CHAPTER III

PREPARATION OF UNIFORM AND NANO-SIZED NaA ZEOLITE USING SILATRANE AND ALUMATRANE PRECURSORS

3.1 Abstract

Nano-sized NaA zeolite was successfully synthesized via sol-gel process and microwave technique. The synthesis parameters, such as, hydroxide ion concentration, seed amount as well as heating time and temperature, were studied to obtain the most uniform and very small size NaA zeolite using the composition of $SiO_2:Al_2O_3:xNa_2O:410H_2O$, $3 \leq x \leq 6$. It was found that hydroxide ion concentration affects the crystal size and heating time, whereas higher amount of seed provides smaller size of NaA zeolite. The zeolite product can be synthesized using a higher temperature for a shorter time or lower temperature for longer time. The best conditions for synthesizing the smallest size, 0.1-0.2 μm, and the most homogeneous NaA zeolite is to use the composition of $SiO_2:Al_2O_3:3Na_2O:410H_2O$ and 3 wt% crystal seed at 80°C microwave heating for 6 h. As synthesized NaA zeolite was characterized using XRD and SEM.

3.2 Introduction

Zeolite A, an aluminosilicate having a small pore size of 4 °A and containing aluminium in the framework, results in a required balancing cations. The common form generally used as a membrane is the sodium form, so called NaA. NaA zeolite has also been employed in gas separation membranes to enhance the selectivity of support[1]. In addition, NaA zeolite are used in many applications such as household products, aquaculture, agriculture, water treatment, etc., due to their adsorption, ion exchange and size selectivity properties[2]. Commercial NaA zeolite is synthesized by both conventional and microwave heating techniques. The microwave technique is used in NaA zeolite synthesis due to its homogeneous heating, resulting in tiny hot spots throughout the synthesis mixture, which reduce synthesis time[3].

The hydrothermal synthesis of aluminosilicate zeolite corresponds to the conversion of a mixture of silicon and aluminum compounds, alkali metal cation, organic molecules and water via alkaline supersaturated solution into a microporous crystalline aluminosilicate[4]. The variables, such as the composition of reaction mixture, temperature and time, have a major influence on zeolite structure crystallized. When the reactants are mixed, these solid phase are dissolve, mediated by the mineralizing agent or alkali. The solution is filled with silicate and aluminate monomer and oligomer which are organized into more extended structure and finally into a crystalline phase. The crystallization process is thermally activated and allows a high yield of crystals to be achieved in an acceptable period of time. The crystallization period can be subdivide into two steps: nucleation of the new population of zeolite crystals and growth of the existing population of crystals.

Seeding is a technique in which the supersaturated system is inoculated with small particles of material to be crystallized. Using this operation, the nucleation stage is by-passed and the induction period is eliminated[4]. Seed crystals are added to a synthesis mixture which may act as pure seeds in that mass is deposited upon them and they grow or give rise to secondary nuclei and hence a new crop of crystals. In the absence of seed crystals, the reaction gives either very low yield or products heavily contaminated with impurity phases[5].

Recently, Wongkasemjit *et al.*[6-8] have developed method to produce uniform zeolites using synthesis silatrane and alumatrane as precursors via sol-gel process and microwave techniques. To produce a strong and efficient film for zeolite membrane application,.the characteristics of being uniformity is crucial. Thus, this work is focus on the producing of NaA zeolite from those atrane precursors cooperating with the seeding technique to reduce crystal size. We also investigate the effect of hydroxide concentration, microwave temperature and time as well as seed wt% on small size and uniform NaA zeolite synthesis.

3.3 Experimentals

3.3.1 Materials

Fumed silicon dioxide (SiO_2), aluminum hydroxide hydrate [$Al(OH)_3$ xH_2O], and triisopropanolamine [TIS, $N(CH_2CH_3CH_2(OH)_3$] purchased from Sigma Aldrich Chemical and Carlo Erba, respectively, were used as reactant. Ethylene glycol (EG,$OHCH_2CH_2OH$) purchased from J.T. Baker Inc. was used as reaction solvent. Sodium hydroxide (NaOH) supplied from EKA chemical was used as base catalyst. Nitrogen gas with 99.99% purity was purchased from Thai Industrial Gases public company (TIG); and acetonitrile (CH_3CN) from Lab-Scan Co., Ltd. All chemicals were used as received.

3.3.2 Instruments

Fourier transform infrared (FTIR) spectra were obtained on Nicolet spectrometer with 16 scans, resolution of 4 cm^{-1} and a frequency range of 4000-400 cm^{-1}. The powder samples were pressed as pellets by mixing with pure and dry potassium bromide (KBr). Thermogravimetric Analysis (TGA) on a Perkin Elmer, TG-DTA, using a platinum pan with a sample weight of 10 μg, was carried out at temperature range from room temperature to 750°C with a heating rate of 10°C/min under nitrogen atmosphere with a nitrogen flow rate of 20 ml/min. Scanning Electron Micrographs (SEM) were obtained on a JEOL 5200-2AE (MP15152001) using a voltage of 15-20 KV at 1500 to 7500 magnification. Wide-Angle X-Ray diffractograms

(WXRD) on D/MAX 2000 series of Rigaku X-Ray diffractometer system were analyzed to identify the zeolite NaA pattern using Cu K_α as a source with 30 mA and 40 KV, a range of 5-50°/min and 0.02° scan step. Microwave thermal treatment was performed on MSP 1000, CEM Corporation Spec 1000 W and 2450 MHz. A sample was heated in a teflon vessel, organic digestion mode and time to temperature program. Surface areas of samples were determined by physisorption of nitrogen at liquid temperature (77 K) using Autosorb I instrument.

3.3.3 Methodology

The synthesis mixture for NaA zeolite was prepared according to the procedure reported previously[6] with the molar ratio of $SiO_2:Al_2O_3:xNa_2O:410H_2O$,$3\leq x\leq 6$. Silatrane and alumatrane synthesized via the OOPS (One Pot Oxide Synthesis) process and characterized by the method of Wongkasemjit's group[9,10] were used to prepared NaA incorporation with the seeding technique. NaA from the same process was also used as crystal seed. The medium were aged for half a day. The effect of parameters (namely, amount of NaOH, microwave heating time and temperature, as well as number of seed crystal on the small size and uniformity of NaA zeolite were studied. The synthesized product were further characterized for their structure and morphology by XRD and SEM, and chemical analysis using SEM-EDX.

3.4   Results and Discussion

3.4.1 Precursor Synthesis

Silatrane [tris (silatranyloxyethyl) amine or Si-TEA] and alumatrane [tris-(alumatranyloxy-1-propyl) amine or AlTIS] were characterized using FTIR and TGA. FTIR confirmed the characteristic peak of silatrane and alumatrane precursors. Silatrane: 3000-3700 cm^{-1} (w, νO-H), 2860-2986 cm^{-1} (s, νC-H), 1244-1275 cm^{-1} (m, νC-N), 1170-1117 cm^{-1} (bs, νSi-O), 1093 cm^{-1} (s, νSi-O-C), 1073 cm^{-1} (s, νC-O), 1049 cm^{-1} (s, νSi-O), 1021 cm^{-1} (s, νC-O), 915-940 cm^{-1} (m, δSi-O-C), 785 and 729 cm^{-1} (s, δSi-O-C) and 379 cm^{-1} (w, Si←N). Alumatrane: 3040 cm^{-1} (b, νO-H),

2937-2881 cm^{-1} (s, vC-H), 2750, 2670, 3700 cm^{-1} (w, NR$_3$ salt Si ◄- N) (w, vC-N),

1259 cm^{-1} (m, vC-O), 1040 cm^{-1} (m, vSi-O), 885 cm^{-1} (s, vAl-O-C), and 659-400 cm^{-1}

(s, δAl-O). Thermal properties and stability were analyzed by thermogravimetric

analysis. The TGA results of alumatrane give two mass loss transitions at 141 and

383°C corresponding to the decomposition of the EG solvent trapped in their

structure and organic ligand, respectively. The ceramic yield, 31.6, corresponding to

the structure of Al(OCHCH$_3$CH$_2$)$_3$N, which is larger than the theoretical (23.72%),

presumably due to the incomplete combustion. Silatrane exhibits only one weight

loss transition at around 400°C corresponding to the decomposition of organic ligand.

The char yield is arround 18.5%, which is close to the theoretical yield of

Si(OCH$_2$CH$_2$)$_3$N$_2$)H$_2$ (18.4%)

3.4.2 Effect of Hydroxide Concentration

From previous study[6], increasing NaOH concentration also increased

the hydroxide concentration, which in turn enhanced the dissolution of the

amorphous gel and nucleation rate leading to the growth of more crystals. In this

study, the effect of hydroxide concentration was investigated parallel to the seeding

effect by fixing microwave heating temperature at 110°C for 2 h 20 min and staring

material composition at SiO$_2$:Al$_2$O$_3$:xNa$_2$O:410H$_2$O, 3≤x≤6.. Figure 3.1 showed that

1 wt% seeding NaA zeolite crystals were observed when X = 3. The crystal sizes

slightly decreased with increasing OH$^-$: Si ratio. At a hydroxide concentration equal

to 3, the average size was 0.7-0.8 μm. When hydroxide concentration is increase to

4, the particle size distribution increased to 0.9-1 μm. However with hydroxide

concentration changed to 5 and 6, the crystal size was as small as 0.4-0.6 μm. The

phase of NaA crystal was confirmed by XRD in Fig 3.2 compared with the

commercial one. XRD data confirmed the reference pattern matching the one when

using hydroxide concentrations equal to 3 and 4. We know that the hydroxide

concentration is decreased with the crystallization time reduction. When hydroxide

concentration is increased to 5 and 6 at the microwave heating time and temperature

2 h 20 min and 110 °C, respectively, the overrun zeolite product occurs. The XRD

pattern (Fig. 3.2) also shows some impurity at 2θ = 18 of NaP zeolite[11]. Referring

to previous study[6], the same condition and without the seeds, NaA zeolite crystals were synthesized by microwave heating at 110°C for 2 h 40 min. By seed operation, the nucleation stage is shorter due to the formation of new nuclei on the seed crystal surface and subsequent growth of the new crystallite of the same phase[12]. Thus crystallization was clearly enhanced because NaA zeolite crystals were observed in the shorter time.

3.4.3 Effect of Microwave Temperature

In general, as crystallization is an activated process, within certain limits temperature has a positive influence on the zeolitization process[13]. Increase of the temperature results in shorter crystallization times, as illustrated in Fig.3.3. With the same formula of $SiO_2:Al_2O_3:3Na_2O:410H_2O$ for a half-day aging time and varying the temperature at 90, 110, 130 and 150°C for 2 h 20 min, the results showed that temperature of 90°C provided mostly amorphous materials with few NaA crystals. Upon increasing the temperature to 110°C, uniform and homogeneous of NaA crystals occurred. However, large crystals with small crystal of NaA from secondary growth emerging on their surface were produced at the high temperature of 130 and 150°C.

Temperature strongly influences the formation of NaA zeolite. The optimal temperature range depends on the Si/Al ratio[14]. It can alter the zeolite phase obtained as well as induction period before the start of crystallization[15]. We fixed the composition at $SiO_2:Al_2O_3:3Na_2O:410H_2O$, aging for half a day, and heating with microwave at 80, 90, 100 and 110°C for 2 h 20 min. The results are shown in Fig. 3.4, which indicates that heating from 80 to 100°C provided mostly amorphous material with few NaA crystals. At 110°C, the uniform and homogeneous NaA crystals were observed.

3.4.4 Effect of Aging temperature

For homogeneous crystal size distribution, it would be favorable to have a short nucleation period. A large number of nuclei would result in small crystals. During the aging period, mixing on a molecular scale is envisaged to allow the formation of nuclei necessary for the crystallization of NaA. During microwave

synthesis, small crystals which are homogeneous in size distribution are received when the synthesis mixture has been aged sufficiently[16]. Aging of the reaction mixture i s frequently carried o ut at room t emperature. H owever, aging has sometimes been carried out at higher elevated temperatures. In this study, to obtained fully grown crystals, the aging time was fixed (half a day), whereas the aging temperature was varied (25 and 40°C) concurrently with the effect of seed crystal. Without seeding, when aging was increased to 40°C, the crystal size was decreased. From the results in Fig. 3.5, c rystal size decreases from 1 μm at 25°C to 0.3-0.4 μm at 40°C. The results differ from those of other research[17,18] and the mechanism is not clear understood.

The XRD pattern (Fig. 3.6) shows only one phase of the synthesized NaA zeolite compared with the commercial one. Aging at 25°C with 3 wt% seed, the crystals formed are small and homogeneous at 0.3-0.4 μm. When the seed wt% was decreased to 1-2, the particle size was changed to ~1 μm with non–uniform characteristics. The reason is the seed crystal provides a surface area on which the required product can grow. As the quantity of added seed material is reduced, the natural supersaturation and consequent self –nucleation will no longer be suppressed and the product crystal size will increase. The XRD results (Fig. 3.7) show only pure NaA zeolite phase without impurities. However, when aging at 40°C with 1-3 wt% seed, the product is rather large (0.8-1 μm) and shows non-uniform crystals. The XRD pattern (Fig. 3.8) also the same results. These phenomena occur due to the growth rate of crystallites, which was strongly influenced by aging temperature due to the fact that the particles formed from the aged solution were agglomerates. Polycrystalline particles have a higher surface area per particle and can therefore assimilate nutrients better than single crystals with regular planar faces[5]. As a result, large crystals grow.

3.4.5 Effect of Microwave Heating Time

Since, in the course of crystallization, the solid product is a mixture of zeolite and unreacted amorphous solids, the crystallinity of the product increases with time. Zeolite crystallization is governed by the occurrence of successive

phase transformations. The thermodynamically, the least favorable phase crystallizes first, and is replaced by more stable phases[19]. In general, crystallization is an activated process, within certain limitation temperature having a positive influence on the zeolitization process. Higher temperature results in shorter crystallization time[20]. Moreover, the effect of variables, viz increasing temperature, hydroxide concentration or adding crystal seeds, can be applied to minimize the crystallization time. Not only the temperature, hydroxide concentration, but also the addition of crystal seeds influences the crystallization time[4]. In our system, we fix the composition at $SiO_2:Al_2O_3:3Na_2O:410H_2O$ with 3 wt% seeding , aging for half a day, and microwave heating at 110°C for 2 h 20 min. The results (Fig. 3.9) indicate that, when the temperature was increased to 110°C, it provided uniform and homogeneous (0.5-0.6 μm) crystals. However, the lower temperature at longer time, such as, 100°C for 4 h or 90°C for 5 h, gives the smaller crystal size as 0.5 or 0.3-0.4 μm, respectively. The most uniform and smallest crystals, 0.1-0.2 μm of zeolite product, were observed at 80°C for 6 h because the higher temperature affects the reduction of induction time, speeding the crystal growth rate[21].

3.4.6 Effect of Seed wt%

Seed crystals are added to the reaction mixture for reducing the synthesis time and directing of the synthesis toward a desired phase[22-24]. The role of seeds in promoting the zeolite crystallization rate is due to the formation of new nuclei on the seed crystal surface, and subsequently growth of these new crystallites of the same phase[11]. In sol-gel system, according to Prabir's work[25], the seed provides the nuclei for crystal growth while the gel's role then is provide a source of nutrients for nuclei growth. For this present work, we thus fixed the composition at $SiO_2:Al_2O_3:3Na_2O:410H_2O$, aging at half a day, varying at 1-3 wt%, and microwave heating at 80°C for 10 h, (see Fig. 3.10). Uniform and small sized crystals were observed, especially in 3 wt% seed. The higher amounts of seed promoted a higher nucleation rate, generating more nuclei, while the rate of both nucleation and growth are know to decrease as the temperature is lowered[26, 27]. Since the growth rate seems to vary more strongly than nucleation rate with temperature, as the temperature is

lowered, the result is the preparation of small zeolite crystals. SEM-EDS results show the Si:Al ratio equal about 1. The Phase of NaA crystal was confirmed by XRD (Fig 3.11) compared with the commercial one. Only one phase was observed.

3.4.7 Surface Area Measurement

The physico-chemistry of small samples is shown in Table 3.1, which indicates that many samples give high surface area compared with the commercial one. Many effects (such as hydroxide ion concentration, seed wt %, microwave temperature and time) on the surface area of as-synthesized product are studied. It is well known that hydroxide concentration enhances the dissolution of amorphous gel and accelerates the crystal growth. When hydroxide ion concentration is increased to 3 with 3 wt% seed, at 80°C microwave heating for 6 h, the average crystal size is 0.1-0.2 μm. When hydroxide concentration is increased to 4, with the same conditions, the average crystal size is 0.3-0.4 μm. A crystal size of ~0.5 μm was obtained when the hydroxide concentration was 5. Seed wt% is the incorporation with NaOH to generate small size NaA zeolite. For hydroxide concentration equal to 3, 4, and 5, as more seed is applied, small size NaA zeolite is obtained due to the seed providing their surface area to assimilate material from the solution for nuclei formation, leading to the small crystal. From Table 3.1, with the same hydroxide concentration, the surface area of NaA zeolite increases when greater seed wt% is applied. An example is that a hydroxide concentration equal to 3 with 1, 2 and 3 seed wt%, higher surface area of 7.3, 9.4 and 11.9 m^2/g, respectively, at a microwave heating temperature of 60°C for 6 h, are shown. Temperature and time can alter surface area of the NaA crystal. Temperature affects factors in zeolite synthesis, reducing the length of induction time and enhancing the crystallization rate when temperature increases. For instance, when the hydroxide concentration equal to 3 with 3 wt% seed, the higher temperature of 90°C for 5 h provides a larger crystal (0.3-0.4 μm) compared with the small crystal (0.1-0.2 μm) obtained from the same condition, but with heating at 80°C for 6 h. Thus, the surface area of the crystal from 80°C / 6 h (11.9 m^2/g) is higher than the one from 90°C / 5 h (9.0 m^2/g). Most of the synthesized

NaA zeolites display high surface areas compared with the commercial one (Sigma Aldrich Co. Ltd).

3.4.8 Moisture Absorption Testing

Moisture absorption of the small size (0.1-0.2 μm, having surface area of 11.9 m^2/g) synthesized zeolite, using SiO_2:Al_2O_3:$3Na_2O$:$410H_2O$ at 80°C for 6 h was determined by the method described elsewhere[6]. The results of water absorption of NaA zeolite synthesized was determined to be 0.1338 g H_2O / g zeolite, which is higher than 0.1186 g H_2O /g zeolite obtained from the commercial one (5.9 m^2/g). The reason is that the smaller size of as synthesized NaA (0.1-0.2 μm) involves higher surface area for absorption of water, more than the commercial one (2 μm).

NaA zeolite is hydrophilic and it has potential for dehydration of an organic mixture. NaA zeolite is thus used for membrane applications. Xu *et al.*[28] synthesized a NaA zeolite membrane by microwave technique in which uniform and small size zeolite was formed from nuclei on the support surface homogeneously and in short duration. A thin layer of NaA zeolite membrane was received, resulting in increasing permeation rate.

3.5. Conclusions

Nanosize NaA zeolite can be successfully synthesized from silatrane and alumatrane by sol-gel process and microwave techniques. The composition of SiO_2: Al_2O_3:$3Na_2O$:$410H_2O$ with 1-3 wt% of seed crystals obtained using the reaction temperatures ranging from 80 to 100°C provides uniform and narrow size distribution of 0.1-0.2 μm of NaA zeolite crystals.

3.6. Acknowledgments

3.7 References

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(a)

(b)

(c)

(d)
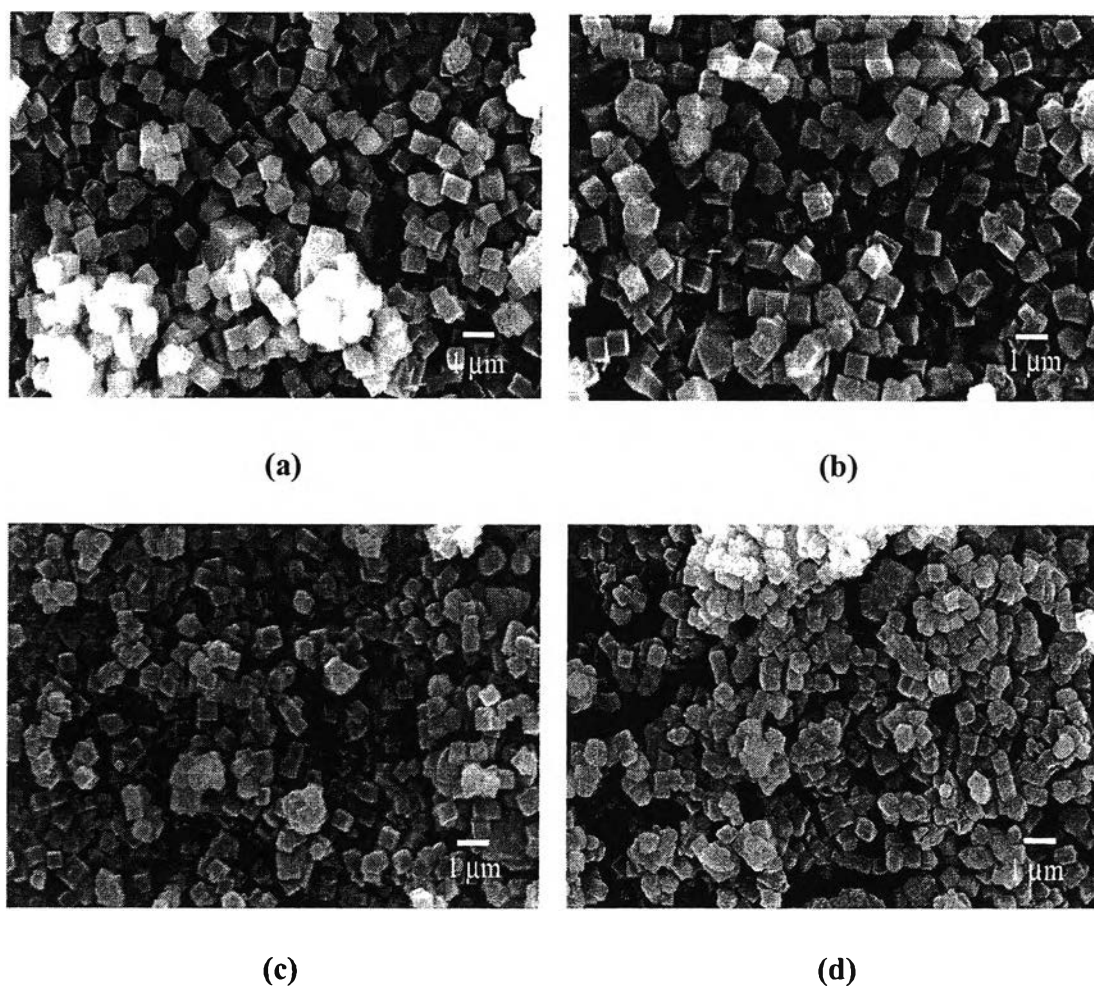
Figure 3.1 The effect of hydroxide concentration on zeolite formation using SiO_2: Al_2O_3:xNa_2O:$410H_2O$, 1 wt% seed, 110°C microwave heating for 2 h 20 min with hydroxide concentration, x, of (a) 3, (b) 4, (c) 5 and (d) 6.
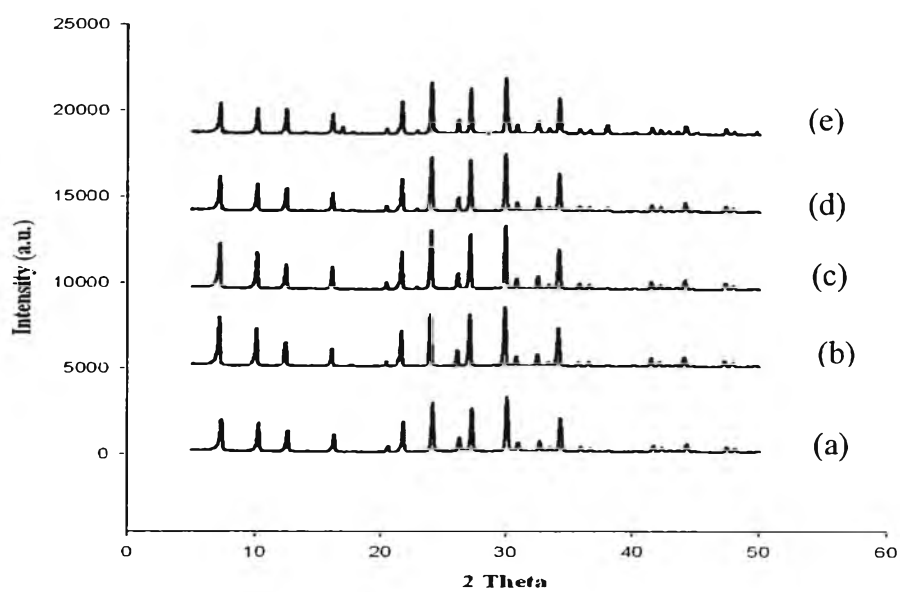
Figure 3.2 XRD spectra of synthesized NaA zeolite using $SiO_2:Al_2O_3:xNa_2O:410$ H_2O, 110°C microwave heating for 2 h 20 min with hydroxide concentration,x,of (b) 3, (c) 4, (d) 5, and (e) 6, compared with the commercial LTA (a).
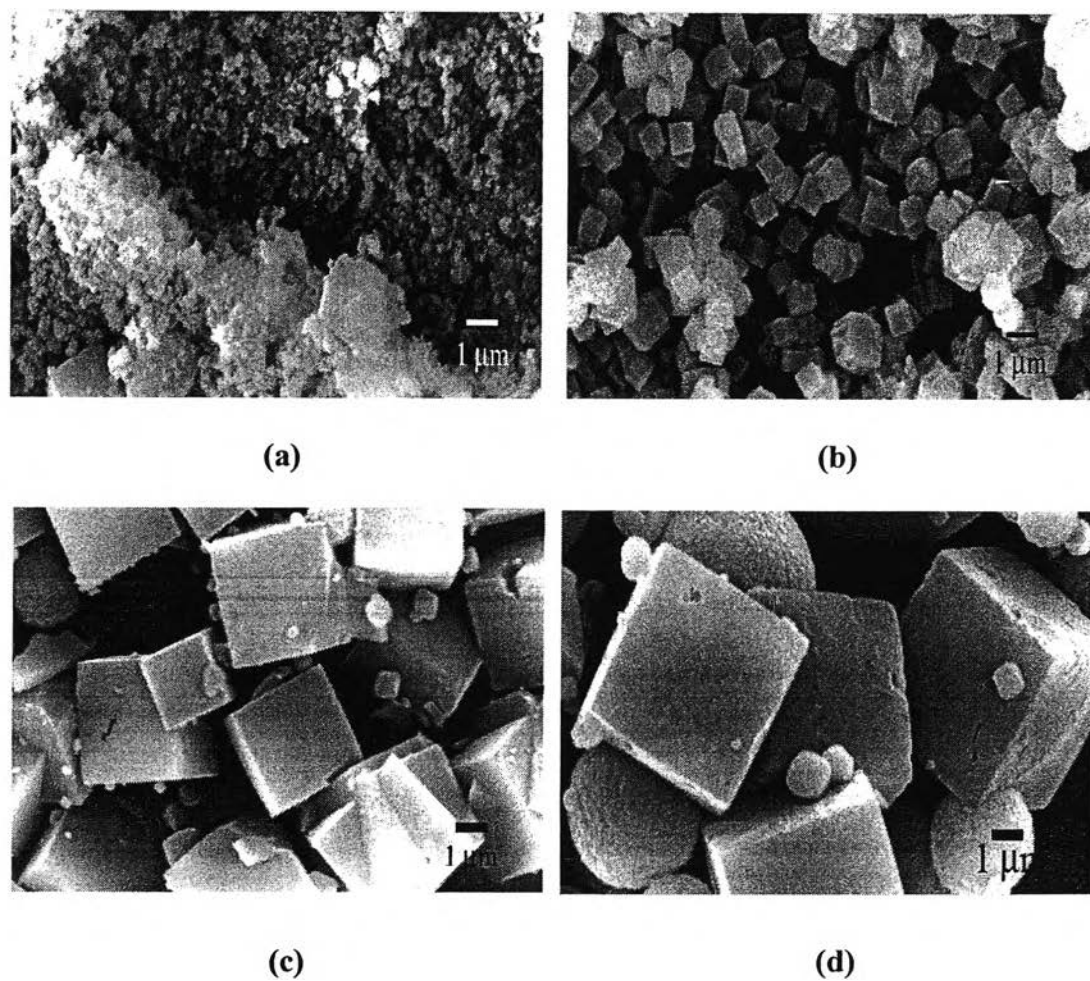
Figure 3.3 Effect of temperature on zeolite formation without seeding using SiO_2: Al_2O_3:xNa_2O :$410H_2O$ at microwave heating temperature of (a) 90°, (b) 110°, (c) 130°, and (d) 150°C for 2 h 20 min.

(a)

(b)

(c)

(d)
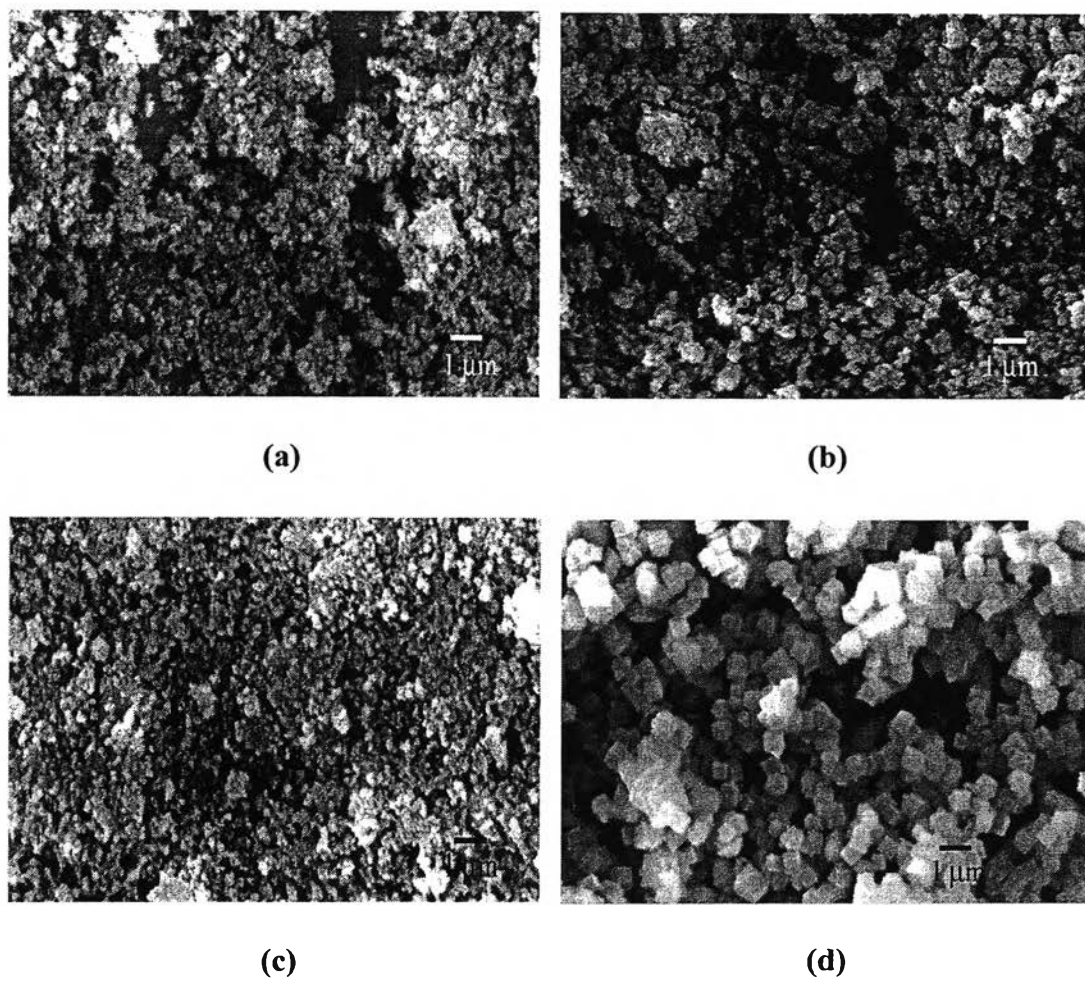
Figure 3.4 SEM micrographs of NaA zeolite synthesized using $SiO_2:Al_2O_3:xNa_2O$:$410H_2O$ with 3 wt% crystal seed at microwave heating temperatures of (a) 80°, (b) 90°, (c) 100°, (d) 110°C for 2 h 20 min.
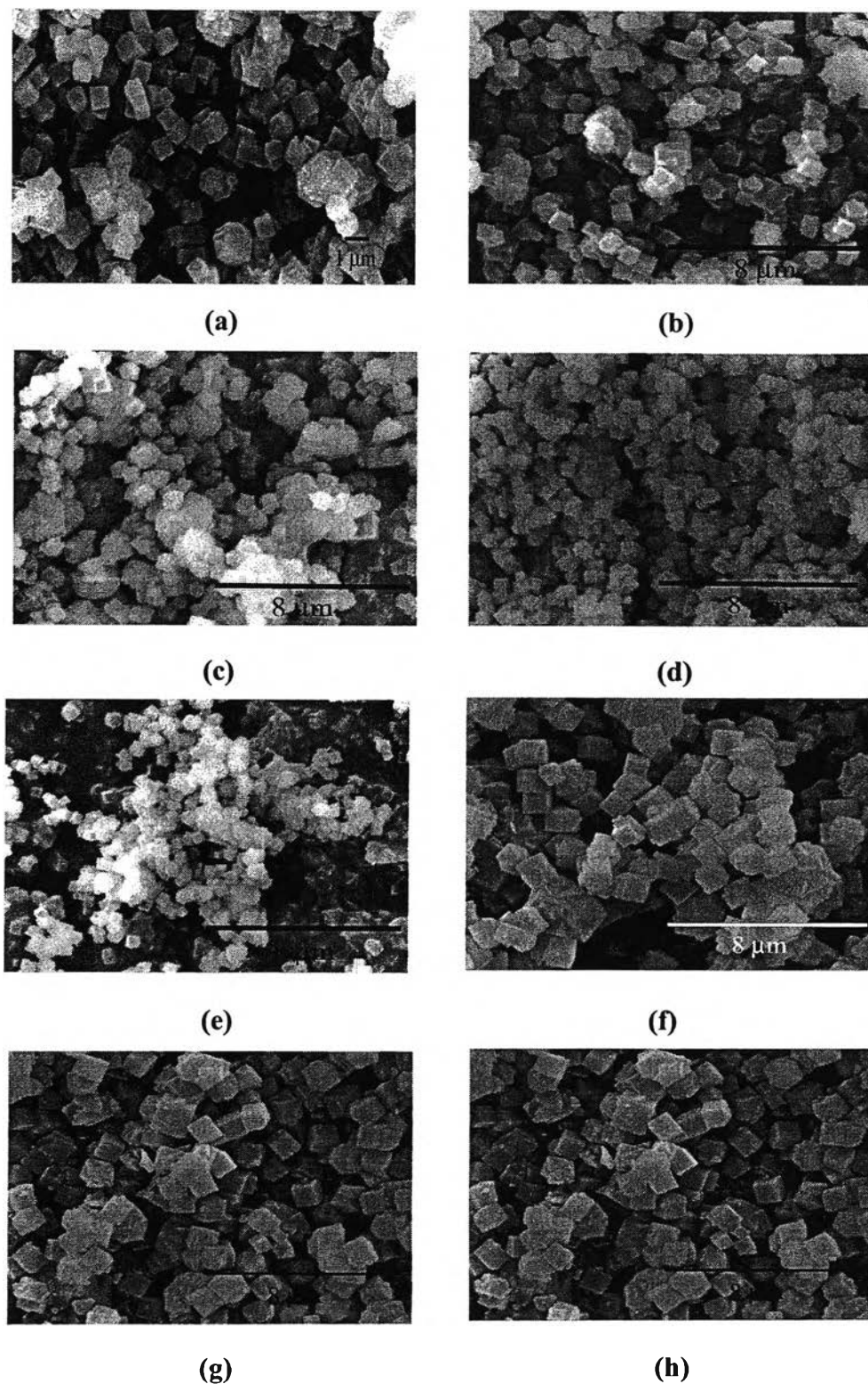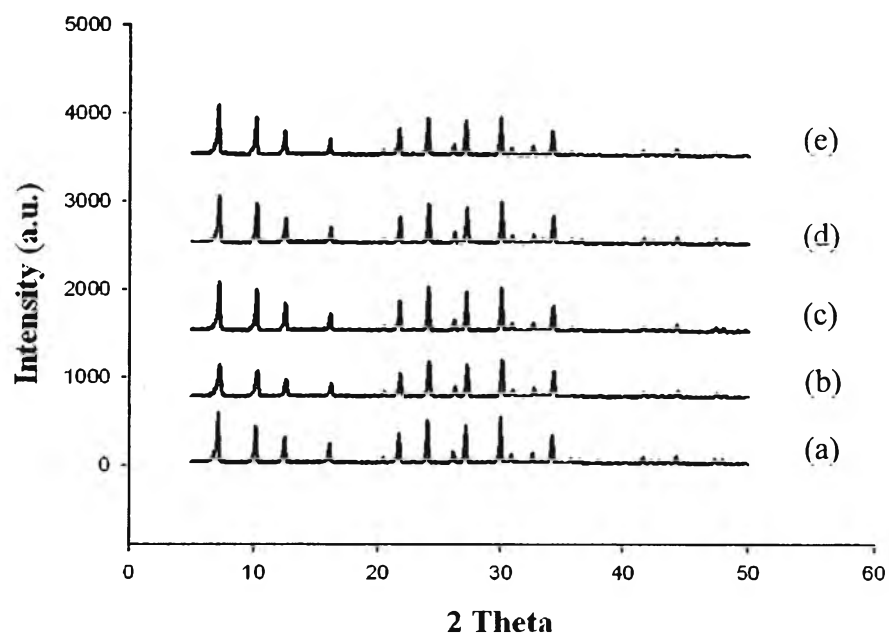
Figure 3.5 SEM micrographs of NaA zeolite synthesized using $SiO_2:Al_2O_3:xNa_2O$:$410H_2O$ at 100°C heating temperature for 2 h 20 min with aging temperature 25°C and seed amount (a) 0, (b) 1, (c) 2 and (d) 3 wt% and with aging temperature 40°C and seed amount (e) 0, (f) 1, (g) 2 and (h) 3 wt%.
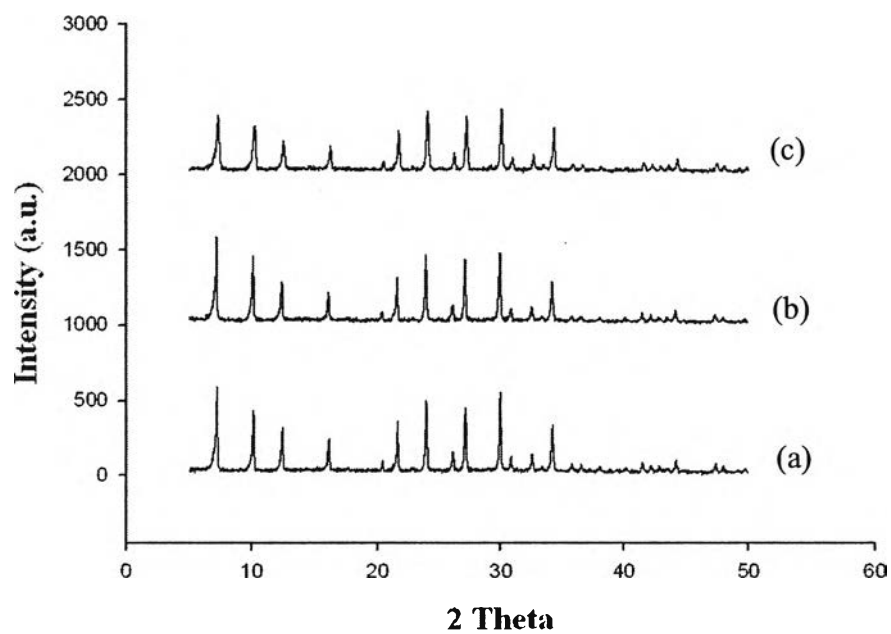
Figure 3.6 XRD spectra of synthesized NaA zeolite using SiO_2:Al_2O_3:xNa_2O:410 H_2O, 110°C microwave heating for 2 h 20 min with aging at (b) 25, and (c) 40°C without Seeding compared with the commercial LTA (a).
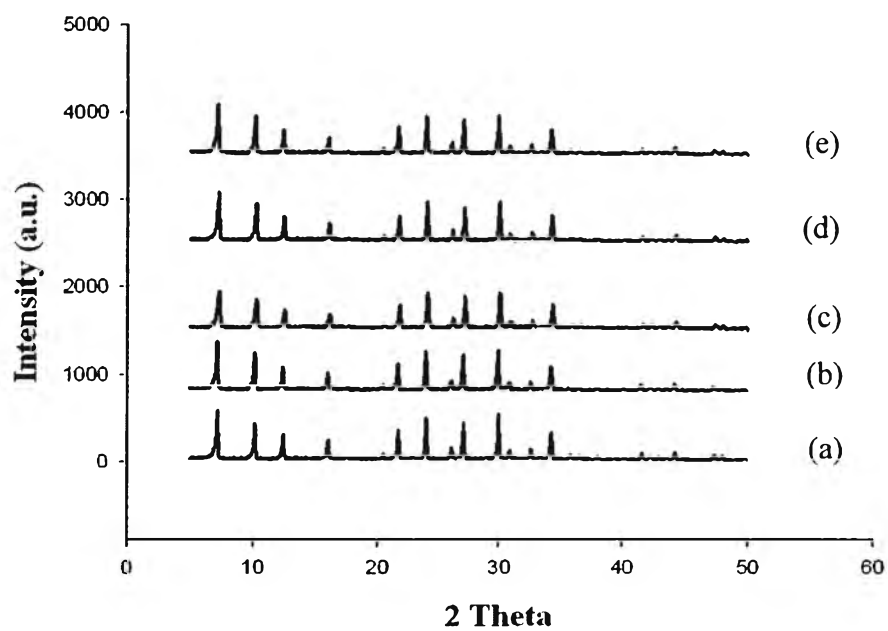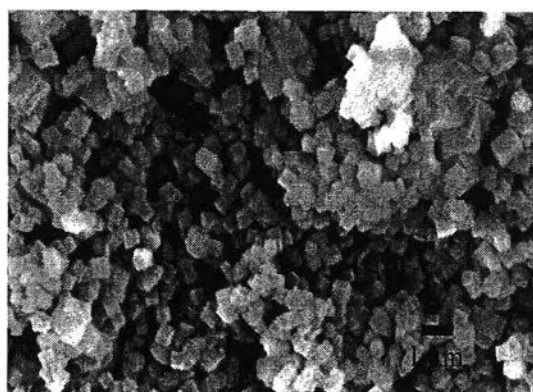
Figure 3.7 XRD spectra of synthesized NaA zeolite using $SiO_2:Al_2O_3:xNa_2O:410$ H_2O, 110°C microwave heating for 2 h 20 min at aging temperature 25°C with (b) 0, (c) 1, (d) 2, (e) 3 wt% seed compared with the commercial LTA (a).
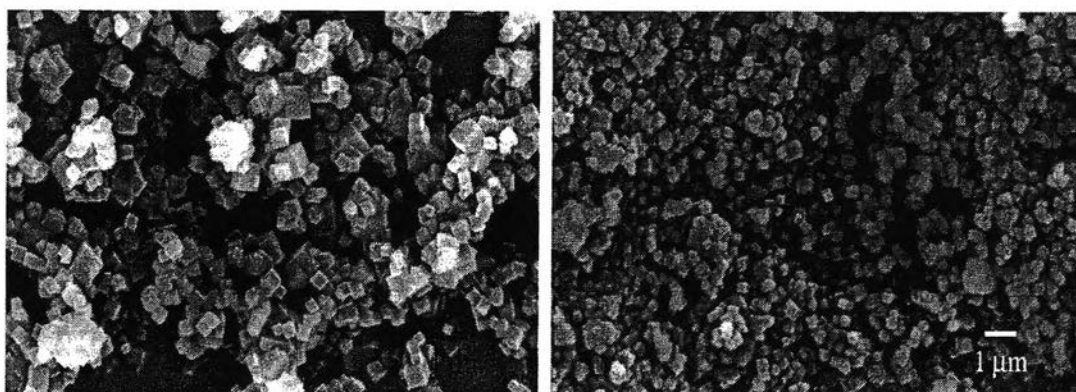
Figure 3.8 XRD spectra of synthesized NaA zeolite using $SiO_2:Al_2O_3:xNa_2O$:410 H_2O, 110°C microwave heating for 2 h 20 min at aging temperature 40°C with (b) 0, (c) 1, (d) 2 and (e) 3 wt% seed compared with the commercial LTA (a).
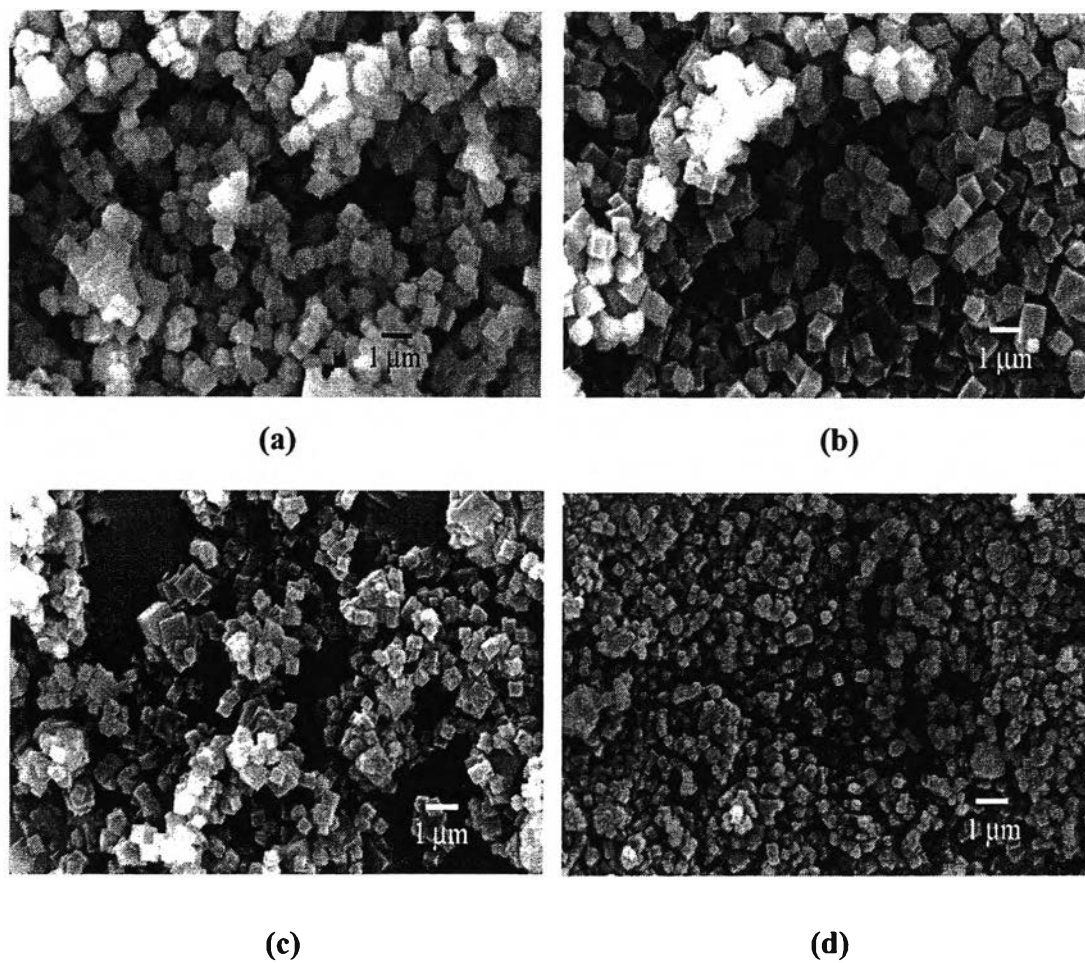
Figure 3.9 SEM micrographs of NaA zeolite synthesized using $SiO_2:Al_2O_3$:xNa_2O :$410H_2O$, 3 wt% crystal seed at microwave heating temperatures and times of (a) 110°C for 2 h 20 min, (b) 100°C for 4 h, (c) 90°C for 5 h, and (d) 80°C for 6 h.

(a)

(b)   (c)

Figure 3.10 SEM micrographs of NaA zeolite synthesized using $SiO_2:Al_2O_3$:xNa_2O :$410H_2O$ at 80°C heating temperature for 6 h with seed amount of (a) 1, (b) 2 and (c) 3 wt%.
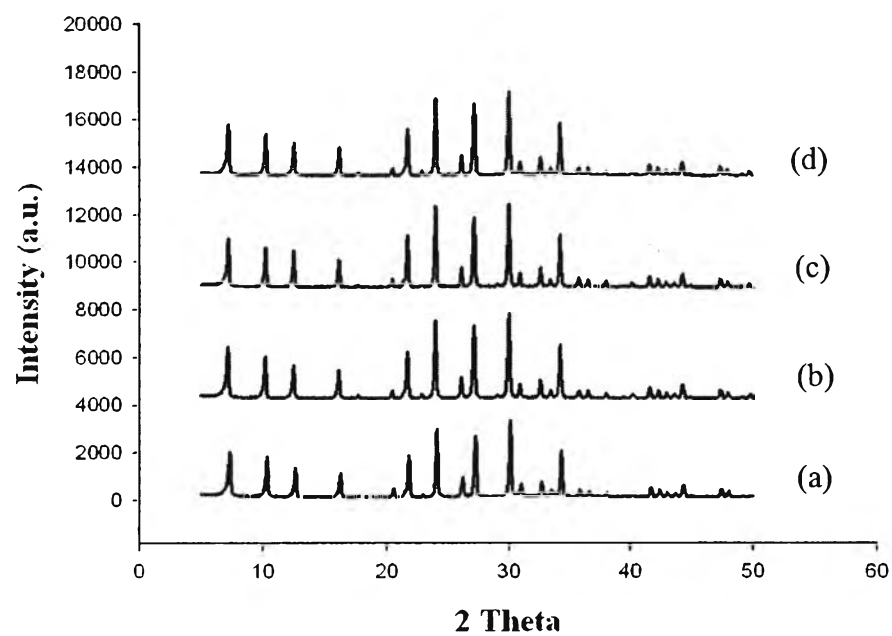
Figure 3.11 XRD spectra of synthesized NaA zeolite using $SiO_2:Al_2O_3:xNa_2O$:410H_2O at 80°C heating temperature for 6 h with seed amount (b)1, (c) 2, and (d) 3 wt% compared with (a) the commercial LTA (a).

Table 3.1 Surface area of as-synthesized NaA zeolite by varying hydroxide ion concentration (3, 4, 5), seed wt% (1, 2, 3) and microwave temperature and time (80°C / 6 h and 90°C/ 5 h) with composition heating temperature for 6 h with SiO_2: Al_2O_3 :xNa_2O :410H_2O; $3 \leq x \leq 5$

NaA synthesis condition			BET surface area
NaOH (mole ratio)	Seed	Microwave temperature / time	(m^2/g)
3	1	80°C-6 h	7.29
3	2	80°C-6 h	9.37
3	3	80°C-6 h	11.87
3	1	90°C-5 h	4.96
3	2	90°C-5 h	6.24
3	3	90°C-5 h	9.04
4	1	80°C-6 h	7.32
4	2	80°C-6 h	7.35
4	3	80°C-6 h	8.75
4	1	90°C-5 h	3.84
4	2 ·	90°C-5 h	5.08
4	3	90°C-5 h	8.71
5	1	80°C-6 h	2.67
5	2	80°C-6 h	3.07
5	3	80°C-6 h	7.93
5	1	90°C-5 h	1.07
5	2	90°C-5 h	1.78
5	3	90°C-5 h	6.21
Commercial NaA (Sigma Aldrich Co.Ltd.)			5.89