NaA zeolite is bigger and irregular size and shape. Thus, NaA zeolite by the direct method is not suitable to be used as crystal seed for the preparation of small and uniform NaA zeolite. However, the direct method can be used for the NaA zeolite preparation only if crystal seeds used have been synthesized from the indirect method.

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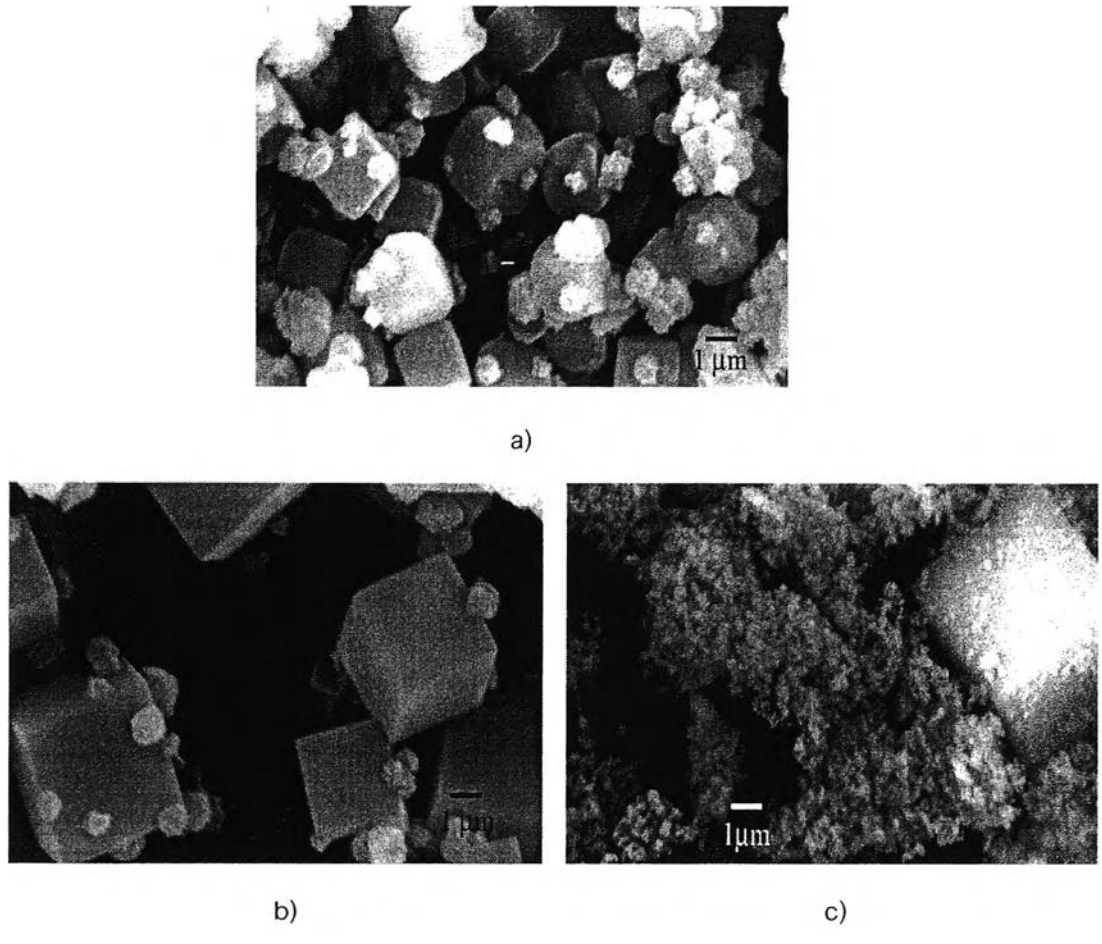


Figure 4.1 SEM micrographs of NaA zeolite synthesized from the direct method at 110°C for 3 h with water amount, z, of a) 200, b) 300, and c) 410.

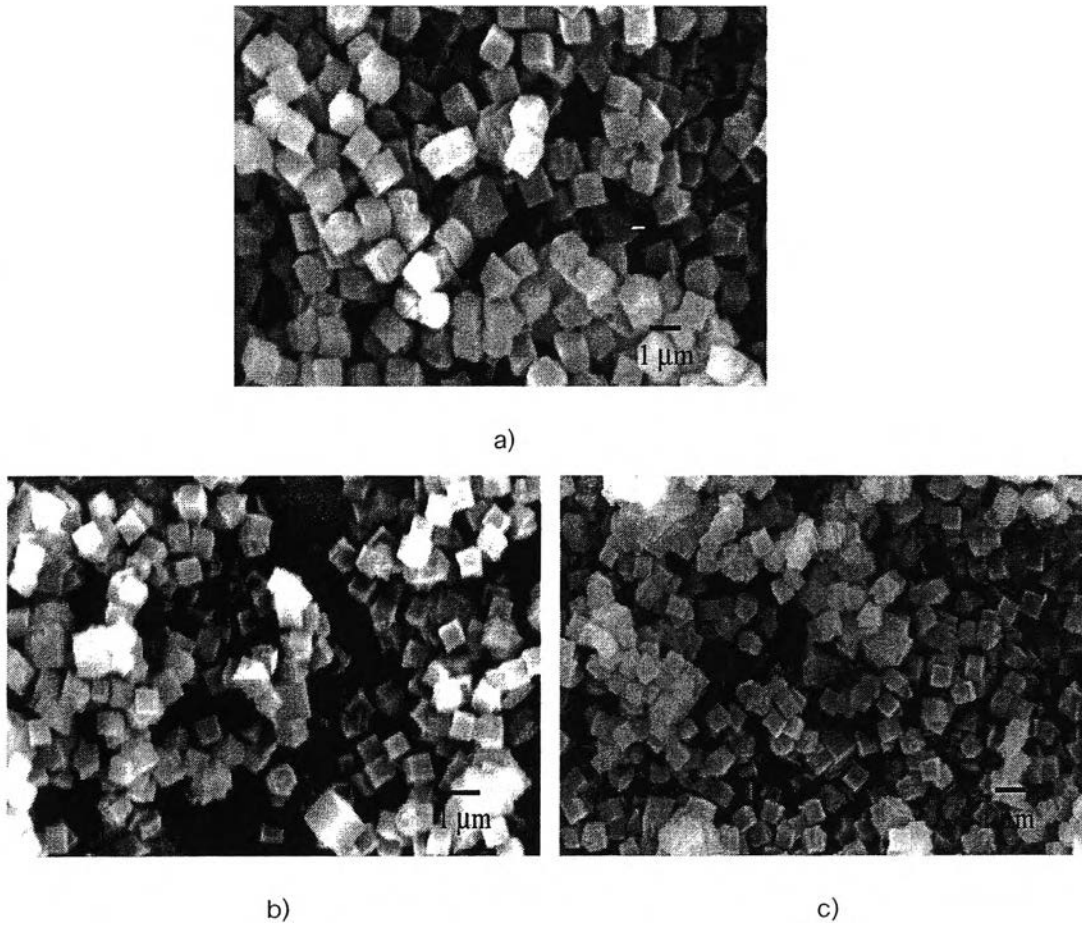
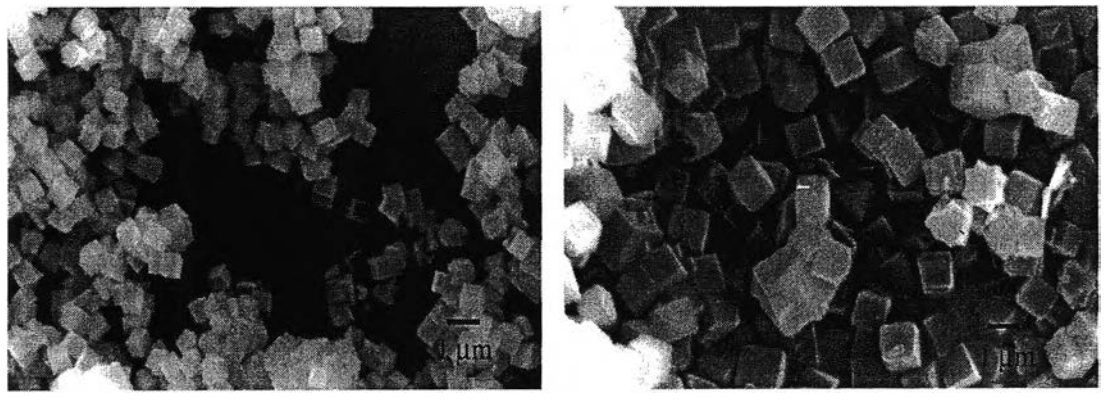


Figure 4.2 SEM micrographs of NaA zeolite synthesized from the direct method with SiO_2:Al_2O_3:$3Na_2O$:$410H_2O$ at 110°C for 2 h with seed amount a) 2, b) 3 and c) 4 wt%.



a) b)

Figure 4.3 SEM micrographs of NaA zeolite synthesized from different of seed sources from a) indirect b) direct methods with SiO_2:Al_2O_3:3Na_2O:410H_2O at 110°C for 2 h 20 min.

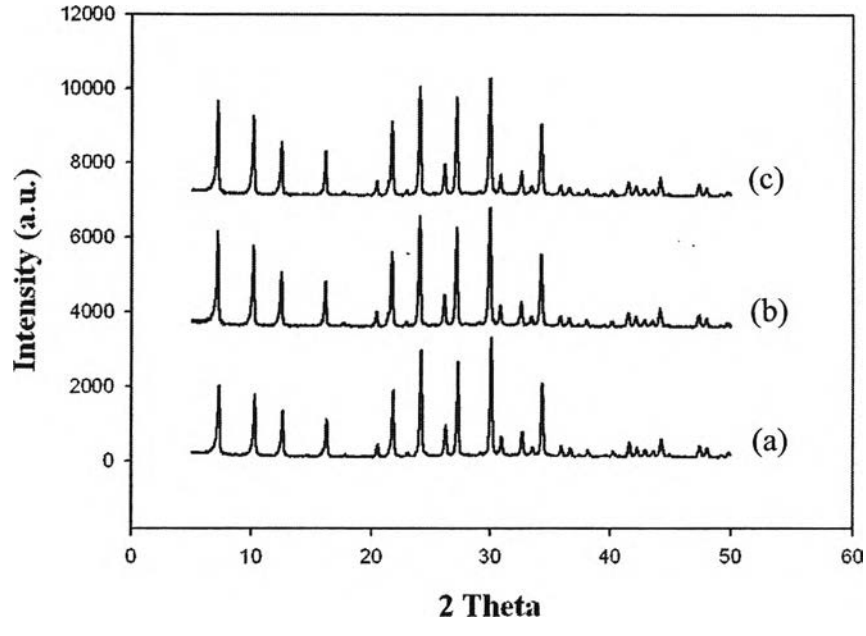
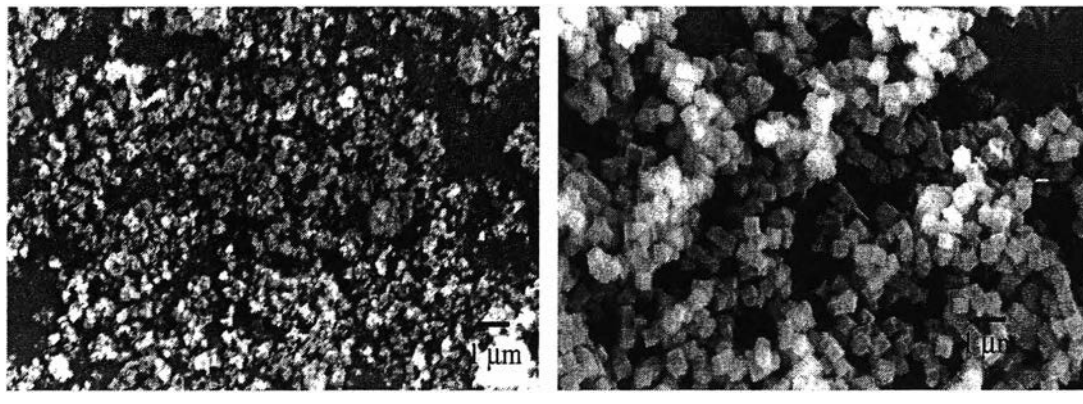


Figure 4.4 XRD spectra of NaA zeolite synthesized from different sources; (a) direct and (b) indirect methods, as compared with (c) the commercial LTA.



a) b)

Figure 4.5 SEM micrographs of NaA zeolite synthesized using 2 wt% crystal seed at microwave heating temperature of a) 90 and b) 100°C for 5 h.

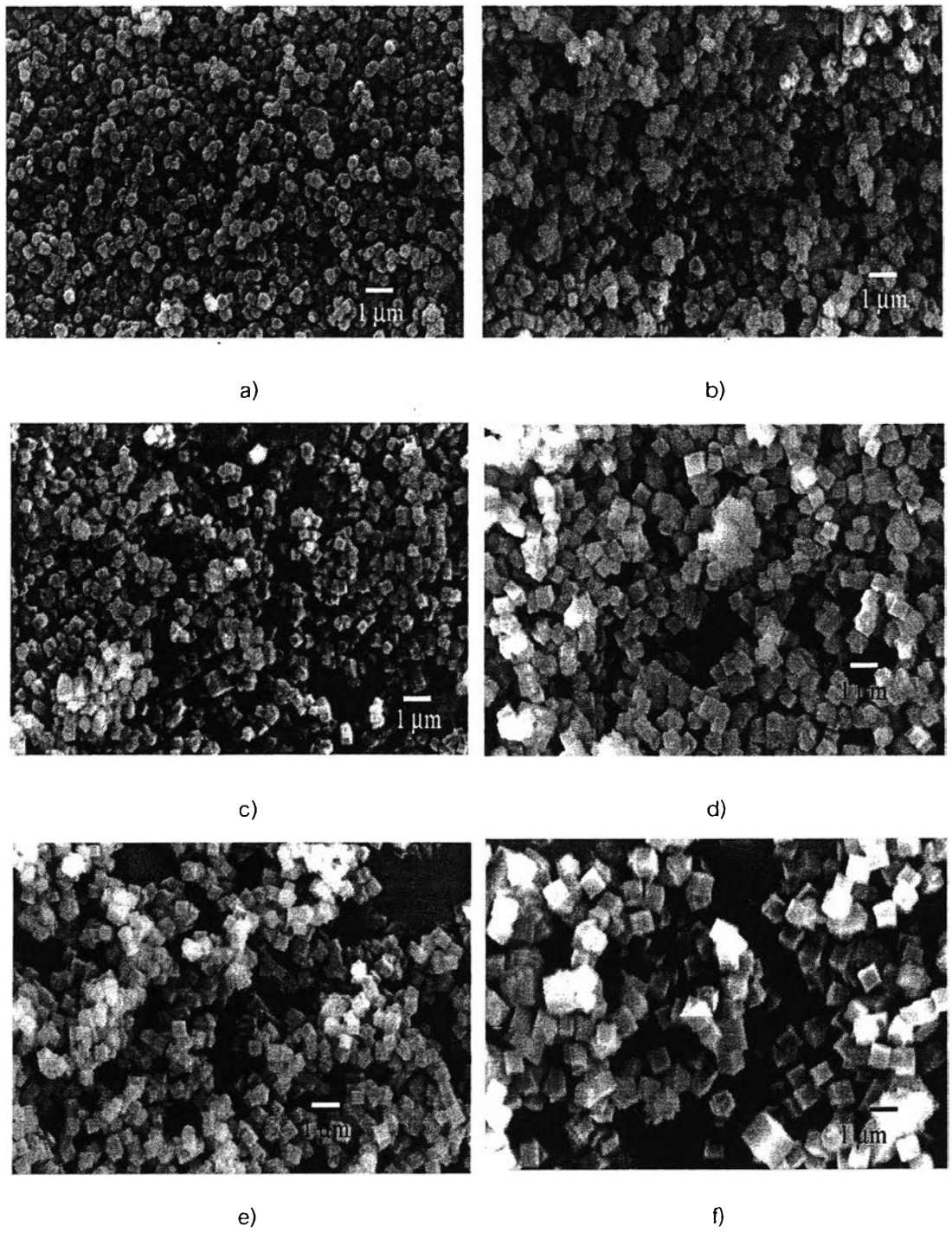


Figure 4.6 SEM micrographs of NaA zeolite using 3 wt% crystal seed at the microwave heating temperature and time of a) 60°C for 10 h, b) 70°C for 7 h, c) 80 °C for 6 h, d) 90°C for 5 h, e) 100°C for 4 h and f) 110°C for 2 h.