CHAPTER IV

ORIENTED NAA ZEOLITE MEMBRANE FORMATION AND PERFORMANCE USING SEEDING AND ELECTROPHORETIC TECHNIQUES

4.1 Abstract

Oriented NaA zeolite membranes have been successfully fabricated on a tubular α-Al_2O_3 support by secondary growth under electrical field. By the aid of seeding and the electric field, the morphology of the zeolite crystals and the membrane performance are improved. A uniform and dense columnar LTA crystal layer was formed. The XRD pattern shows the strong peak {222} of the preferred orientation in the overall membrane ranging from surface to porous alumina support layer. The effects of seeding time and electrical potential on the performance of the membrane were investigated. It was found that the preferred orientation affected the performance of NaA zeolite membrane, and high quality NaA zeolite membrane prepared using 1.5 min seeding time before crystallization at 333 K under 2V electric field gave the best membrane performance with a separation factor greater than 10,000 and 0.61 $kg/m^2.h$ of the flux.

4.2 Introduction

Recently, zeolite membranes have attached a great deal of attention due to their uniform microporous structure, good thermal stability, high mechanical strength, and high resistance to relatively extreme chemical environments [1, 2]. Several methods have been used to synthesize the membranes, such as hydrothermal synthesis [3-6], secondary growth [7-9], microwave synthesis [10-12], and the electrophoretic technique [13, 14]. The hydrothermal method usually needs only a single step; however, it was found to have some disadvantages, such as difficulty in controlling the nucleation on the surface support [15]. The obtained membranes are randomly oriented. Another technique in making a NaA zeolite membrane, called the secondary growth or seeding method, has been introduced as an alternative approach to grow zeolite crystals preferentially on a support surface [16]. Microwave synthesis is an alternative not only for limiting the synthesis duration, but also for improving the properties of the zeolite membrane [17-19]. However, the performance of the zeolite membrane prepared by this method still fluctuates without the aid of the seeding technique [20].

Electrophoresis deposition has been found to be a simple and effective technique for thin film preparation [21-22]. The charged particles can migrate to the support surface homogeneously and rapidly under the action of the applied electric field, resulting in uniform and dense membranes [20]. This technique is not only for coating the charged particle on the substrate before hydrothermal treatment, but is also for driving the zeolite particles to migrate to the support surface during hydrothermal synthesis [23-24], resulting in the formation of an oriented, continuous layer of zeolite seeds on the support to act as nuclei for the crystal growth step [15]. For application, the performance of zeolite membranes and sensors is influenced by the orientation of zeolite crystals of the film. The orientation will affect the diffusion path through the membrane and the adsorption kinetics of a chemical sensor consisting of a supported zeolite film [25].

In this paper, we demonstrate that, with the aid of the seeding technique, highly oriented NaA zeolite membranes can be prepared on α-Al_2O_3 support using the electrophoretic technique. The effects of potential and crystal seeds on membrane morphology, orientation and thickness were investigated, and the performance of the synthesized membranes, relative to those effects, is also studied using the pervaporation technique.

4.3 Experimental

4.3.1 Materials

Fumed silicon dioxide (SiO_2, surface area 474 m^2/g, average particle size 0.007 μm) and aluminum hydroxide hydrate ($Al(OH)_3.xH_2O$, surface area 51 m^2/g)

were purchased from Aldrich, Co. Ltd. Sodium hydroxide (NaOH) from Lab-Scan Co., Ltd. was used as the base catalyst. Homemade porous α alumina tubes (11 mm outer diameter, 9 mm inner diameter, 6 mm length, 0.3 μm pore radius on average with 38% porosity) were used as supports and were supplied by MTEC.

4.3.2 Equipment

All samples were characterized using scanning electron micrographs (SEM) on a JEOL 5200-2AE (MP15152001) and wide angle X-ray diffractograms (WXRD) on the D/MAX 2000 series of the Rigaku X-Ray Diffractometer system using CuK_α as a source. The separation factor calculated from the quantities of water and ethanol was determined using gas chromatography (Win Lab III, Perichorm).

4.3.3 NaA zeolite membrane synthesis

The porous Al_2O_3 tube was cleaned and washed with deionized water by ultrasonication for 15 min to remove any dirt on the surface. The support was dried at 363 K for 24 h and calcined at 673 K for 3 h to burn off any impurities on the support surface before coating with seed crystals. Membrane synthesis was carried out by first coating the NaA zeolite crystal on the alumina substrate, followed by immersing the coated substrate into a vessel containing the solution mixture for further microwave heat treatment.

Vacuum seeding [26] was used to coat the NaA seed onto the support tube. The suspension was prepared by dispersing 7 g of NaA zeolite (particle size ~0.1-0.2 μm) synthesized using the SiO_2:Al_2O_3:$3Na_2O$:$410H_2O$ formula described in ref. 27, into 1000 ml of water with ultrasonic treatment. The seeding layer was coated onto the outer surface of the support tube using 0.0325 MPa for 1.5, 2, and 3 min. The seeded support was dried in air at 383 K for 24 h before characterization using SEM.

The cleaned Al_2O_3 tubes were placed vertically in a stainless steel autoclave containing the precursor solution ($5SiO_2$:$Al2O_3$:$50Na_2O$:$1000H_2O$), prepared according to ref. 28, and using an electric field, as studied in ref. 15. After crystallizing at 333 K for 10 h, repeated synthesis (multistage synthesis) was carried out in order to improve the quality of the NaA zeolite membrane. The synthesized membrane was washed several times with deionized water and then dried in air at 363 K for a few days before characterization using SEM and XRD.

4.3.3 Pervaporation

The efficiency of the synthesized membrane on the support tube was determined, including the separation factor and the water flux, by the pervaporation, using an ethanol/water mixture (95/5) at a feed rate of 0.898 l/min, 10 mmHg vacuum pressure, and 343 K. The quantities of the water and the ethanol were determined by a gas chromatograph equipped with an HP plot Q capillary column at 433 K TCD detector temperature and 180 kPa helium gas flow rate.

4.4 Results and Discussion

4.4.1 NaA zeolite formation on the support

The most important factor during zeolite membrane formation under electric field is the surface attractive force of the zeolite particle on the support [15]. Before crystallizing, the α-Al_2O_3 support was seeded using 7 g/l of the NaA zeolite (0.1-0.2 μm) in water for 2 min seeding time. Figure 4.1 is the SEM images of the synthesized NaA zeolite membranes prepared by hydrothermal synthesis (Figure 4.1b,c) and electrophoretic technique (Figure 4.1d,e) using electric potential (1.0 V) and heating at 333 K for 10 h. As can be seen from the SEM results, more uniform crystals were formed on the support surface when using the electrophoretic technique while less uniform crystals with a size of about 1-3 μm and a thickness of about 12-13 μm were obtained when using conventional heating. The reason for this less-uniform crystal formation in the conventional heating comes from zeolite particles generated and irregularly and slowly transported to the support surface by the action of gravity and the hydrodynamic effect, as it is schematically presented in Figure 4.2a [15].

For the electrophoretic technique, the seeded support surface provided enough nuclei for crystals to grow during hydrothermal treatment. When applying an electric field, the charged zeolite particles migrate onto the support surface orderly and regularly, providing a uniform and dense zeolite membrane (Figure 4.2b). After crystallization, the crystal sizes (about 1-2 μm) became uniform on the support surface and covered thoroughly with 13-14 μm thickness, as shown in Figure 4.1d,e.

The XRD patterns (Figure 4.3) show that NaA zeolite synthesized using the electrophoretic technique was fabricated (see the reflection of {222}) as oriented-like membrane [29]. The {222} peak was one of the strong peaks at all x-ray incident angle, indicating the preferred orientation in the overall membrane ranging from surface to porous alumina support layer [29]. In general, θ - 2θ scan XRD patterns indicate average information on a membrane owing to low resolution to resolve the structure of the membrane, unlike grazing incidence 2 scan diffraction analysis (GIXRD) [29]. However, in our case, the structure of the preferred orientation was detected simply using the θ - 2θ scan XRD pattern for the first time. Furthermore, the columnar LTA crystal layer was clearly observed in the SEM result (Figure 4.1e). The oriented membrane was obtained by gradually and orderly moving negatively-charged NaA zeolite to the support within the applied field [30], unlike NaA zeolite membrane produced from conventional heating, showing typical randomly oriented NaA-type pattern which was reported by several researchers [23,26].

4.4.2 Effect of seeding time on membrane properties

The seeding, or secondary growth, method involves the deposition of zeolite nanosized seed crystals on the substrate before hydrothermal growth, leading to the formation of an inter-grown film. It is well known that the presence of seeds on the support surface provides better control of the membrane formation process by forming a gel layer over the seed layer, causing crystal nucleation and growth with shortened crystallization time [26, 31, 32].

In addition, the secondary growth method ensures the growth of the zeolite crystals on the support rather than in the solution and limits the nucleation from transforming to other crystals [33, 34]. However, the most important factor in zeolite membrane preparation is the fabrication of a very thin film with a defect-free membrane layer in order to obtain a high efficiency of flux and separation. The seeds indeed have a significant effect not only on the quality, but also on the performance of the synthesized membrane. In our study, we fix the seed concentration and vary the seeding time (1.5, 2, and 3 min). Figure 4.4 b-g is the SEM images of Al_2O_3 substrates coated with 7 g/l of the seed in water at a coating pressure of 0.0325 MPa for 1.5, 2, and 3 min coating time, respectively [27]. It can be clearly seen that 1.5 min seeding time was enough to completely cover (Figure 4.4b) the substrate. The longer time, especially the 3 min seeding time, resulted in a denser and thicker layer.

Figure 4.5 shows the SEM images of the synthesized NaA zeolite membrane fabricated by the electrophoretic technique using 2V electric potential at 333 K for 10 h. It was found that the seeding time influences the membrane thickness. All of the coating times gave a fully covered α-Al_2O_3 support surface with homogeneous NaA zeolite crystals (1-2 μm). The membrane thickness was about 15-17 μm. When the seeding time was 2 min, the denser and thicker membrane was obtained. A possible explanation is that the secondary growth of the NaA seeds seals the inter-crystalline gaps and forms a continuous and tightly-packed film. In fact, this phenomenon is necessary for membrane application [35]. The longer seeding time (3 min) also provided thicker seeding layer, resulting in cracks.

Figure 4.6 is to show that the synthesized membranes fabricated for different seeding times (1.5, 2, and 3 min) on the α-Al_2O_3 support before crystallizing under applied electric field were indeed pure NaA zeolite membranes. All NaA zeolite membranes show the strong {222} peak in the XRD pattern, indicating the preferred orientation in the overall membrane, ranging from the surface to the porous alumina support layer [29].

4.4.3 Effect of applied electric potential on membrane properties

Shan et al. [22] fabricated the zeolite film by electrophoretic deposition in a non-aqueous medium and investigated the effect of voltage and time on the zeolite film. They reported that the film thickness increased with higher voltage at the same deposition time, similar to the work done by Huang et al. [15]. For our case, the SEM images of the synthesized NaA zeolte membrane prepared by the electrophoretic technique at 333 K for 10 h with different electrical potentials (1-2 V) also show the same trend. It can thus be concluded that the applied electrical potential has a great effect on the thickness of the synthesized NaA zeolite membrane. The SEM image in Figure 4.7a shows that, at 1.0 V the α-Al_2O_3 substrate was fully covered with the NaA zeolite with 1-3 μm crystals and 13-14 μm thickness.

With increasing the electrical potential, the synthesized membranes became denser, with columnar characteristics, and thicker (Figure 4.7c-f). This is owing to the particles possessing higher electric mobility in the more intensive electric field [22]. At 2.0 V electric field (Figure 4.7e-f) the membrane became more packed and the crystal seemed to be smaller because the zeolite particles migrate on the surface rapidly before growing into larger ones [15]. The thickness of the zeolite membrane was also increased to 17-18 μm.

4.4.4 Effect of applied electric potential on membrane performance

According to well-defined properties for separation purposes, the coating layer should be as thin as possible and free of any pinholes for optimal performance [31]. Thus, controlling the thickness and the texture of the membrane is a significant task in determining the performance of the system. Characterization using XRD and SEM can only indicate whether a continuous membrane forms on the support, but cannot confirm whether a defect-free zeolite membrane was obtained. To evaluate the quality of the synthesized membranes, the pervaporation technique was used. Table 4.1 summarizes the effects of the seeding time and the electrical potential on the membrane performance. Without application of the electrical field, the formation of the NaA zeolite membrane is promoted by the seed layer on the support surface. The zeolite nuclei forms gel layers and grows into zeolite crystal, followed by intergrowth of the zeolite crystals to eventually form a membrane [27, 29]. As shown in Table 4.1, the seeding time has a great effect on the zeolite membrane performance. When the seeding time is too long, the seeding layer is too thick, creating cracks which result in poor separation properties. On the contrary, when the seeding time is short, the seed amount on the support is not enough to produce a sufficient number of nuclei to convert into a denser zeolite film, also resulting in poor performance. The suitable seeding time for the hydrothermal treatment is 2 min, giving a much better performance with a separation factor >10,000. Under the action of the electric field and hydrothermal treatment, a more uniform and denser zeolite membrane was formed, especially, at the highest electric field; and the best performance was obtained. This is because the charged particles can migrate to the support surface homogeneously and rapidly [15]. As discussed previously, the applied electrical potential plays a significant role in the crystal growth and the membrane thickness [15, 22]. The pervaporation results in Table 4.1 indicate that under the same electric field potential, the 1.5 min seeding time provided the best quality membrane, while a longer seeding time caused the membrane to be too thick, creating cracks and providing poor performance.

4.5 Conclusions

Oriented, uniform, and dense NaA zeolite membranes were successfully prepared on an alumina substrate by seeding and electrophoretic techniques. Both the morphology and the performance of the membranes were improved. The applied electric potential has an important effect on the membrane layer, as well as on the membrane thickness, of the NaA zeolite. More homogeneous and more uniform crystals were formed on the alumina support surface, with a size of 1-3 μm. With increasing applied electrical potential, smaller crystal sizes and denser NaA zeolite membranes were obtained, with better performance. The seeding time is also responsible for the zeolite membrane thickness and performance. A longer seeding time generates a NaA zeolite membrane that is too thick and contains cracks, causing poorer performance. All of the synthesized membranes were oriented-like membranes, confirmed by the preferred orientation in the overall membrane ranging from surface to porous alumina support of the strong {222} peak in the XRD pattern. The best NaA zeolite membrane was prepared using 1.5 min of seeding time on the alumina support before crystallizing at 333 K under an electrical field of 2 V, giving a separation factor > 10,000 and 0.61 kg/m^2.h flux.

4.6 Acknowledgments

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4.7 References

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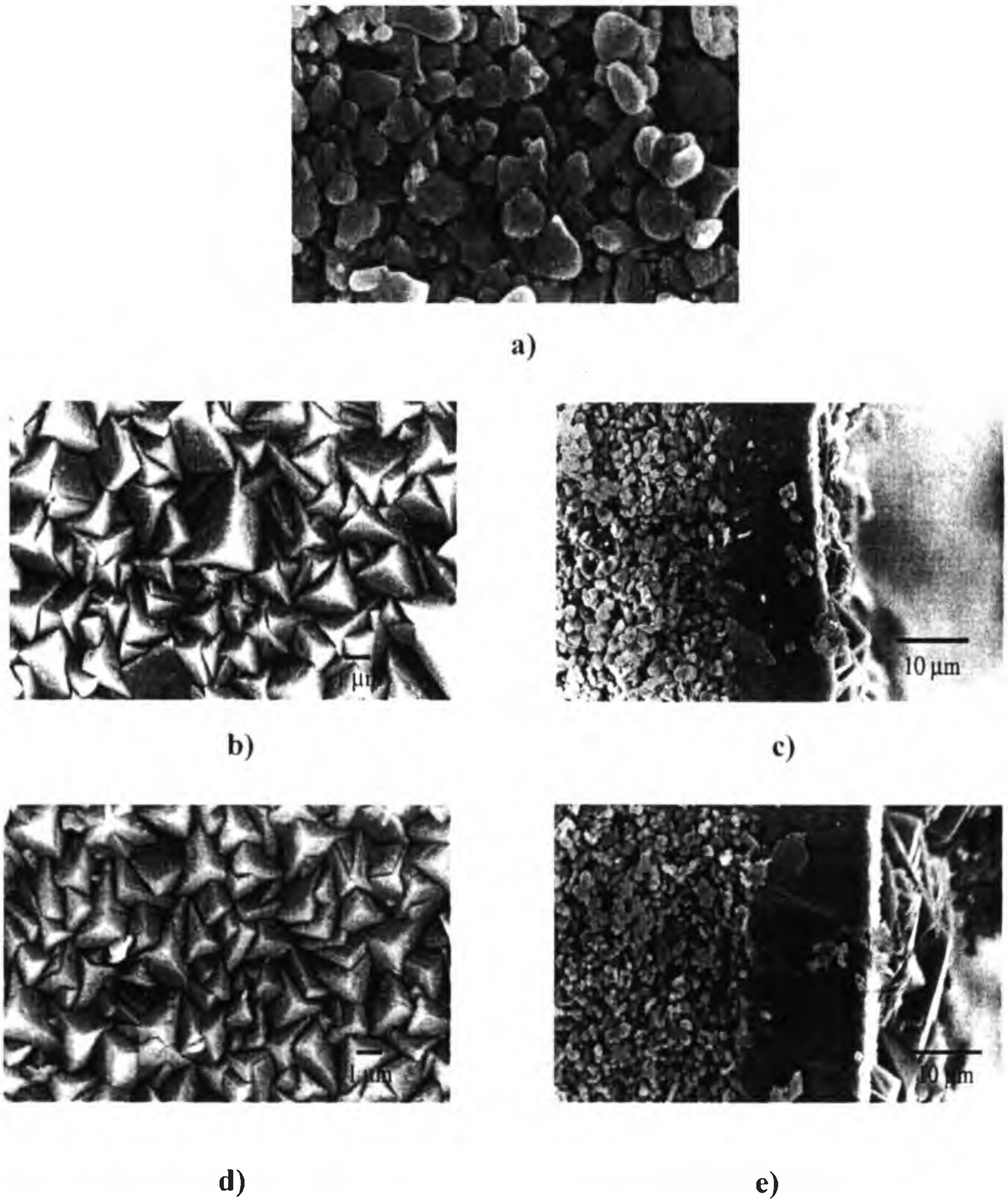


a)

b)

c)

d)

e)

Figure 4.1 SEM micrographs of a) α-Al_2O_3 support, b) and c) NaA zeolite membrane prepared by hydrothermal synthesis method and, d) and e) by electrophoretic technique.

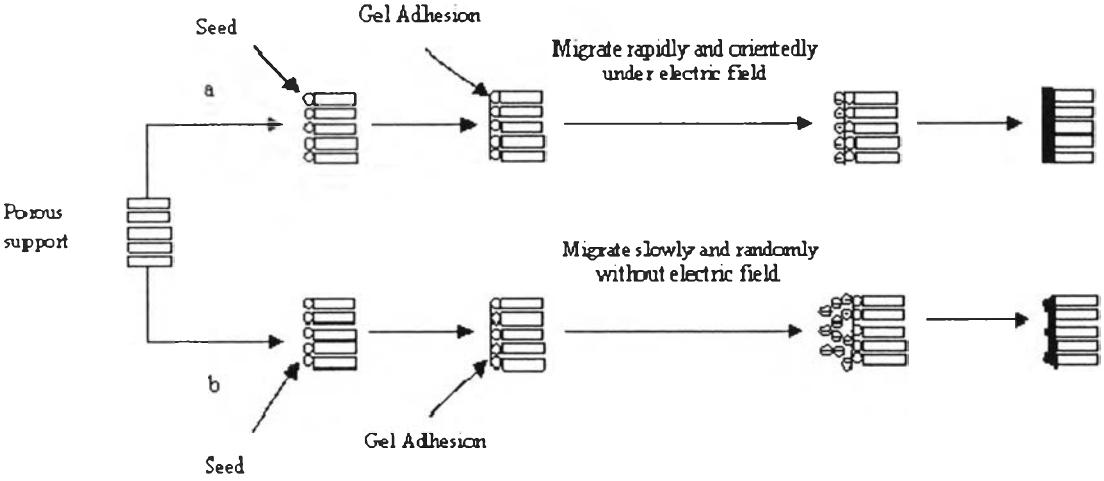


Figure 4.2 Comparison of NaA zeolite membrane prepared on alumina support surface by hydrothermal synthesis under electric field (a) and without electric field (b).

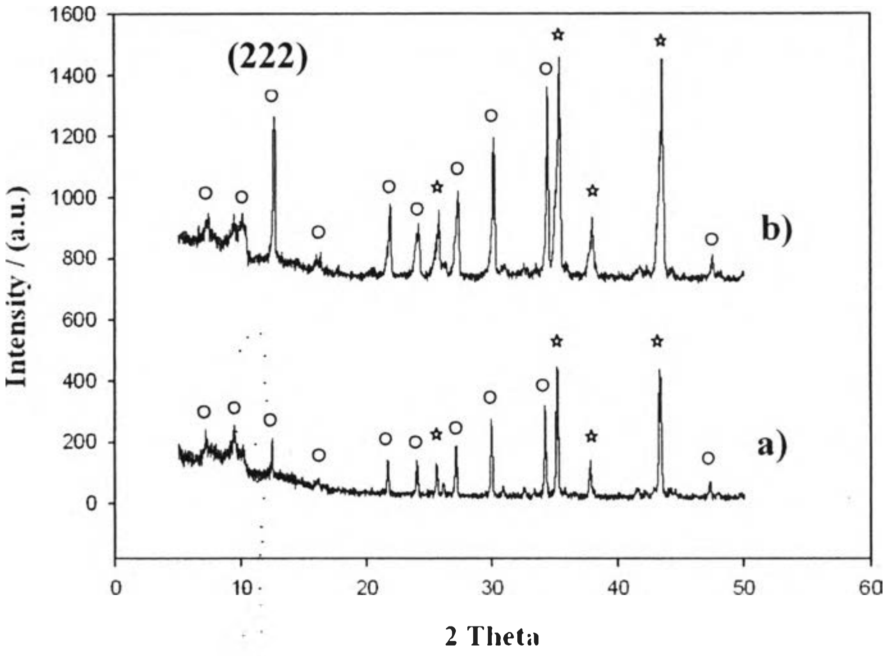


Figure 4.3 XRD pattern of the as-synthesized membrane of 2 min seeding on porous α-Al_2O_3 support before crystallizing by: a) hydrothermal method; b) electrophoretic technique; 1 V. (☆) alumina substrate; (○) NaA Zeolite.

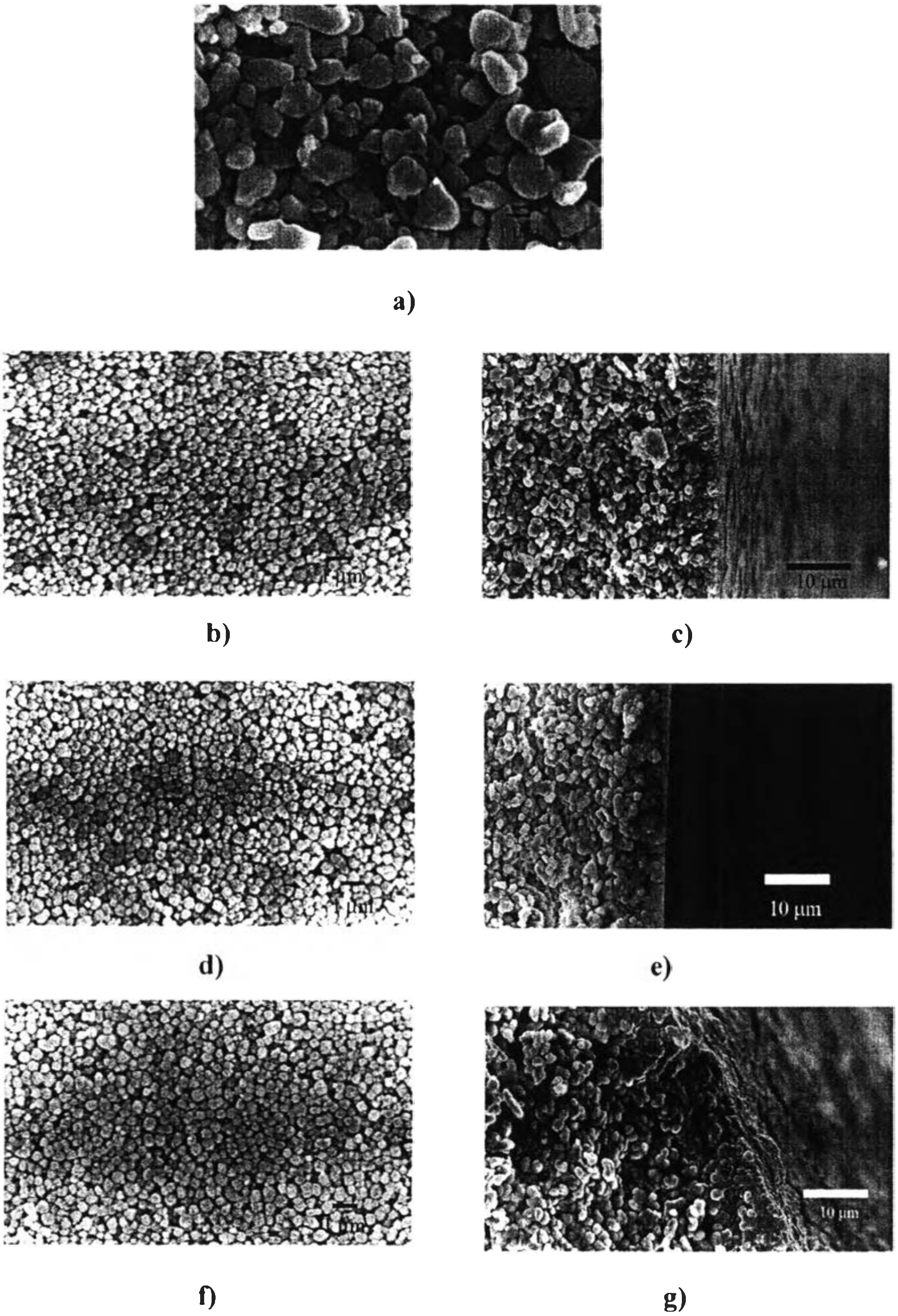
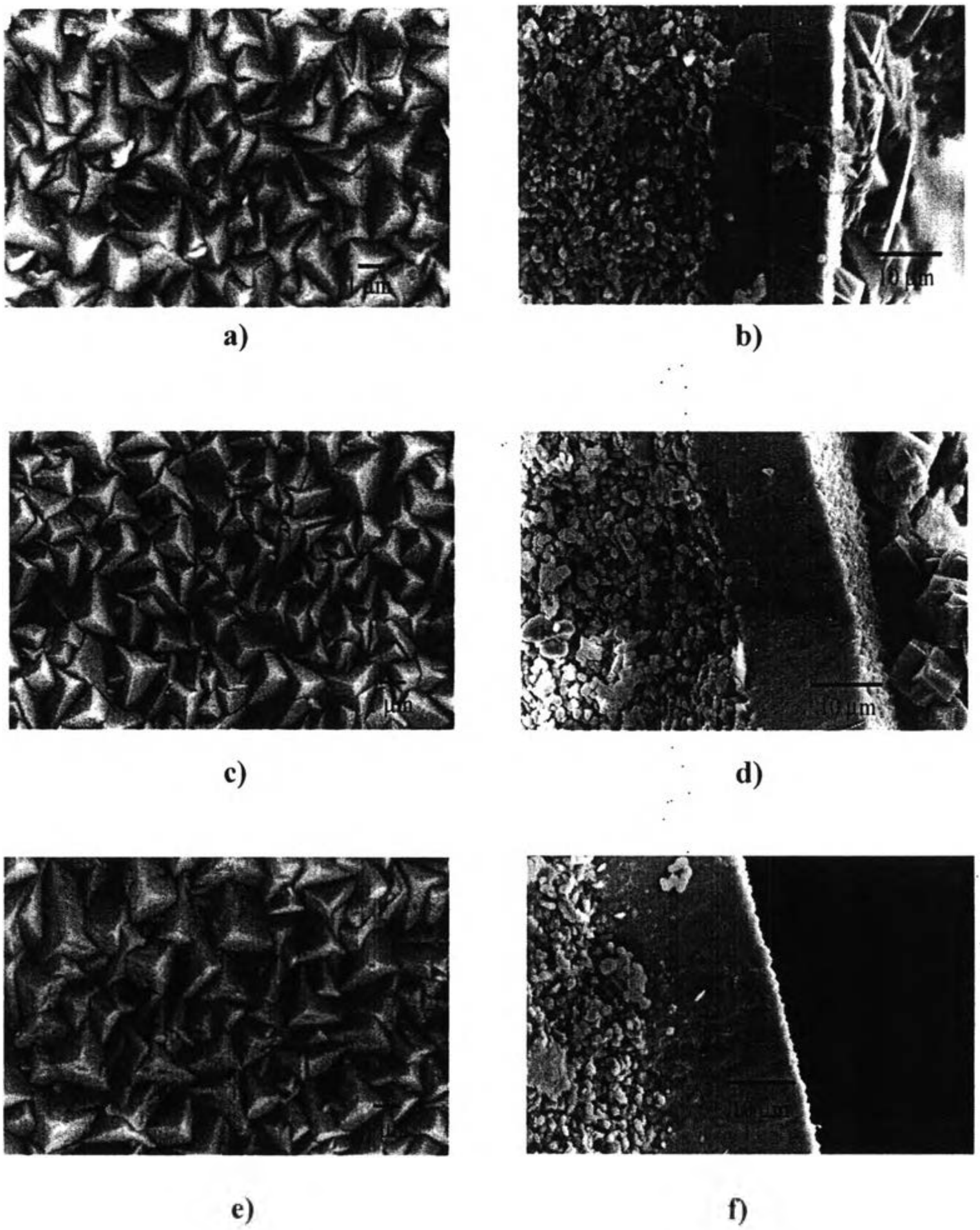


Figure 4.4 SEM micrographs of: a) α-Al_2O_3 substrate; and b), c) and d) NaA crystal seed (7 g/l) seeded by vacuum seeding on the α-Al_2O_3 substrate using 1.5, 2, and 3 min., respectively.



a) b) c) d) e) f)

Figure 4.5 SEM micrographs of NaA zeolite membrane synthesized on substrateusing a seed concentration of 7 g/l with seeding times of a) and b) 1.5 min., c) and d) 2 min, and e) and f) 3 min., under 333 K and electric field 2 V.

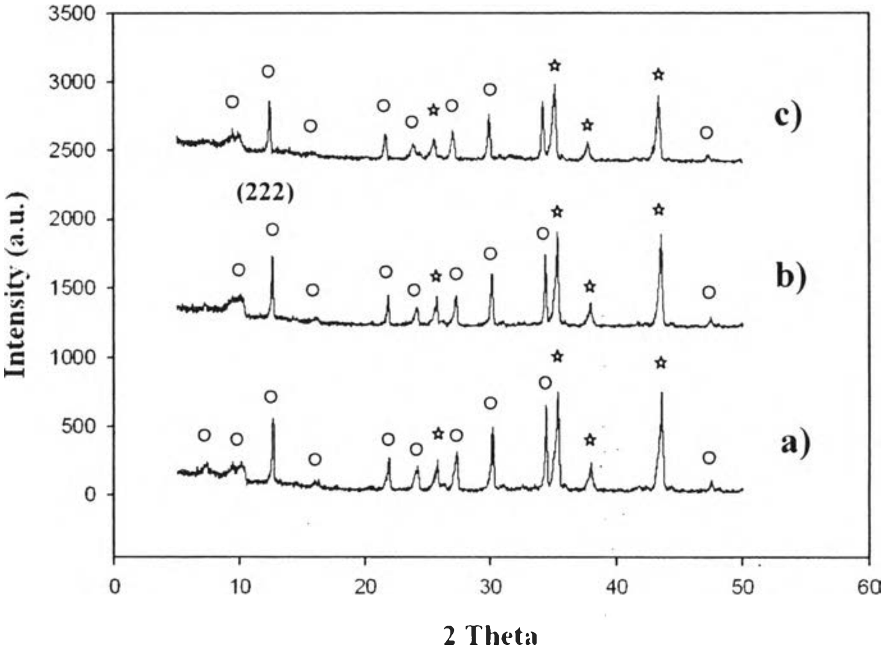


Figure 4.6 XRD patterns of NaA zeolite membrane synthesized on substrate using a seed concentration of 7 g/l with seeding times of a) 1.5, b) 2, and c) 3 min., under 333 K and electric field 2 V. (☆) alumina substrate; (○) NaA Zeolite

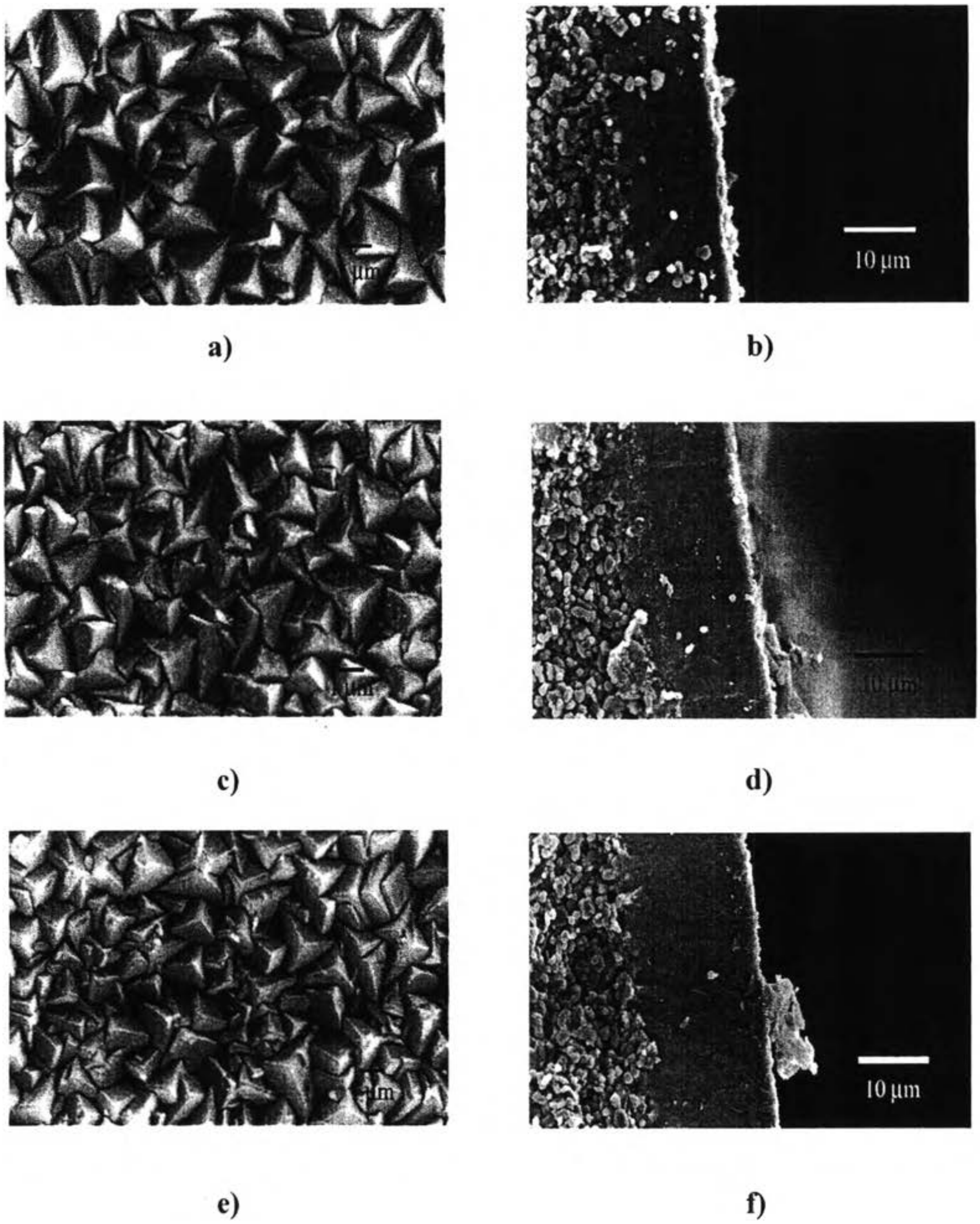


Figure 4.7 SEM micrographs of NaA zeolite membrane synthesized on Al_2O_3 support using a seed concentration of 7 g/l with a seeding time of 1.5 min and varying the electric field: a) and b) 1.0 V; c) and d) 1.5 V; and e) and f) 2 V.

Table 4.1 Pervaporation properties of as-synthesized NaA zeolite membrane using different seeding times parallel to several electrical potentials.

Conditions		**Membrane performance**		
Electrical potentials (V)	**Seeding time (min)**	**Zeolite layer (μm)**	**Total water flux (kg/m^2.h)**	**Separation factor**
0	1.5	11-12	1	90.18
	2	12-13	0.74	402.03
	3	14-15	0.95	208
1.0	1.5	13-14	0.98	432.31
	2	13-14	0.95	109.38
	3	16-17	0.80	75.15
1.5	1.5	16-17	0.74	2973.12
	2	18-19	0.75	324.58
	3	19-20	0.70	97.49
2.0	1.5	17-18	0.61	>10,000
	2	19-20	0.81	844.64
	3	20-21	1.2	633.92