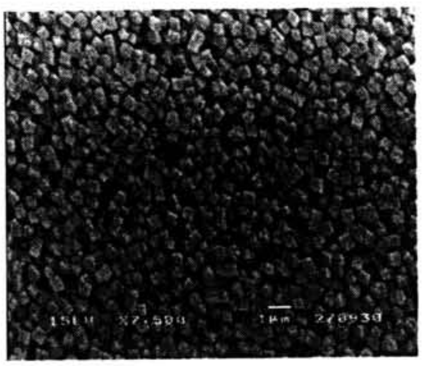
CHAPTER IV
RESULTS AND DISCUSSION

4.1 NaA Zeolite Crystal Seed

To fabricate thin film without any defect on surface membrane, seeding technique is used to form seeding layer on the substrate before a secondary growth step. Therefore, the preparation of small and uniform particle size of crystal seed is important. Generally, in order to get a good seeding layer, the seed size should be comparable with the support pore, i.e. the seed size should be as small as possible, but big enough to avoid penetrating into the support pore (Huang, A. *et al.*, 2004). In this study the synthesized NaA crystal, having the size about 0.3 – 0.6 μm, which is closely to the size of support pore, 0.3 μm, was characterized using SEM and XRD in fig.4, as compared with LTA database.



(4.1a)

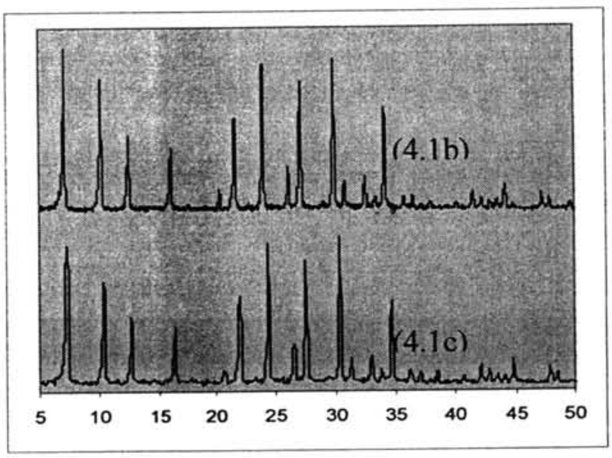


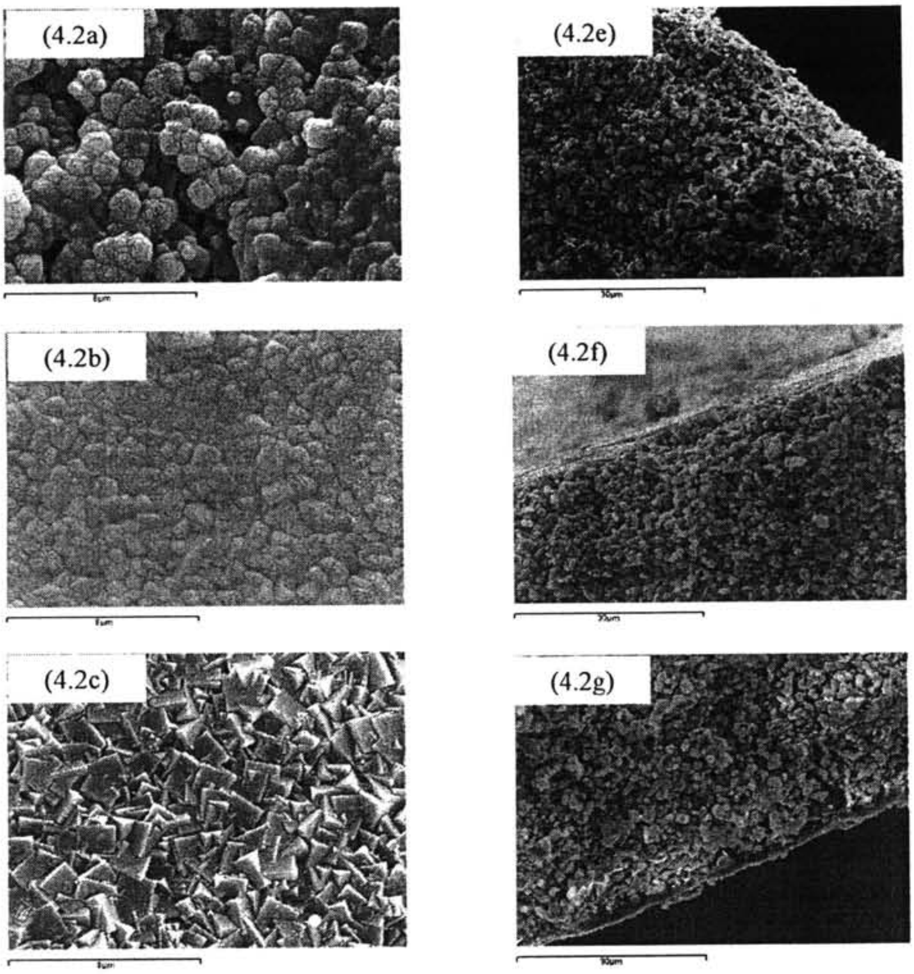
Figure 4.1 a) SEM micrograph of the synthesized NaA crystal, b-c) XRD patterns of the synthesized NaA crystal and LTA database, respectively.

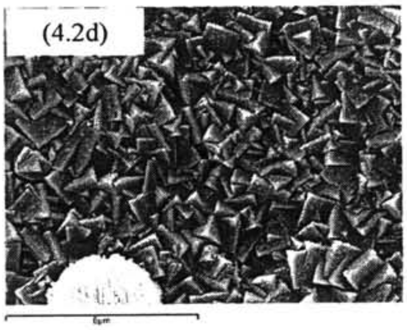
4.2 NaA Zeolite Membrane Synthesis by Static Method of Microwave Technique

As mentioned previously, the important advantage of using microwave is the shorter synthesis time. In this work, the Na A zeolite synthesis is mainly focused on the use of microwave at various synthesis time, synthesis temperature, seed suspension concentration and seeding time.

4.2.1 Effect of synthesis time

The layer development of NaA zeolite crystal on the support surface is studied at various synthesis times. Fig. 4.2 (a-d) shows morphology of NaA zeolite membranes synthesized, using 1g of seed in 1000 mL of water for 3 min seeding time, 60°C microwave temperature for 30, 60, 90 and 120 min, respectively. Figure 4.2a shows an initial stage of induction time (Gora, L *et a*l., 1997)(Wijnen, P.W.J.G. *et a*l., 1994). During this stage, the aging-matured precursor species in solution, consisting of alkali ions, aluminate, silicate and aluminosilicate monomers dimers and oligomers, rearrange into amorphous gel particles. The seed layer can be still seen and an amorphous gel layer is deposited on the support surface. These colloidal particles are agglomerated and are brought to the support surface by Brownian motion and are then deposited onto the surface in a thin amorphous gel film (Koegler, J.H. *et a*l., 1997). This stage is associated with the formation of the gel film, the formation of nuclei within the film and the exposure of viable nuclei to the surrounding solution as the gel phase starts to dissolve during continuous hydrothermal treatment (Koegler, J.H. *et a*l., 1997). When the synthesis time increases to 1 h, the characteristics of zeolite membrane formed depends on the formation of primary zeolite particles (nuclei). All nuclei were formed within the matrix of the gel film because of the high supersaturation of nutrients in the gel (Gora, L *et a*l., 1997). Small crystallites appear and are grouped together to build hemi-sphere shape clusters (Fig. 4.2 b). Each small semicrystalline cluster is closely packed and crystallizes to form a matrix of crystallite cluster in close proximity to each other (Zah, J. *et a*l., 2006). Figure 4.2 c shows that the crystals become the well-known cubic morphology of NaA crystal which are intergrowth to form NaA membrane, and Fig. 4.2 d indicates that additional time to 2 hours does not affect the cubic morphology, but inter-crystalline gaps has developed to form defect free layer.





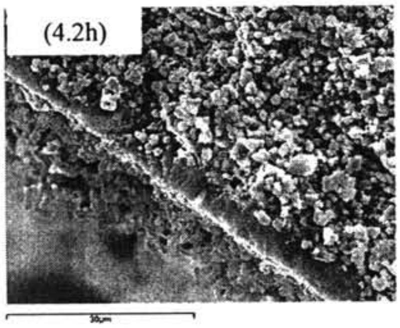


Figure 4.2 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of 1g/1000ml and vacuum seeding for 3 min under microwave radiation by static method at 60°C for a) 30, b) 60, c) 90 and d) 120 min with the layer thickness of e) 0 (only substrate), f) 0.81, g) 1.20 and h) 4.21 μm.

Fig. 4.2 e, f, g and h demonstrate the thickness of the membrane growth taken place for 30, 60, 90 and 120 min, respectively. There is no thickness in the induction stage and next stage is non-continuous membrane. The thickness gradually increases when synthesis time increases. The thickness of these membranes shown in Fig. 4.2.1f, g and h are 0.81, 1.20 and 4.21 μm, respectively.

Fig. 4.3 a, b, c and d show the morphology of NaA zeolite membrane synthesized at 75°C for 15, 30, 45 and 60 min, respectively, using the same seed amount (1g/1000 mL water) seeding time (3 min). The results are similar to those grown at 60°C, except that the synthesis time to reach the well-known cubic morphology is shorter because of the higher temperature. At 30 min of the synthesis time the crystallization process began to build the cubic crystal shape while still keeping small size of crystals. However, at the 45 min synthesis time (Fig. 4.3 c) intergrowth of cubic crystals occurred over the whole support surface, causing bigger crystal size. When the synthesis time is long enough, 60 min (Fig. 4.3 d), the second layer partially began to form on the top.

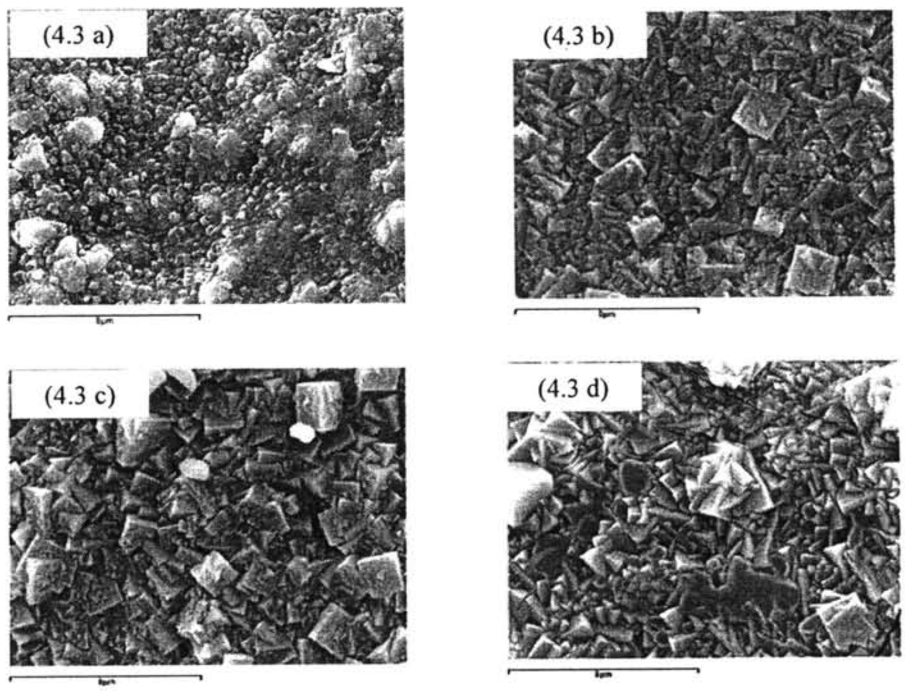


Figure 4.3 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed concentration of 1g/1000ml and vacuum seeding for 3 minunder microwave radiation by static method at 75°C for a) 15, b) 30, c) 45 and d) 60 min.

The results of the NaA zeolite membrane synthesis at higher temperature, 90°C, for 5, 10, 15, 20, 25 and 30 min, using the same conditions of the seed amount and the seeding time are shown in Fig. 4.4 a, b, c, d, e and f, respectively. The morphology becomes well-defined intergrowth in 25 min synthesis time (Fig. 4.4 e). Although the synthesis time reaches 30 min, no changing of the morphology can be seen.

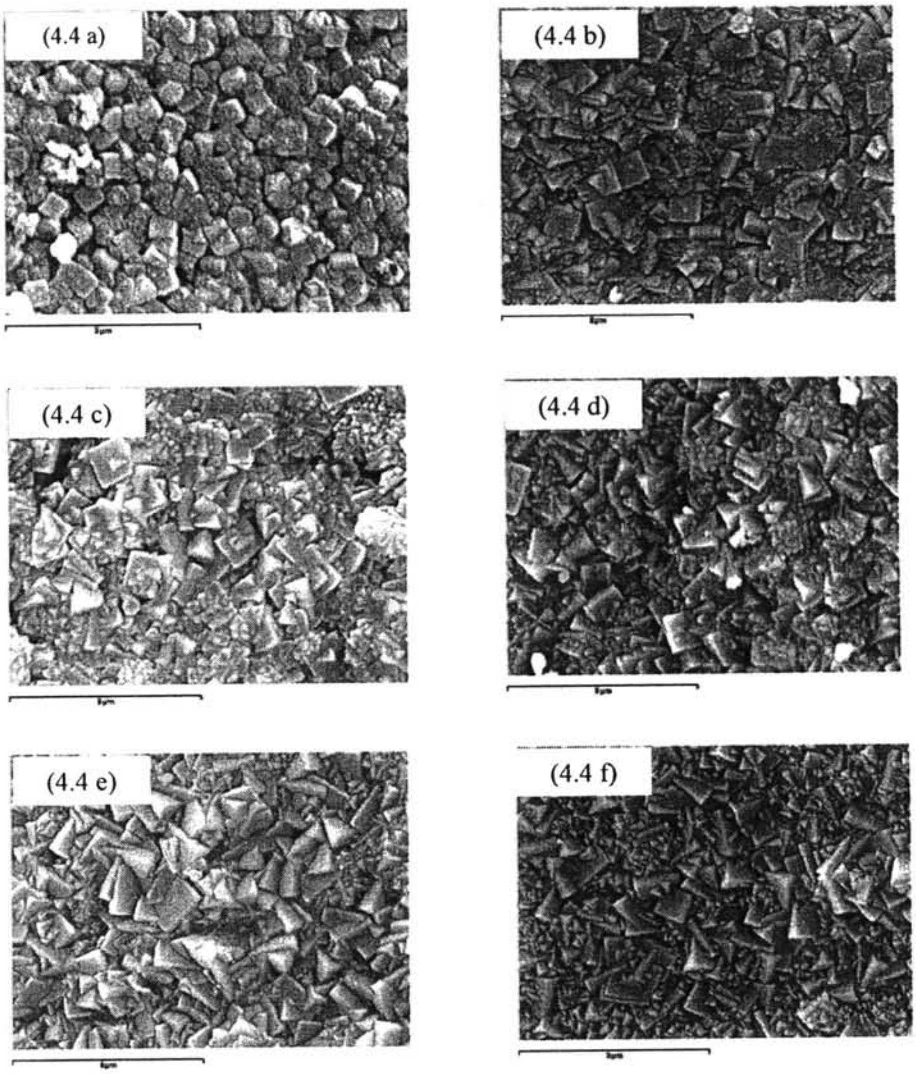
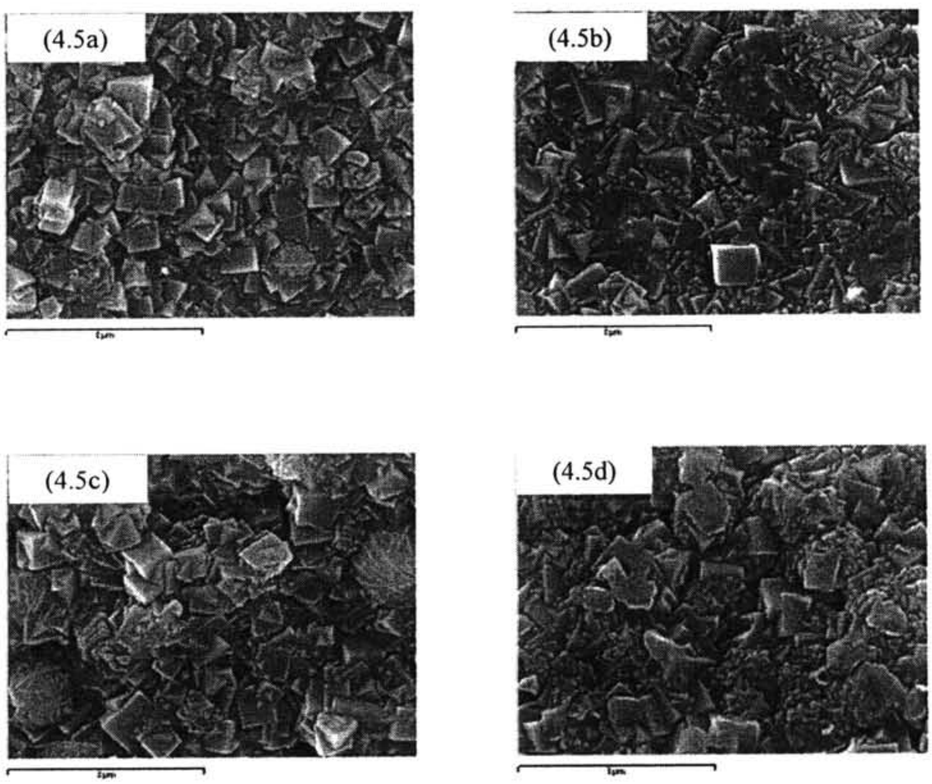
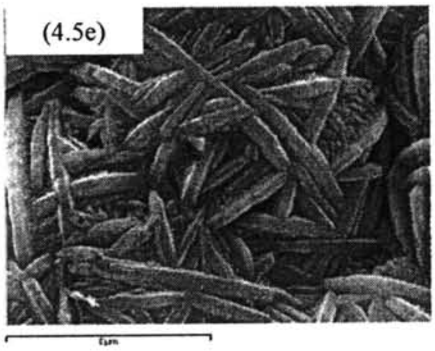
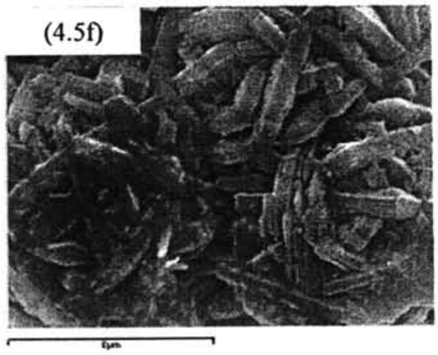


Figure 4.4 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of 1g/1000ml and vacuum seeding for 3 min under microwave radiation by static method at 90°C for a) 5, b) 10, c) 15, d) 20, e) 25 and f) 30 min.

The results of the NaA zeolite membrane synthesis at 105°C for 5, 10, 15, 20, 25 and 30 min, as shown in Fig. 4.5 a, b, c, d, e and f, respectively, indicate that the NaA membrane layer occurs within 5 min and 10 min synthesis time results in the second layer (Fig 4.5 a). The second layer of NaA crystal grows more when synthesis time is in between 15 to 20 min (Fig. 4.5 c and d). However, Fig. 4.5 c shows some another phase that commonly found, as a ball of yarn called hydroxy-sodalite crystal, as also discovered by Xiaochun Xu et al. (Xu, X. *et al.*, 2004), when the temperature was increased to 90°C within 15 min by microwave treatment. At this time, the synthesized membrane consisted of NaA zeolite along with hydroxy sodalite. Pure-hydroxy sodalite was observed after heated for 45 min. This sodalite phase was observed over the support surface in Fig. 4.5 e and f. It can be indicated that at higher temperature and longer time, the NaA phase was transformed to hydroxy-sodalite phase that was confirmed by XRD as show in Fig 4.5 g.







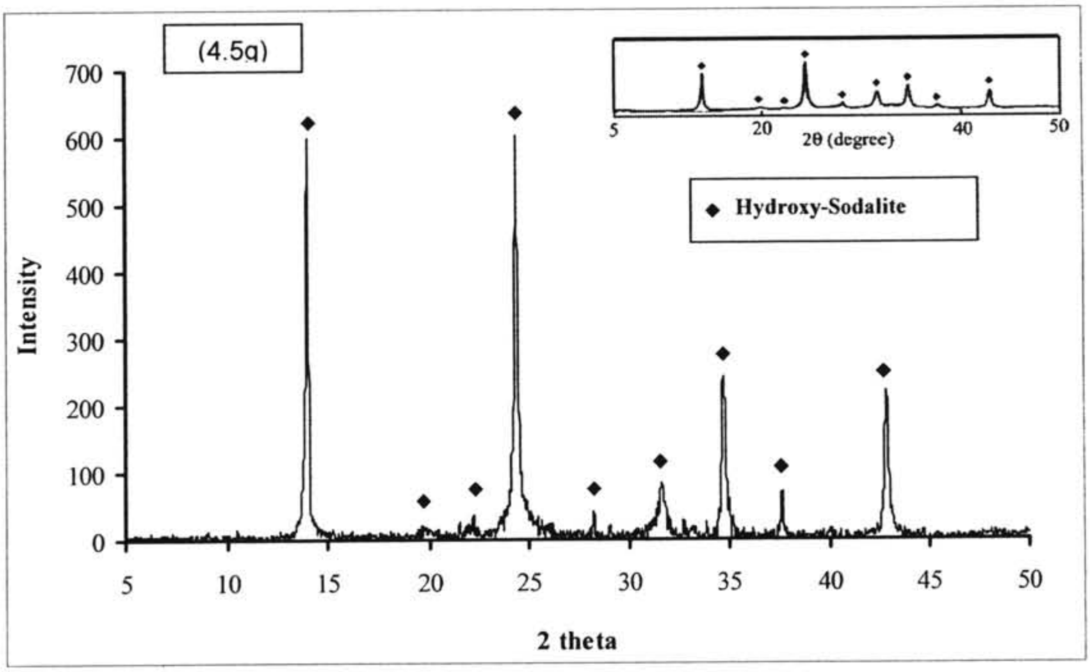


Figure 4.5 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of 1g/1000ml and vacuum seeding for 3 min under microwave radiation by static method at 105°C for a) 5, b) 10, c) 15, d) 20, e) 25, f) 30 min and g) XRD pattern of hydroxyl-sodalite phase.

4.2.2 Effect of synthesis temperature

It is well known that synthesis temperature influences other factors in the zeolite synthesis and the zeolite formation. For example, a decrease of the induction time length and an increase of crystallization rate are resulted from the increase of the synthesis temperature (Kuanchertchoo, N. *et al.*, 2006).

In this work, the effect of synthesis temperature at 60°, 75°, 90° and 105°C was studied with fixing the formula of precursor solution (SiO_2:Al_2O_3:3Na_2O: 410H_2O), the suspension concentration of NaA seed crystal (1 g/water 1000 mL) and the seeding time (3min). For the growth mechanism, the amorphous gel layer can transform to the crystalline layer, inter-growth of cubic layer, that is resulted form an increase of the synthesis time. Although the well-defined crystalline layer is not completely presented, the inter-growth of cubic morphology of NaA begins to form at 90 min when the synthesis temperature is 60°C (Fig. 4.2c). If the synthesis temperature increases to higher, 75°, 90° and 105°C, the synthesis times needed are only 30, 10 and 5 min, respectively, to form the inter-growth cubic layer. Thus, the increase of the synthesis temperature leads to a decrease of the synthesis time. An increase of the temperature results in a shortening of the crystallization time because crystallization is an activated process, within certain limits, temperature has a positive influence on the zeolitezation process (Renso, F. *et al.*, 1998.).

4.2.3 <u>Effect of seeding suspension concentration</u>

Suspension concentration has significant effect on the quality of the seeding layer and the performance of the zeolite membranes. When the suspension concentration is too low, the support surface was not completely covered. Therefore, the seeded support surface cannot provide enough nuclei to form a continuous zeolite membrane (Huang, A. *et al.*, 2004). In this experiment, the suspension concentrations of 1, 2, 3 g/l were used for vacuum seeding. The support was seeded with constant seeding pressure difference of 0.0325 MPa for 3 min seeding time.

Figures 4.6 a-c, are the micrographs of the as-synthesized membrane prepared at 60°C microwave temperature for 90 min, using seed suspension of 1, 2 and 3 g/l, respectively. It was shown that the suspension concentration of 3g/l gave another layer on the top of the first one and started to form cluster.

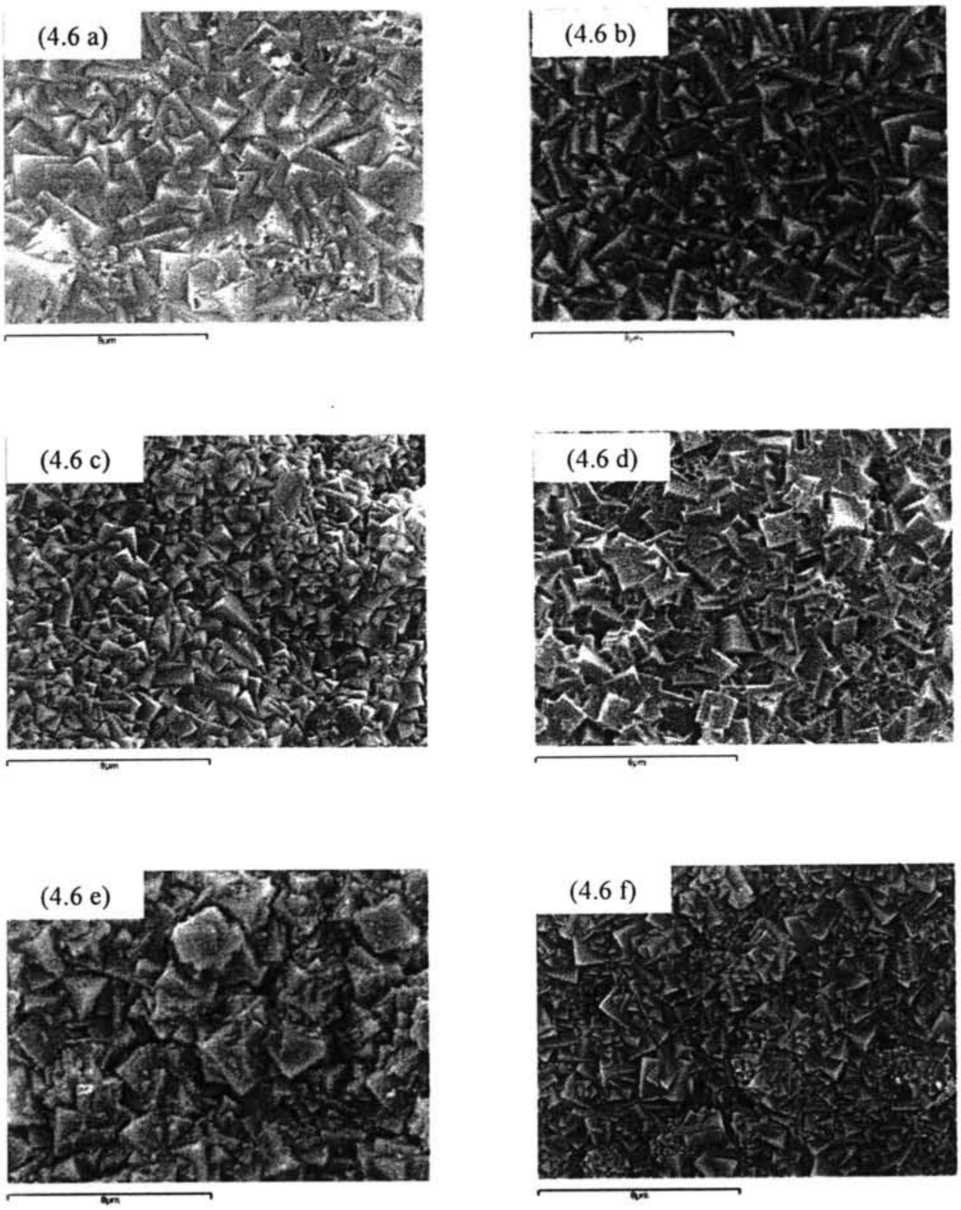


Figure 4.6 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of a)1, b) 2 and c) 3g/1000ml and vacuum seeding for 3 min under microwave radiation by static method at 60°C for 90min and d) 1, e) 2 and f) 3g/1000ml under microwave radiation by static method at 75°C for 45 min.

When increasing microwave temperature to 75°C for 45 min, the growth trend was similarly to those carried out at 60°C. Figures 4.6d-f show NaA membrane synthesized from using seeding suspension concentration of 1, 2 and 3 g/l, respectively. It was found that the membrane layers were not completely covered to form continuous membrane when less than 3 g/l of suspension concentration (Fig. 4.6d-e) was used, comparing to continuous membrane and cluster of second layer obtained from using 3 g/l of suspension concentration (Fig. 4.6f).

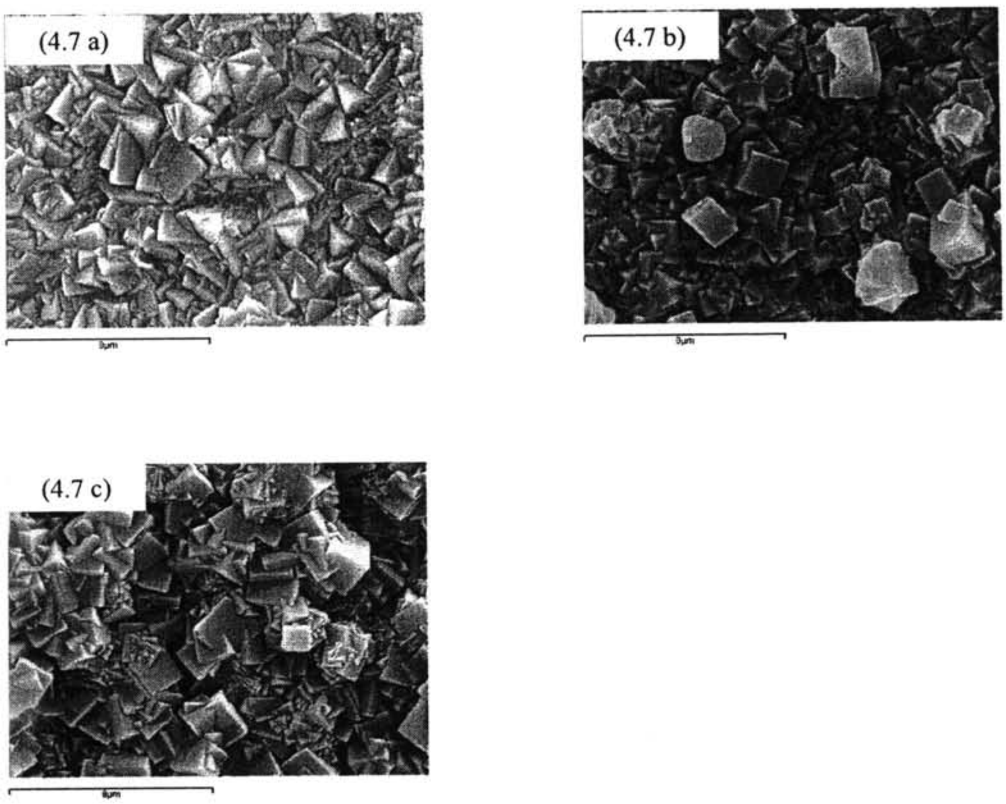


Figure 4.7 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of a) 1, b) 2 and c) 3g/1000ml and vacuum seeding for 3 min under microwave radiation by static method at 90°C for 25 min.

Figures 4.7a-c show membrane layer synthesized at 90°C for 25 min with seeding suspension concentration of 1, 2 and 3 g/l, respectively, for 3 min seeding time. The growth trend was similarly to the results obtained at 60° and 75°C microwave temperature. However, increasing the temperature to 105°C, NaA zeolite was transformed to hydroxy-sodalite phase. Moreover, if seeding suspension concentration increased, hydroxy-sodalite crystal size would also increase, as shown in fig. 4.8 a-c for the seeding suspension concentration of 1, 2 and 3 g/l, respectively.

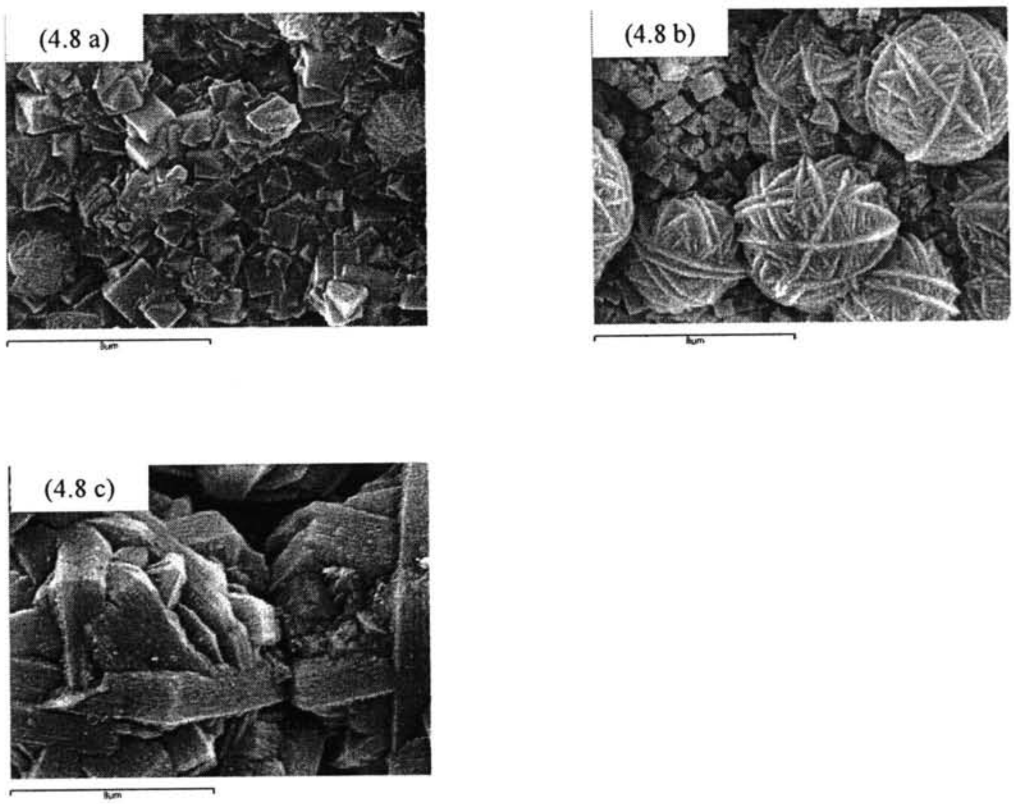


Figure 4.8 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of a) 1, b) 2 and c) 3g/1000ml and vacuum seeding for 3 min under microwave radiation by static method at 105°C for 25 min.

As indicated above, seeding suspension concentration is one important factor of seed crystal arrangement on zeolite membrane. When seeding suspension concentration is too low, the support surface is not continuously covered. On contrary, when seeding suspension concentration is higher, the seeding layer is more compact and dense.

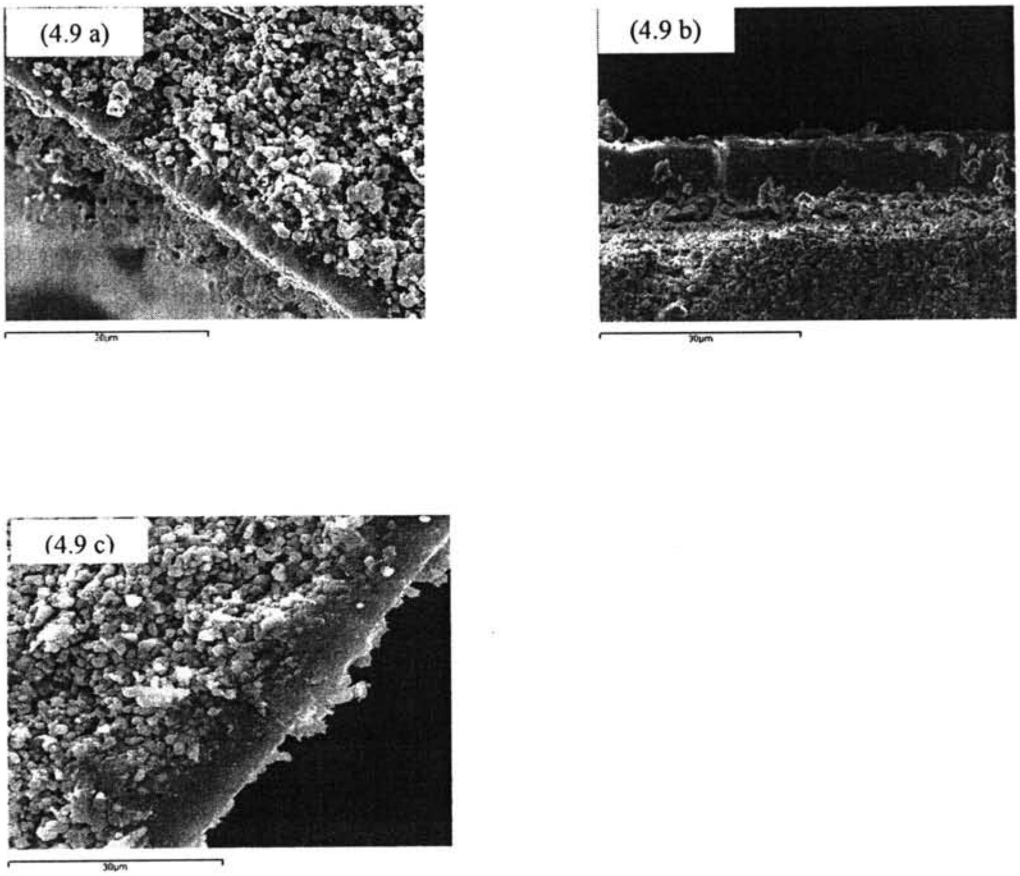


Figure 4.9 SEM micrographs of thickness 0f NaA zeolite membrane synthesized on substrate using vacuum seeding time 3 min and seed suspension concentration of a)1g/1000ml, b)2/1000ml and c)3/1000ml under microwave radiation by static method at 60°C for 150 min with the membrane layer thickness of a)3.9-4.2, b)7.8-8.4 and c) 9.6-9.7 μm.

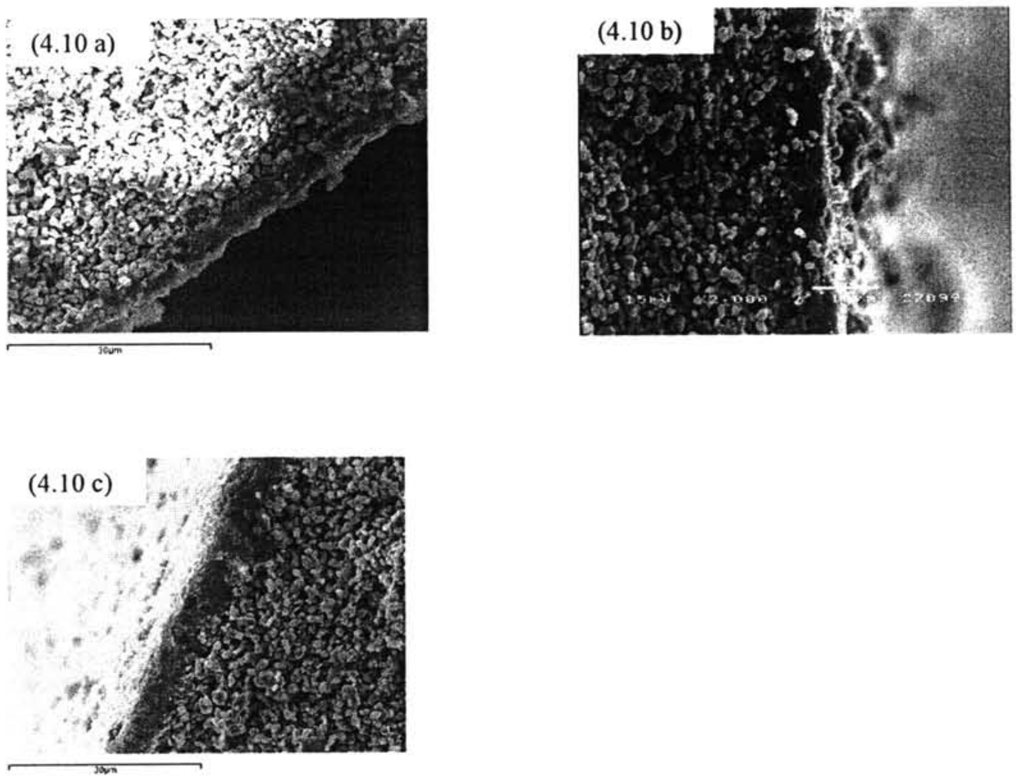


Figure 4.10 SEM micrographs of thickness of NaA zeolite membrane synthesized on substrate using vacuum seeding time 3 min and seed suspension concentration of a)1g/1000ml, b)2/1000ml and c)3/1000ml under microwave radiation by static method at 75°C for 60 with the membrane layer thickness of a)3.0-3.2, b)4.7-5.3 and c) 6.1-7.7 μm.

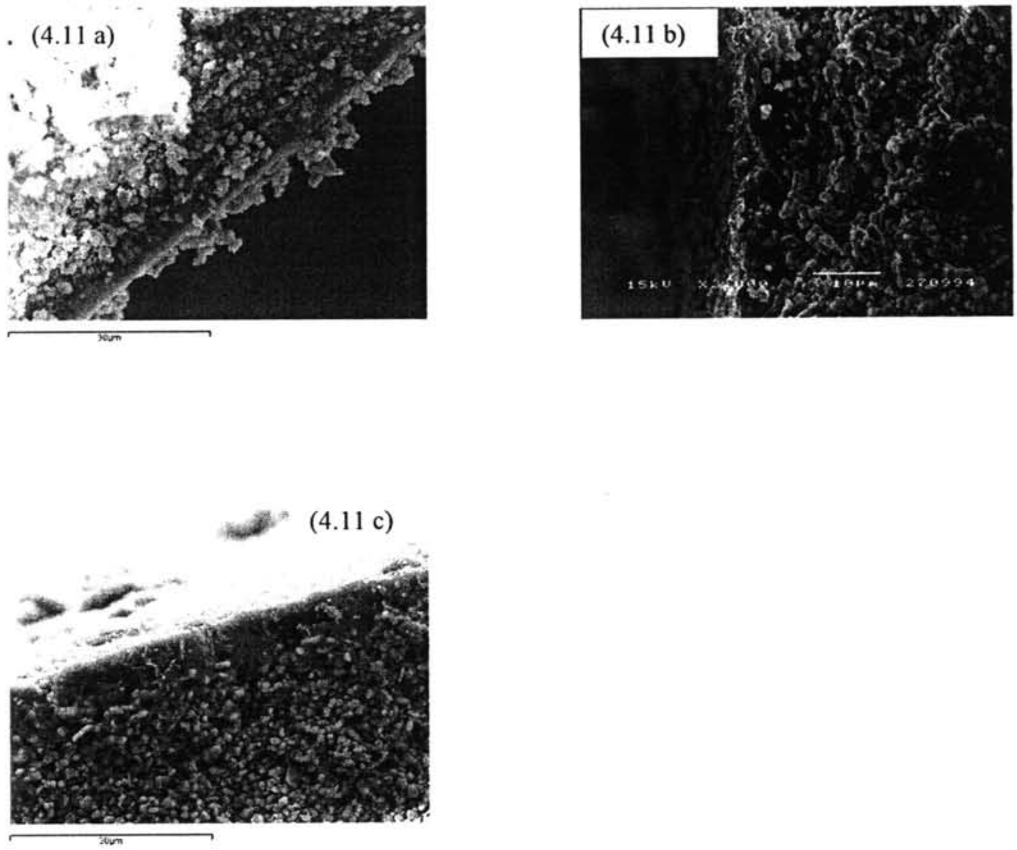


Figure 4.11 SEM micrographs of thickness 0f NaA zeolite membrane synthesized on substrate using vacuum seeding time 3 min and seed suspension concentration of a) 1g/1000ml, b) 2/1000ml and c) 3/1000ml under microwave radiation by static method at 90°C for 15 min with the membrane layer thickness of a)2.70, b)5.9 and c) 6.6-6.8 μm.

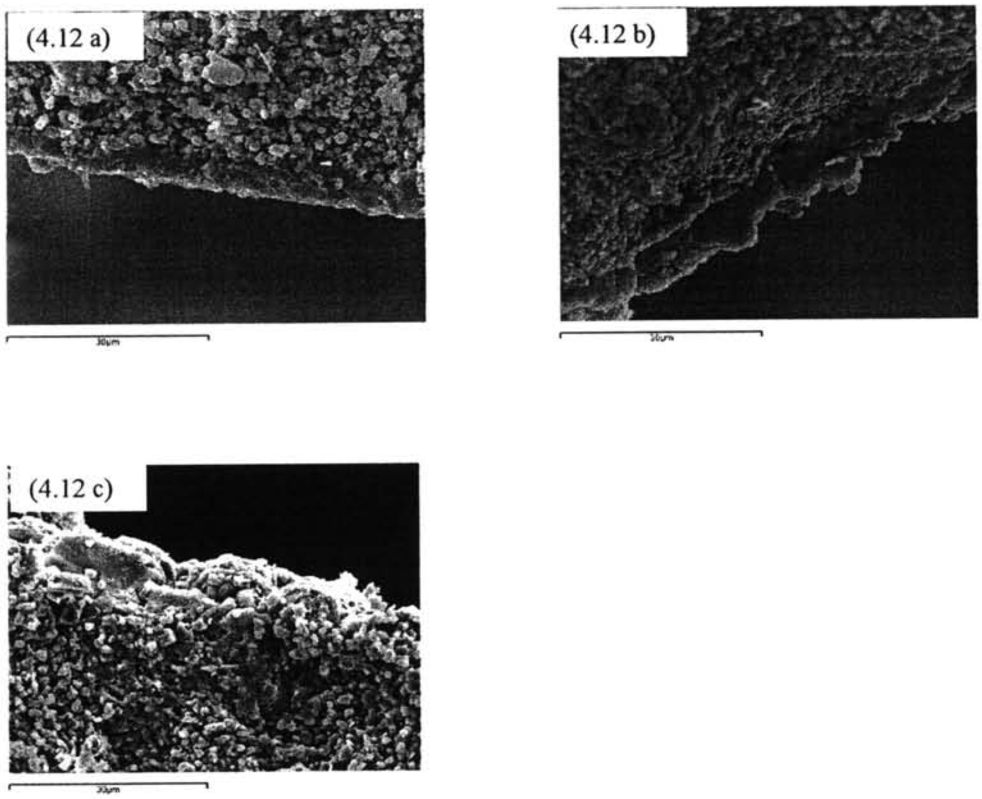


Figure 4.12 SEM micrographs of thickness 0f NaA zeolite membrane synthesized on substrate using vacuum seeding time 3 min and seed suspension concentration of a)1g/1000ml, b)2/1000ml and c)3/1000ml under microwave radiation by static method at 105°C for 15 min with the membrane layer thickness of a) 4.5, b) 6.1 and c) 7.7 μm.

Table 1 Thickness of as-synthesized membranes synthesized using different conditions

Synthesis temperature & Synthesis time	Membrane thickness (μm)		
	1g/l seed Suspension Concentration	2g/l seed Suspension Concentration	3g/l seed Suspension Concentration
60°C for 150 min	3.9-4.2	7.8-8.4	9.6-9.7
75°C for 60 min	2.5-3.2	3.6-4.0	3.8-5.1
90°C for 15 min	2.7	5.9	6.6-6.8
105°C for15 min	4.5	6.1	7.7

Fig.4.9 , 4.10, 4.11 and 4.12 showed the thickness of NaA zeolite membrane layer that were varied on time. However, each of temperature was varied on seed suspension concentration from 1, 2 to 3 g/l. The results showed the same trend in all set of temperature that the thickness membrane will increase when increase seed suspension concentration.

4.2.4 Effect of seeding time

Seeding time also influences on the properties of the seeding layer and the zeolite membrane. The seeding layer is too thick and some cracks easily occur when the coating time is too long, resulting in zeolite membranes with poor separation properties. Contrarily, the seeding layer is non-continuous when the coating time is too short, also resulting in the zeolite membrane with poor performance (Huang, A., *et al.*, 2004).

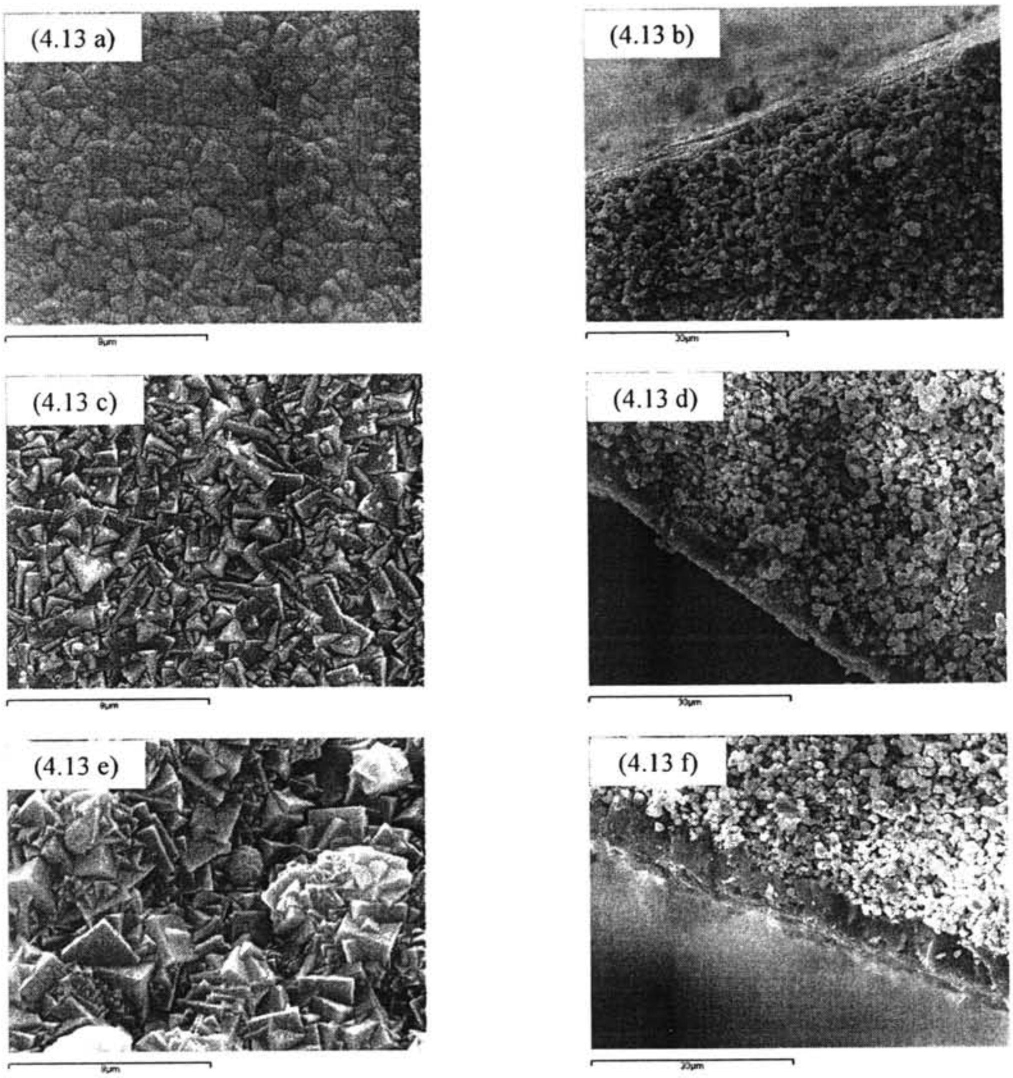
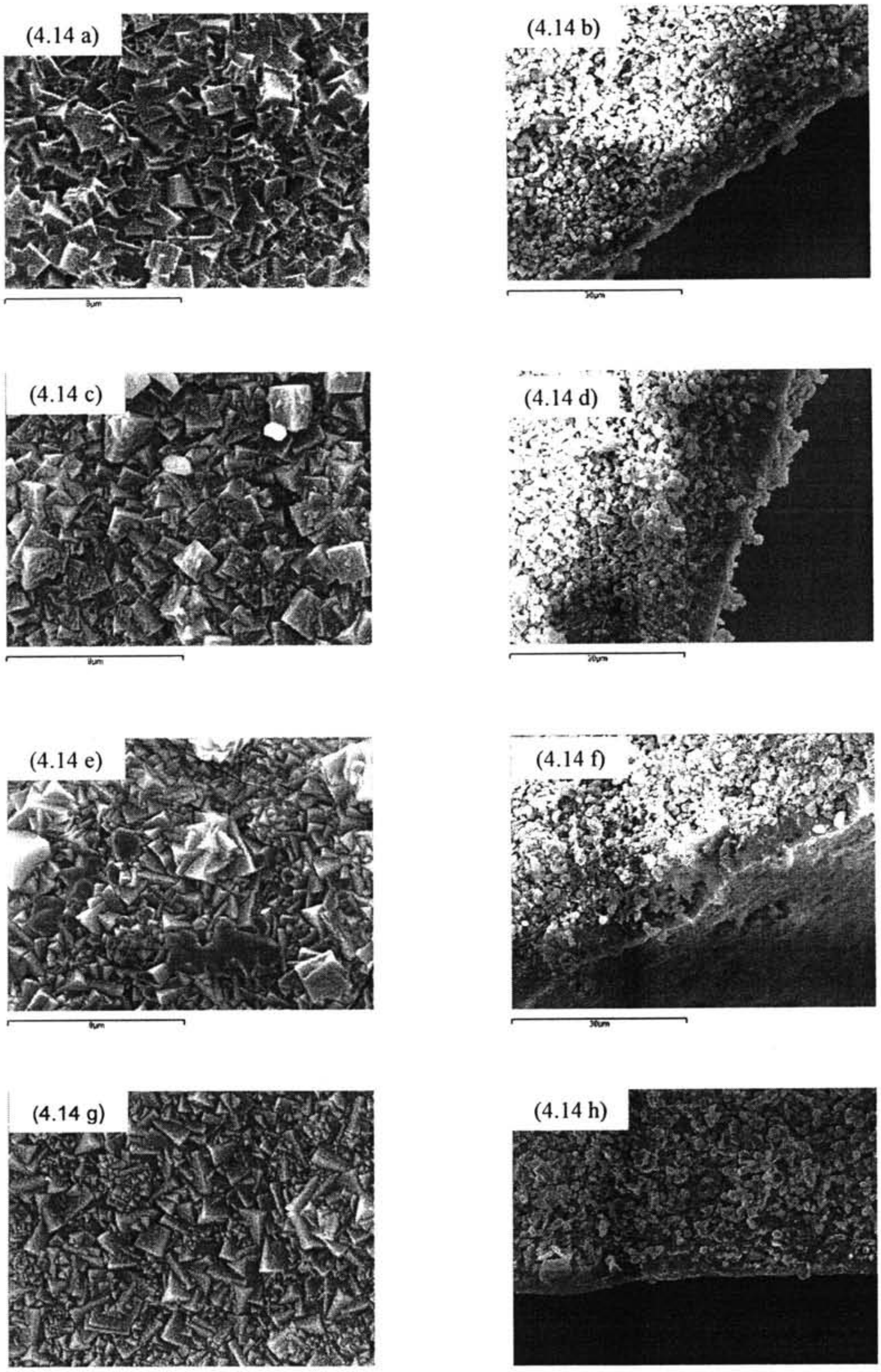


Figure 4.13 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of 1g/1000ml and vacuum seeding for a) 3, c) 4, e) 5 min under microwave radiation by static method at 60°C for 60 min with the layer thickness of b)0-1.3, d)3.3-4.1 and f)5.3-5.8 μm.

Figures 4.13 a, c and e show NaA membrane synthesized using 3, 4 and 5 min. seeding time, respectively, 1g/l seeding suspension concentration, 60°C microwave temperature for 60 min synthesis time. The results indicate that 5 min seeding time provides denser NaA seeding layer.


(4.14 a)
(4.14 b)
(4.14 c)
(4.14 d)
(4.14 e)
(4.14 f)
(4.14 g)
(4.14 h)

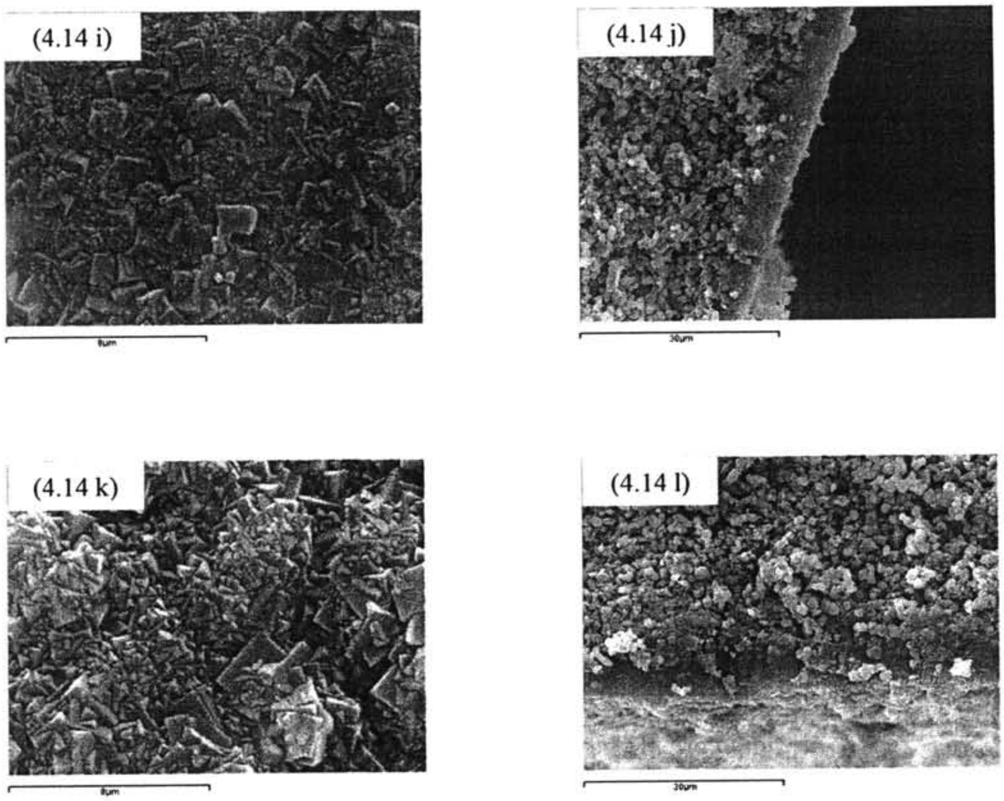


Figure 4.14 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of 1g/1000ml and vacuum seeding for a) 3, c) 4, e) 5 min under microwave radiation by static method at 75°C for 60 min with the membrane layer thickness of b) 2.5-3.2, d) 3.6-4.0, f) 3.8-5.1 µm, and vacuum seeding for g) 3, i) 4 and k) 5 min under microwave radiation by static method at 90°C for 30 min with the membrane layer thickness of h) 1.6-2.3, j) 4.5-5.3 and l) 5.7-6.6 µm.

Figures 4.14 a, c and e (synthesized at 75°C for 60 min) and Fig. 4.14 g, i and k (synthesized at 90°C for 30 min) show NaA membrane synthesized using 1g/l of seeding suspension concentration for 3, 4 and 5 min. seeding time, respectively. The results also show that 5 min seeding time provides dense NaA layer with another layer.

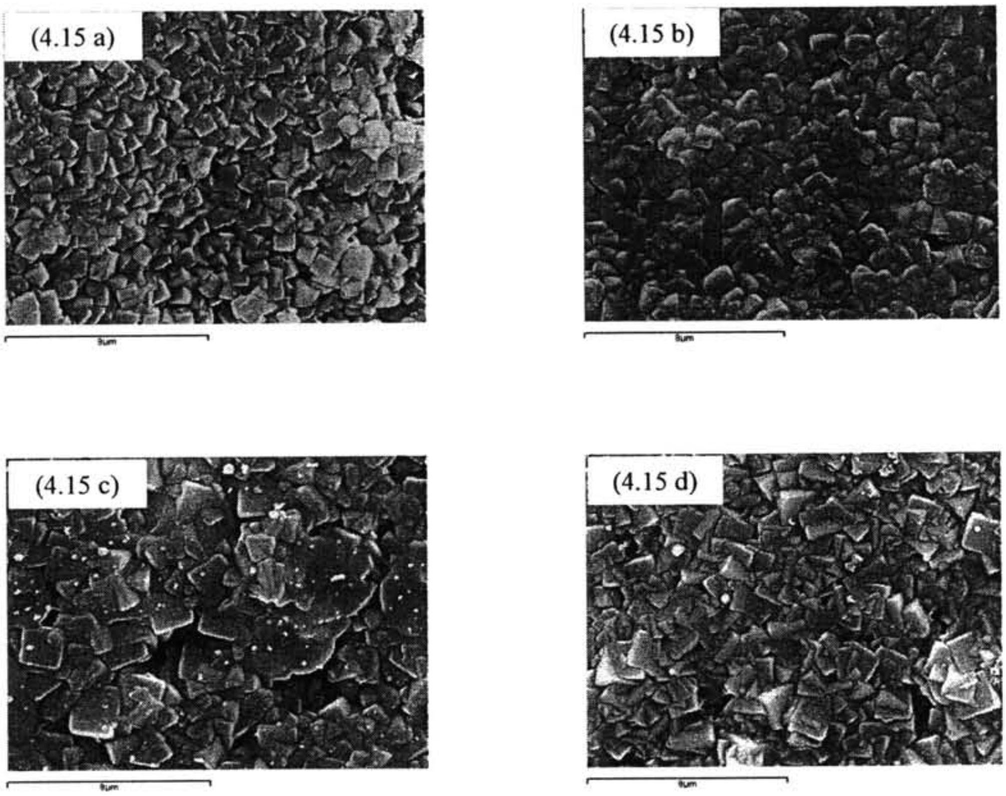
Table 2 Thickness of as-synthesized membranes synthesized using different conditions

Synthesis temperature& Synthesis time	Membrane thickness (μm)		
	3 min seeding time	4 min seeding time	5 min seeding time
60°C for 60 min	0-1.3	3.3-4.1	5.3-5.8
75°C for 60 min	2.5-3.2	3.6-4.0	3.8-5.1
90°C for 30 min	1.6-2.3	4.5-5.3	5.7-6.6

In case of the membrane thickness, fig. 4.13 a, c, e, and fig. 4.14 a, c, e, g. i and k, it was found that the thickness increased with an increase of the seeding time, as summarized in table 1. Figures 4.13 f, 4.14 f and 4.14 l display the seeding layer thickness resulted from long seeding time. The thickness of synthesized membrane obtained from using high synthesis temperature, long synthesis time and long seeding time, as can be seen in fig. 4.14 l, demonstrates a few cracks. It can be concluded that if membrane is too thick, some cracks may easily occur, giving poor performance of membrane. On contrary, the thickness layer may be disable to measure due to too thin or non-continuous layer resulted when the seeding time is too short. An example can be seen in fig. 4.13b showing the SEM image of the membrane synthesized at low synthesis temperature and low synthesis time using 3 min seeding time. This condition is not enough to form continuous membrane, as compared to the one using 4 min seeding time (fig. 4.13d).

4.3 NaA Zeolite Membrane Synthesis by Dynamic Method of Microwave Technique

In a previous report (Tsutsumi, K. *et al.*, 2000) NaA zeolite membrane synthesized by circulated method using plate heater showed the globular morphology. A-type zeolite crystals grew with globular crystal of about 10 mm in diameter piling up on each other on the glass substrate and 5 mm in diameter on PTFE substrate. These globular crystals were found to further agglomerate, forming globular lumps of 30–60 mm and combining with each other. In this experiment, it is thus focused on the morphology comparison of NaA zeolite membrane synthesized between static and dynamic methods using microwave technique. Furthermore, degree of stirring is studied to observe the morphology effect.



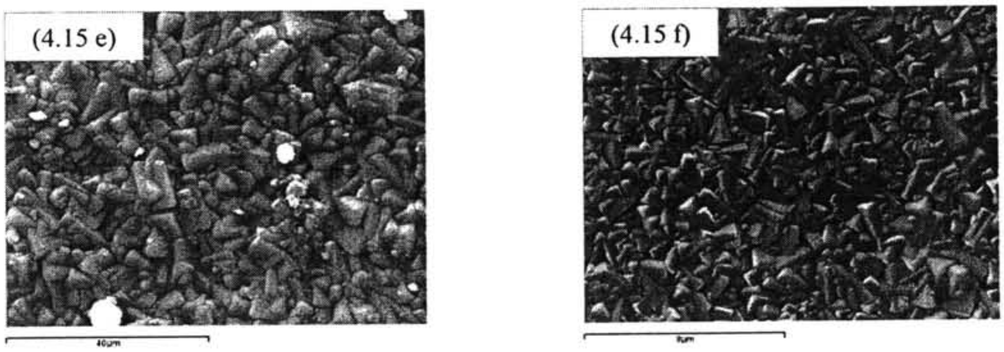
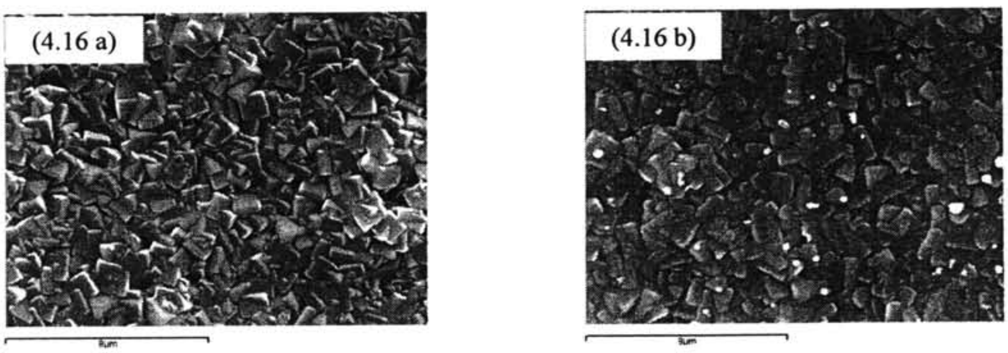


Figure 4.15 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of a) 1, b) 2 and c) 3g/1000ml, and vacuum seeding for 3 min under microwave radiation by static method at 90°C for 25 min.

Figures 4.15a-f show the morphology of NaA membrane synthesized at 90°C for 5, 10, 15, 20, 25 and 30 min, respectively, by the static method using microwave hydrothermal treatment. In the case of the dynamic method, the obtained morphology is not as round as observed in the report of Tsutsumi, K. *et al.*, 2000. The reason might be from the fact that the magnetic stirrer used in the vessel springs throughout the reaction time instead of moving around.



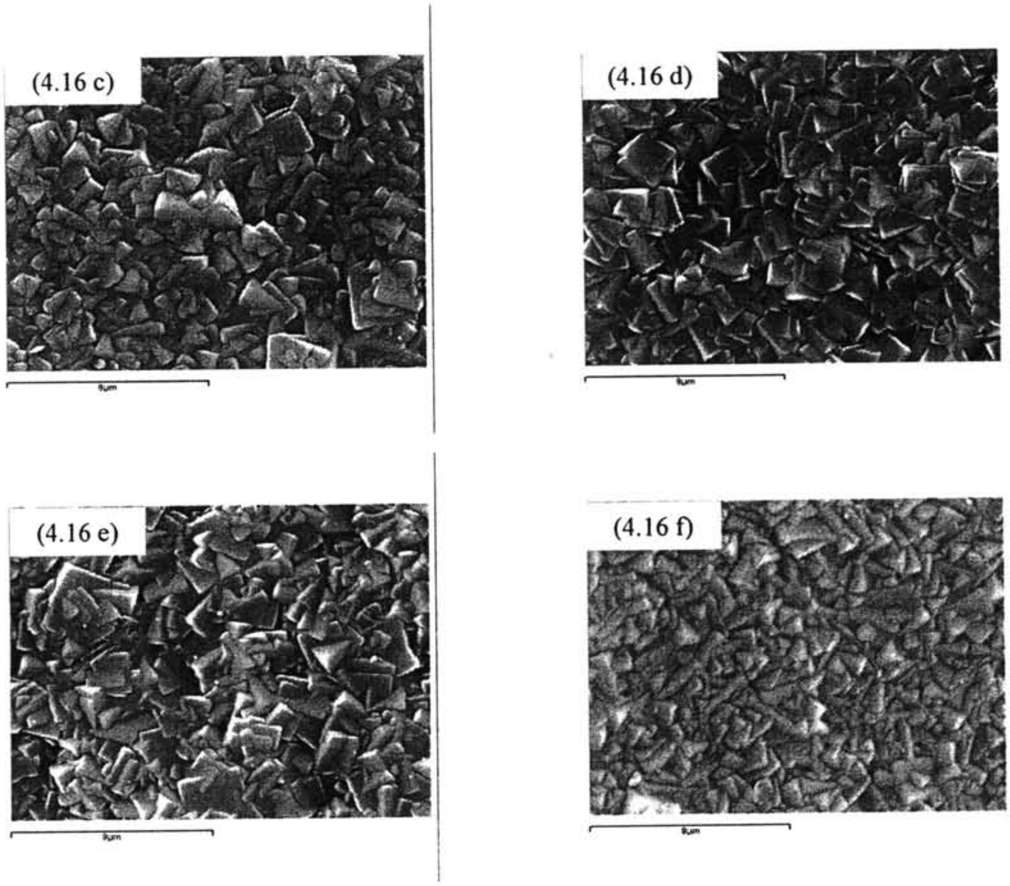


Figure 4.16 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration 3g/1000ml and vacuum seeding for 3 min under microwave radiation by dynamic method (30% stirring) at 90°C for a) 5, b) 10, c) 15, d) 20, e) 25 and f) 30 min.

Figures 4.16 a-f show the morphologies of NaA membranes synthesized at 90°C for 5, 10, 15, 20, 25 and 30 min, respectively, by dynamic method of microwave hydrothermal treatment with 30% stirring. The results indicate no difference on morphology when compared with the static method. NaA zeolite is still rectangular shape, as found in the static system. It is different from Tsutsumi's study, showing spherical shape (Tsutsumi, K. *et al.*, 2000). As given earlier, the reason is due to the small magnetic stirrer jumping all over the vessel and a little force created the magnetic stirrer, only agitating the solution, not stirring.

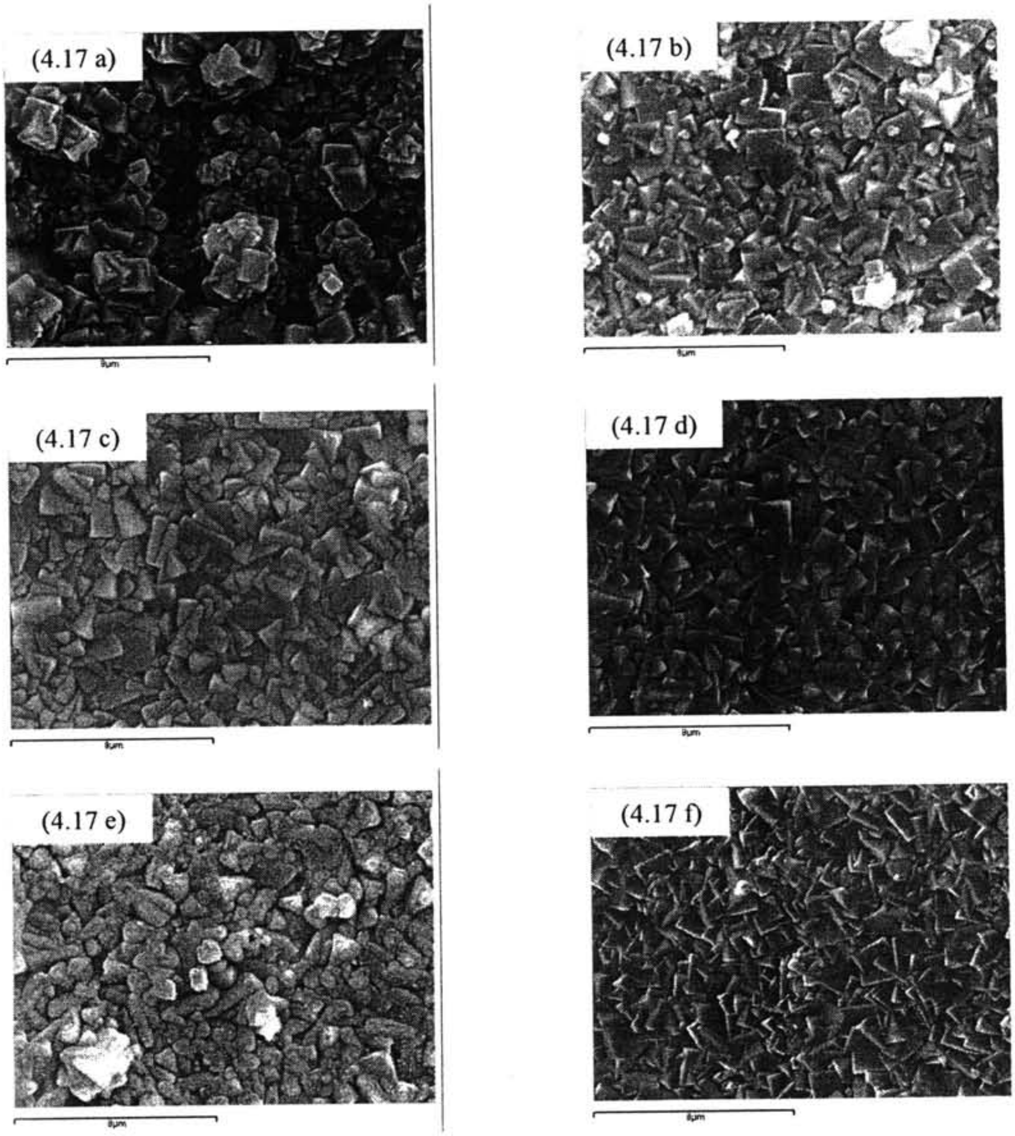
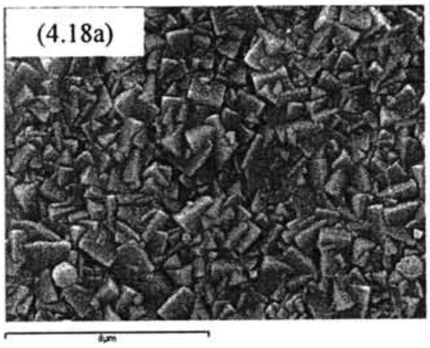
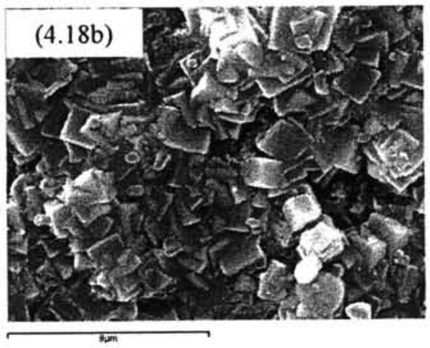


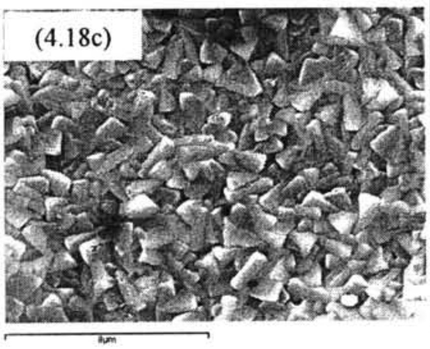
Figure 4.17 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of 3g/1000ml and vacuum seeding for 3 min under microwave radiation by dynamic method (60% stirring) at 90°C for a) 5, b) 10, c) 15, d) 20, e) 25 and f) 30 min.

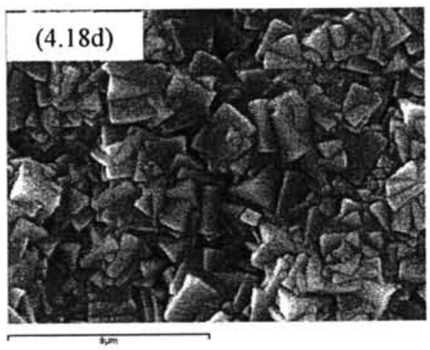
Figures 4.17 and 4.18 show the morphology of NaA membrane synthesized at 90°C for 5, 10, 15, 20, 25 and 30 min, respectively, by dynamic method of microwave hydrothermal treatment with 60 and 90% stirring. The morphology was still the same in rectangular shape although the degree of stirring was increased.

However, the stirring degree slightly influences the size of crystals on membrane, as summarized in table 2.









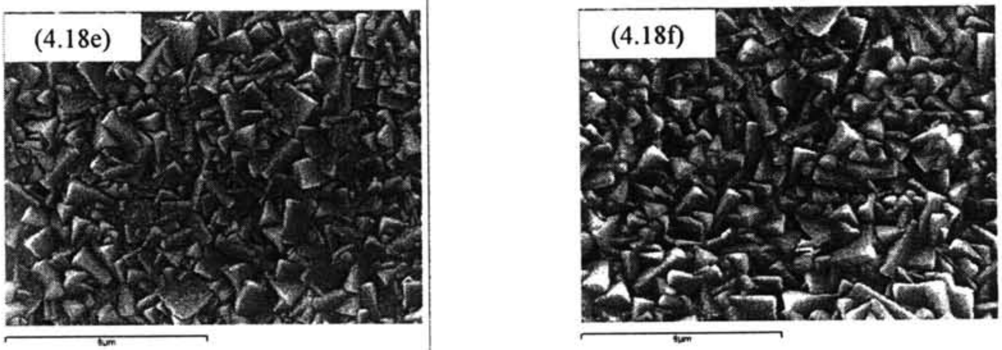


Figure 4.18 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of 3g/1000ml and vacuum seeding for 3 min under microwave radiation by dynamic method (90% stirring) at 90°C for a) 5, b) 10, c) 15, d) 20, e) 25 and f)30 min.

Table 3 Effect of agitation on the average crystal size of NaA zeolite membrane synthesized for 30 min synthesis time

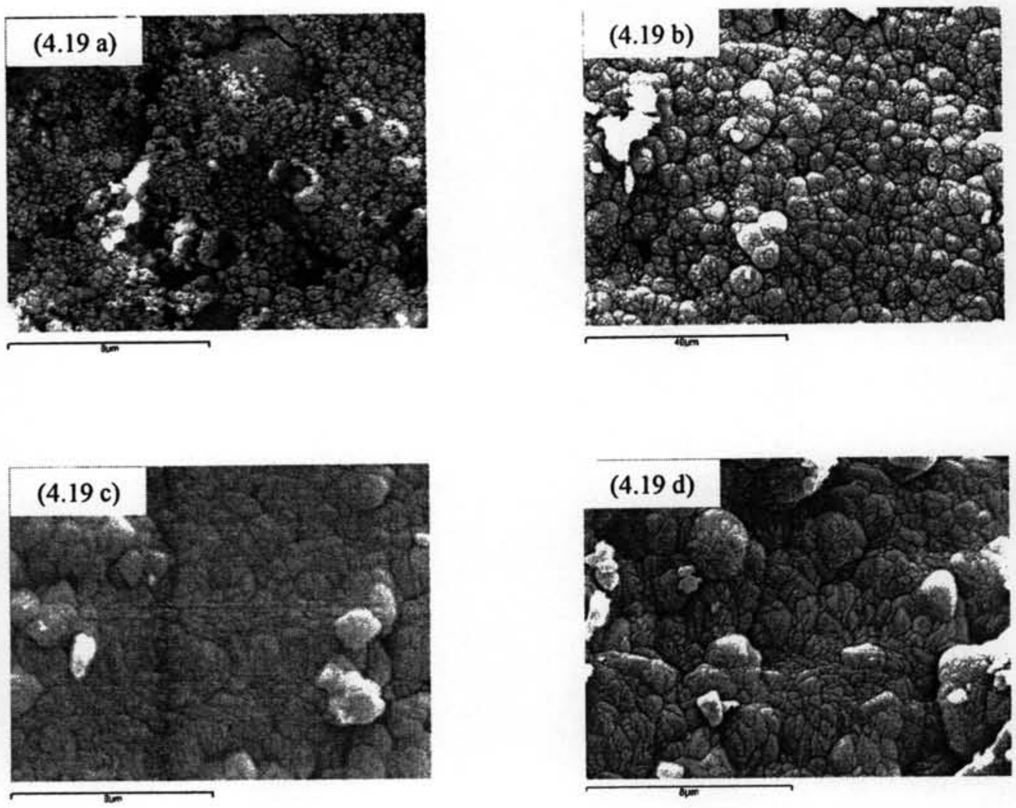
Synthesis Method	Average Crystal Size of NaA zeolite on membrane(μm)
Static	1.7-1.9
Dynamic (30% stirring)	1.5-1.7
Dynamic (60% stirring)	1.2-1.4
Dynamic (90% stirring)	1.6-2.0

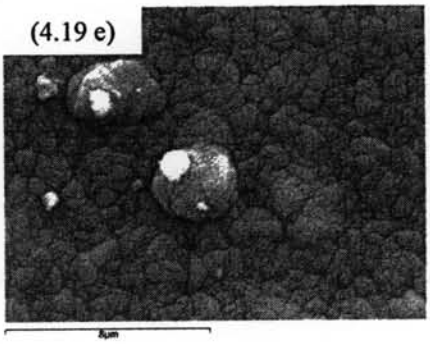
The results show that increasing degree of agitation affects to a decrease of the particle size. The average crystal size of agitation state is smaller than the static state. From the static stage up to 30% stirring stage, average crystal size decrease about 0.2 μm. Increase stirring percentage from 30 to 60 results in the average crystal size decrease about 0.3 μm. On the other hand, increase of the stirring percentage to 90 causes the inversion. The average crystal size not only increases, but also has the similar size to those obtained using the static stage. The assumption could be that the stirring is too fast to agitate the precursor solution, or is close to the static stage, giving the size alike.

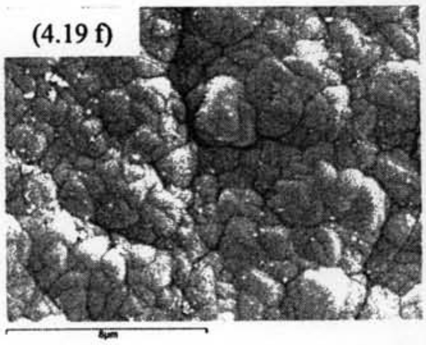
4.4 NaA Zeolite Membrane Synthesis by Conventional Hydrothermal and Electrophoresis Techniques.

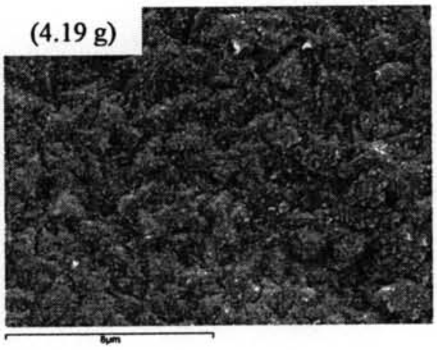
4.4.1 <u>NaA Zeolite Membrane Synthesis by Conventional Hydrothermal Technique</u>

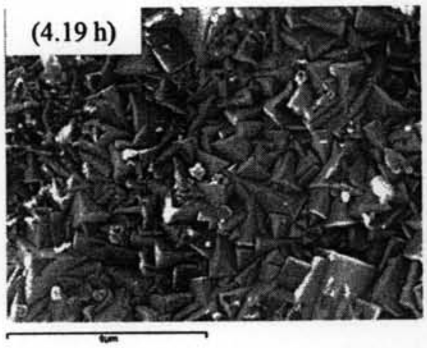
With this technique, various synthesis times from 1 to 24 h were studied at 60°C synthesis temperature. The support tube was seeded by vacuum seeding with 3 g/l seed suspension concentration for 3 min.

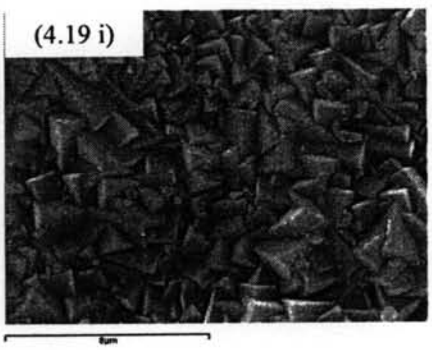


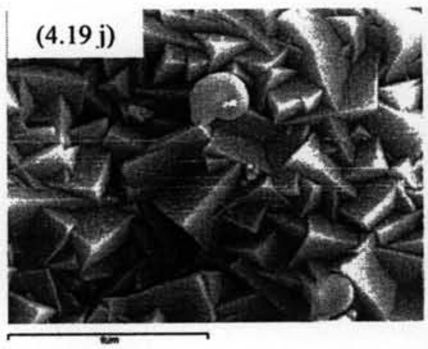

(4.19 e)

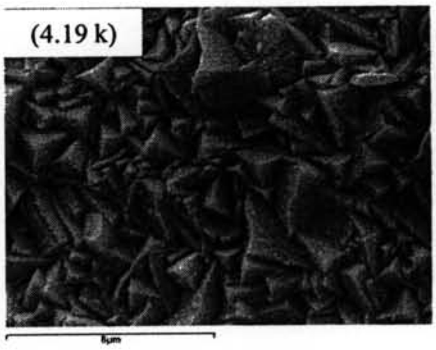

(4.19 f)


(4.19 g)


(4.19 h)


(4.19 i)


(4.19 j)



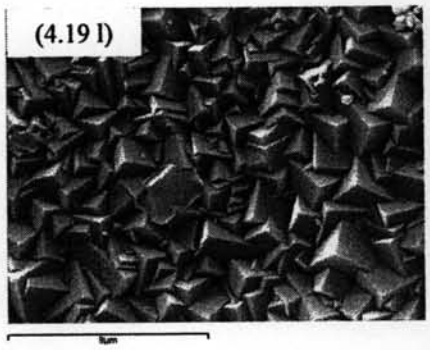
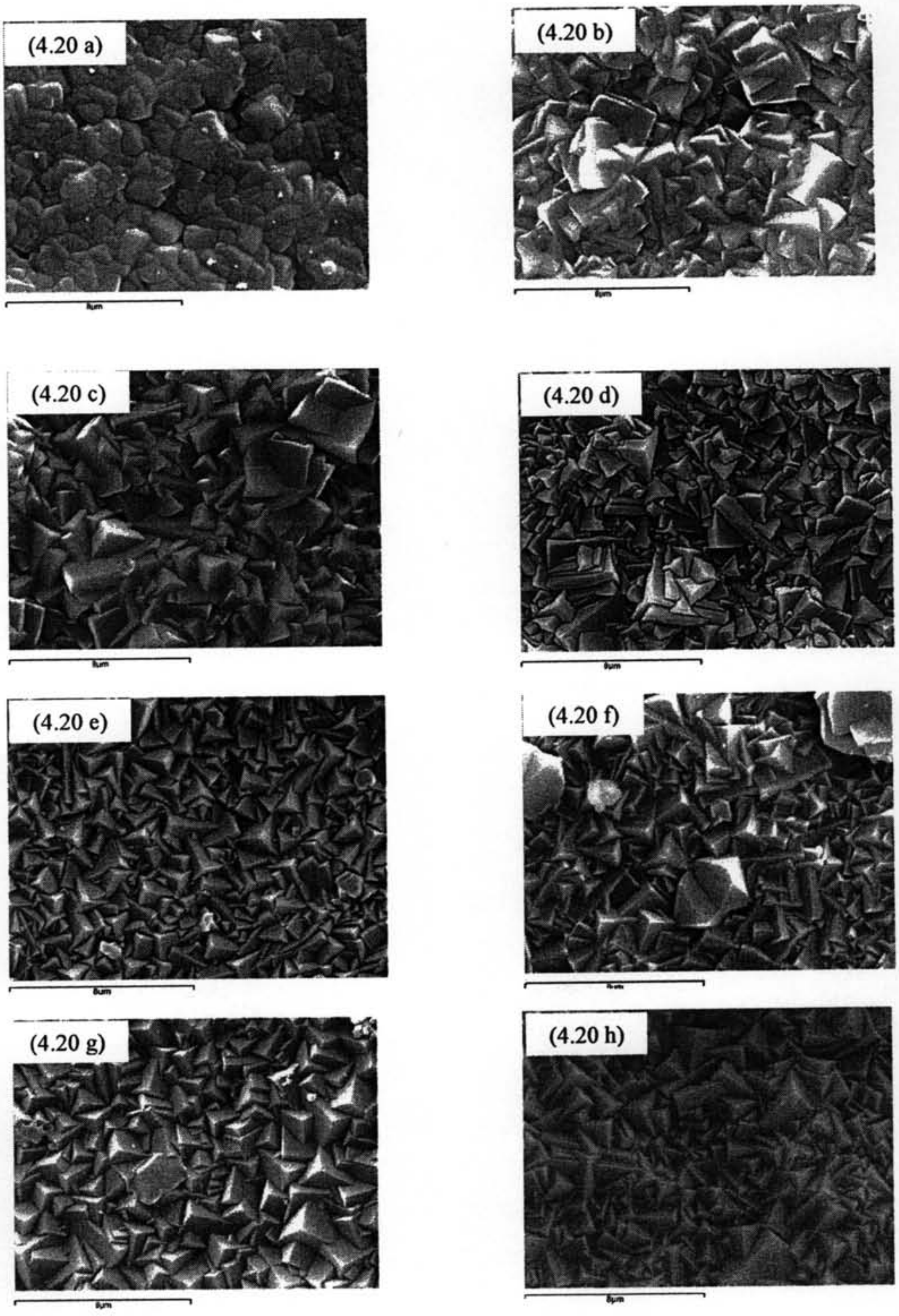


Figure 4.19 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of 3g/1000ml and vacuum seeding for 3 min under conventional hydrothermal technique at 60°C for a) 1, b) 2, c) 3, d) 4, e) 5, f) 6, g) 9, h) 12, i) 15, j) 18, k) 21 and l) 24 h.

Figures 4.19 a-l are the SEM images of NaA membranes synthesized for 1, 2, 3, 4, 5, 6, 9, 12, 15, 18, 21 and 24 h synthesis time, respectively. The results show that the NaA zeolite crystal in globular shape of about 0.6-0.9 μm in diameter was found within 2h. When the synthesis time goes on, these globular crystals were found to further agglomerate, forming globular lumps of 1.4-1.8 μm and combining with each other within 6 h. The NaA zeolite cystal started to grow in the cubic shape in 9 h. Within 12 h, the cubic crystal displayed the intergrowth layer, but it did still not give complete surface. The edges of cubic were sharp ridge at 18h. Even crystallization is performed for a longer period of time, 24 h, NaA zeolite membrane was formed without generation another phase. Instead, it showed complete intergrowth cubic membrane.

4.4.2 <u>NaA Zeolite Membrane Synthesis by Electrophoresis Technique</u>

With this technique, various synthesis times from 1 to 24 h were studied at a fixed synthesis temperature of 60°C. The support tube was seeded by vacuum seeding with 3 g/l seed suspension concentration for 3 min, similar to the study by the conventional hydrothermal technique.


(4.20 a)
(4.20 b)
(4.20 c)
(4.20 d)
(4.20 e)
(4.20 f)
(4.20 g)
(4.20 h)

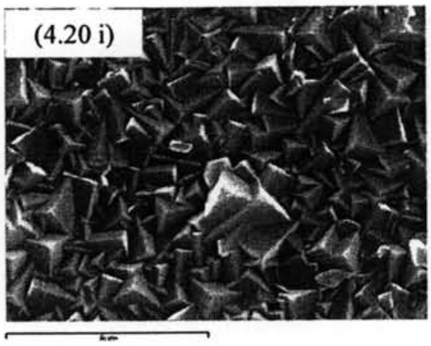


Figure 4.20 SEM micrographs of NaA zeolite membrane synthesized on substrate using seed suspension concentration of 3g/1000ml and vacuum seeding for 3 min under electrophoresis technique at 60°C for a) 1, b) 3, c) 6, d) 9, e) 12, f) 15, g) 18, h) 21 and i) 24 h.

Figures 4.20 a-i are the SEM images of NaA membranes synthesized at 1, 3, 6, 9, 12, 15, 18, 21 and 24 h synthesis time, respectively. Only 1 h, the membrane obtained was close to the cubic shape. It showed edges even they were still not sharp. However, these crystals were agglomerated and were more cubical than globular shape. The cubic layer was obtained within 3h, but it was obviously intergrown within 6 h. With this technique, even the synthesis time was increased continuously until 24 h, the secondary phase was not observed.

4.5 Comparison of NaA Zeolite Membranes Synthesized by Conventional Hydrothermal, Electrophoresis and Microwave Techniques.

Based on the above results, NaA zeolite membrane can be successfully synthesized using different techniques, viz. conventional hydrothermal technique, electrophoresis technique and microwave technique. The microwave technique provided the best performance in terms of using the shortest synthesis time because the thermal energy can transfer to the volume of material while the heat from conventional technique only transfers to the surface by convection, conduction and radiation (Bonaccorsi, L. *et al.*, 2003). Between the electrophoresis and the conventional hydrothermal techniques, the latter technique uses longer synthesis time than the other one to form the cubic NaA shape. The conventional hydrothermal treatment uses at least 9 h to form cubic shape while electrophoresis technique uses only 3 h. This reason could be rationalized that electrophoresis technique uses both the voltage and the current heat up, helping zeolite nuclei in the precursor solution move to the seeded support surface rapidly, as discussed in report of Huang, A. *et al.*, 2007.

In the case of the membrane characteristics, conventional and electrophoresis techniques provide more dense membrane than microwave technique. Moreover, most membranes also show better well-intergrowth and layer was defect free.