SYNTHESIS OF LOW SILICA/ALUMINA ZEOLITE MEMBRANES IN A FLOW SYSTEM

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ABSTRACT

SYNTHESIS OF LOW SILICA/ALUMINA ZEOLITE MEMBRANES IN A FLOW SYSTEM

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Zeolite A-type membranes are usually synthesized from hydrogels and rarely synthesized from clear solutions mostly in batch systems. Few studies were carried out using semi-continuous systems for zeolite A membrane synthesis. Zeolite A membranes are mainly used in pervaporation processes for separation of water from water/organic mixtures because of their hydrophilic property.

In this study, zeolite A membranes were synthesized on α-alumina supports from a clear solution with a molar composition of $49Na_2O$: $1Al_2O$: $5SiO_2$: $980H_2O$. Synthesis was done both in a batch system and in a flow system in which solution was circulated through the support under atmospheric pressure. Effects of synthesis temperature, time, flow rate and seeding on membrane formation were investigated. The membranes were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), single gas permeation measurements and pervaporation tests.

In batch system, pure zeolite A membranes having cubic form of zeolite A was obtained for the syntheses carried out at 60°C for 24 h and 80°C for 8 h. Thicknesses of the membranes synthesized at 80°C and 60°C were about 2 μm and

4 μm, respectively. N_2 permeances were $2*10^{-8}$ mol/m^{2}sPa and $8*10^{-8}$ mol/m^{2}sPa for of the membranes synthesized in the batch system at 60°C and 80°C, respectively. When synthesis was carried out in flow system pure and continuous zeolite A membranes were obtained for all conditions. Membranes synthesized at 60°C and 80°C had thicknesses of about 1.5 and 2 μm, respectively. Lower N_2 permeations were obtained for the membranes synthesized in flow system. It was observed that flow rate and seeding did not significantly affect the thickness of the membrane layer. The membranes synthesized in this study are significantly thinner than the membranes reported in the literature. Single gas permeation tests at 25°C for the membranes showed that comparable membranes with the ones in literature were obtained in this study. For a double layer membrane synthesized in flow system at 80°C for 8h separation factor about 3700 was obtained for the separation of 92:8 (wt.%) ethanol/water mixture at 45°C.

Keywords: zeolite A, synthesis in flow system, zeolite membrane, clear solution, pervaporation

ÖZ

AKIŞLI SİSTEMDE DÜŞÜK SİLİKA/ALÜMİNA ORANLI ZEOLİT MEMBRAN SENTEZİ

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Zeolit A membranları genellikle kesikli sistemde, hidrojellerden ve nadiren berrak çözeltilerden sentezlenmektedir. Son zamanlarda yapılan birkaç çalışmada zeolit A membran sentezi için sürekli sistem de kullanılmıştır. Zeolit A membranları susever özelliklerinden dolayı genellikle su/organik karışımlarından suyun pervaporasyon ile ayrılmasında kullanılmaktadırlar.

Bu çalışmada zeolit A membranları α-alumina destekler üzerinde kompozisyonu $49Na_2O$: $1Al_2O$: $5SiO_2$: $980H_2O$ olan berrak çözelti kullanılarak sentezlenmiştir. Sentez hem kesikli sistemde hem de çözeltinin destek üzerinde devinim yaptığı akışlı sistemde gerçekleştirilmiştir. Sentez sıcaklığının, süresinin, akış hızının ve tohumlamanın membran üzerindeki etkileri incelenmiştir. Membranlar X ışını kırınımı (XRD), taramalı elektron mikroskopu (SEM), tek gaz geçirgenlik ölçümleri ve pervaporasyon ile karakterize edilmiştir.

Kesikli sistemde küp zeolit A kristallerine sahip saf zeolit A membranları 60°C ve 24 saat ile 80°C ve 8 saatte sentezlenmiştir. Membran kalınlıkları 80°C ve 60°C sentez için 2 µm ve 4 µm olarak ölçülmüştür. Tek gaz geçirgenliklerinde 60°C'de sentezlenen membran yaklaşık $2*10^{-8}$ mol/m^2sPa azot geçirgenliği gösterirken bu değer 80°C'deki membran için $8*10^{-8}$ mol/m^2sPa olarak ölçülmüştür. Sentez akışlı sistemde yapıldığında saf ve sürekli zeolit A tabakası bütün koşullarda elde edilmiştir. Burada 60°C ve 80°C'de sentezlenen membranların kalınlıkları 1.5 ve 2 µm olarak ölçülmüştür. Akışlı sistemde kesikli sistemdekine göre daha düşük azot geçirgenlikleri elde edilmiştir. Akış hızının ve tohumlamanın membranın kalınlığına etkisi olmadığı gözlemlenmiştir. Bu çalışmada sentezlenen membranlar literatürdekilere kıyasla çok daha incedir. Bu membranların 25°C'de yapılan tek gaz ölçümlerinde literatürdekilerle kıyaslanabilir sonuçlar elde edilmiştir. Akışlı sistemde 80°C ve 8 saatte yapılan çift katlı tüp membran ile 92:8 (%) etanol/su karışımının 45°C'deki ayrımında yaklaşık 3700 seçicilik elde edilmiştir.

Anahtar kelimeler: zeolit A, akışlı sistem, zeolit membran, berrak çözelti, pervaporasyon

To My Parents

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TABLE OF CONTENTS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

CHAPTER 1

INTRODUCTION

Zeolites are microporous, crystalline materials with well-defined structures that contain aluminum, silicon, and oxygen in their framework. Zeolites are also called molecular sieves since they have well defined, molecular sized pores. Zeolites can be classified with respect to their pore sizes. Large pore zeolites, e.g. faujasite, have a pore size of about 0.74 nm. Medium pore size zeolites like ZSM-5 has a pore size of nearly 0.55 nm. Finally, small pore zeolites such as zeolite A has pores with only 0.42 nm [1].

Due to molecular sized pores, zeolites can be used to prepare membranes for use in gas and liquid separation. Moreover they can be used as catalysts, adsorbents and ion exchangers.

Zeolite membranes are thin films of zeolites that are synthesized on thick macroporous supports. The support is needed to obtain mechanical strength [2]. Many different support materials such as glass [3], steel [4], alumina [5-7] and titania [8] with different geometries like disks or tubes were used in the preparation of zeolite membranes.

Zeolite membranes generally synthesized in batch systems. Support where the membrane will be grown on is inserted into the synthesis solution in an autoclave, which is then is placed in an oven to keep the synthesis mixture at desired temperature. Many types of zeolite membranes were synthesized in batch systems like MFI [9] , zeolite X [10] and zeolite A [7, 11-13] etc.

However, batch system may introduce some disadvantages to be used for industrial production of zeolite membranes. For industrial application of zeolite membranes, membranes are likely to be long tubes with small inside diameters, so that effective membrane area for permeation can be extended. In batch systems, synthesis on long supports can yield membranes with non-homogenous characteristics because of the concentration gradients that may occur along the support [5] . Besides, crystals that will form in the bulk mixture fall onto the support due to gravity so that the membrane thickness can be non-uniform.

Synthesis of zeolite membranes in a continuous flow system can be an alternative to conventional batch synthesis. In this synthesis settling of the crystals can be prevented and more homogenous solution can be provided since the synthesis mixture flows around the support. Therefore membranes with large surface area can be synthesized in continuous systems. There are only few studies that perform synthesis in continuous systems. Yamazaki et al. [14] synthesized flat zeolite A membranes by pumping the synthesis solution on the heated substrate. Pina et al. [5] studied the synthesis of zeolite A membranes in a semi-continuous system. In another study performed by Richter et al. [15], MFI type membranes were synthesized by flowing the synthesis solution into the autoclaves continuously. In 2006 Çulfaz et al. [16] studied MFI type membrane synthesis in a flow system in which the synthesis solution was recirculated throughout the system. Finally Pera-Titus et al. [17] synthesized zeolite A membranes in a continuous flow system where the synthesis mixture was sent to the support by gravity.

Zeolite A membranes have been studied widely because of their affinity to water. These membranes are mostly synthesized from gels on seeded supports and mainly used for dehydration of ethanol-water mixtures due to their hydrophilic property in pervaporation process which is a membrane based separation technique for separation azeotropic mixtures [7, 18-20]. Zeolite A membrane is the only commercialized membrane. Mitsui Engineering produces zeolite A membranes having length of 80 cm and area of 300 m^2. These are used in pervaporation separation of ethanol/water mixtures and have selectivity about 10000 and flux 8 kg/m^{2}h [21].

Mainly gel has been used for synthesis of zeolite membranes in the continuous systems. However, homogeneity in the gel could be lost easily because of poor mixing. The alternative for gel is that use of clear solutions for zeolite A membrane synthesis. However, previous studies showed that in clear synthesis solutions other types of zeolites can easily formed [22, 23].

In this study zeolite A membranes were synthesized from clear synthesis solutions using a recirculated flow and batch systems at atmospheric pressure. Syntheses were carried out on seeded and unseeded disc and tubular α-alumina supports. Synthesis was performed at temperatures between 50°C and 95°C and at different flow rates of synthesis solution between 6 and 48 ml/min to investigate the effect of temperature and flow rate on membrane morphology. Membranes were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) for identification of phase and morphology of the membranes, respectively. Single gas permeation and pervaporation tests were applied to test the membranes. In literature this study is the first one that used clear synthesis solution in a recirculated flow system for the synthesis of zeolite A membrane. This method can be further developed for the preparation of zeolite A membranes with enlarged surface areas.

CHAPTER 2

LITERATURE SURVEY

2.1. Description of Zeolite A

Zeolite A, which is also called Linde Type A (LTA), has the typical oxide formula of $Na_2O:Al_2O_3:2SiO_2:4.5H_2O$. The Si/Al ratio for zeolite A is equal to one, which is the lowest silica alumina ratio among all zeolites. Zeolite A is composed of truncated octahedrons (β-cage) and double four rings (D4Rs) as shown in Figure 2.1. By combination of β-cages and D4Rs, a large cavity, called α-cage, forms. The α-cage has pore opening of 0.42 nm, and the β-cage has a pore opening of 0.22 nm [1].

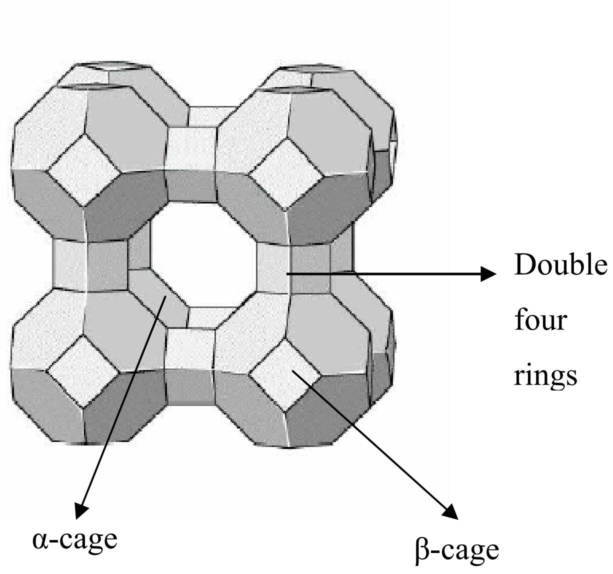


Figure 2.1: Structure of zeolite A [1].

The pore size of zeolite A can be tuned by ion exchange. Zeolites have negatively charged framework because of aluminum that they have. This negative charge is balanced by the cations which are exchangeable. The pore size of zeolite A can be tuned by exchanging the cation present in the framework. Sodium form of zeolite A is called as 4A or NaA, and has pore size of about 0.42 nm. When potassium is exchanged with sodium, zeolite is called as zeolite 3A or KA and the pore size becomes 0.3 nm. When calcium is exchanged, pore size increases to 0.50 nm and it is called as zeolite 5A or CaA [1].

2.2. Synthesis of Zeolite A Membranes

Syntheses of zeolite A membranes were mainly performed on tubular or disc shaped supports in batch systems. Seeded supports were mostly used in syntheses since seeding increases the zeolite growth on the support while inhibiting the formation of zeolite in the bulk [24, 25].

In batch synthesis, gel was poured into the autoclave in which seeded or unseeded support was inserted vertically or horizontally. Then the autoclave was put into oven to keep the solution at the desired temperature. In some studies, microwaves were used to keep the synthesis solution at desired temperature [6]. Syntheses of zeolite A membranes were performed at different temperatures between 20°C and 175°C [1]. Thicknesses of the membranes changed between from 3 to 30 μm.

Kita et al. [7] synthesized zeolite A membrane from gel on seeded supports at 100°C for 3.5 h. They obtained membranes with a thickness of 30 μm. They tested the membranes in pervaporation process using 10:90 (wt.%) water/ethanol mixture at 75°C. Membranes showed high selectivity and flux in separation of water. Flux about 2 kg/m^2h and separation factor about 10000 was obtained.

In another study performed by Aoki et al. [26] zeolite A membranes with a thickness of 3 μm were synthesized on seeded supports at 100°C for 20h. They characterize the membranes in gas permeation test. Ideal selectivity of H_2/N_2 was observed higher than Knudsen diffusion ratio (3.74) as 4.5-4.8 for membranes.

Several researchers performed multi-stage synthesis [23, 27]. In multi stage synthesis, gel or solution in the autoclave was renewed after each synthesis. Application of multi stage synthesis generally resulted with membranes having fewer defects. Kumakiri et al. [27] obtained zeolite A membranes showing separation factor in pervaporation of ethanol/water mixture more than 10000 after performing several sets of batch synthesis.

The only large scale produced membrane is zeolite A membrane which is produced by Mitsui Engineering. Synthesis of these membranes was reported by Morigami et al. [21]. Membranes were synthesized on tubular supports having 80 cm length and 300 cm^2 area. Seeded supports were used for crystallization of zeolite A membrane at 100°C for 3-4 h and thickness of the membranes were about 20-30 μm. Mitsui engineering in Japan uses these membranes for pervaporation separation of water from organic mixtures.

As described in introduction part, there are some disadvantages for the synthesis of zeolite membranes in batch system. Moreover multiple synthesis steps are required to obtain defect free membrane. The alternative method to solve these problems is using continuous system. In this system more homogenous conditions can be provided so desired membranes can be synthesized in a single step. Also synthesis can be carried out by using lower amounts of raw materials. Membranes, which synthesized in a single step by using small amount of raw materials, are preferred in industry so continuous system is an alternative method for synthesis of zeolite membranes.

There have been few studies performed in continuous system for synthesis of zeolite A membranes. Pina et al. [5] synthesized zeolite A membranes in a semi-continuous system in which synthesis gel was periodically renewed. Dry nitrogen with a pressure of 10 bar was used to supply the gel to the autoclave and the solution in the autoclave was removed by pneumatic valves. During the synthesis, the gel was renewed by this way at different renewal rates (from 13 min to 75 min). Membrane formation was performed at 90°C for 5 h on the outer surface of the seeded tubular alumina supports. Synthesized membranes had thickness about 10 μm and showed pervaporation separation factors of 94-3603 and fluxes of 2.2-3.8 kg/m^{2}h for 10%water / 90%ethanol liquid mixtures.

In 2006, Pera-Titus et al. [28] used the same system to synthesize zeolite A membranes on the inner side of the seeded tubular supports. Synthesis was carried out at 363-373 K for 5 h. In this study, fresh gel was renewed in every 10 min. Synthesized membranes with two cycles showed selectivity about 16000 and flux about 0.5 kg/m^{2}h for pervaporation separation of 90:10 (wt.%) ethanol/water mixture.

Recently, Pera-Titus et al. [17] synthesized zeolite NaA membranes on the inner side of titania tubular supports using a continuous flow system. In this system, the action of gravity was used to circulate the synthesis solution with a flow rate of 1.5-4 ml/min. After synthesis at 358 K for 6-7 h, membranes having thickness about 10-20 μm was obtained. For pervaporation separation of 92:8 (wt.%) ethanol/water mixtures, seeded synthesis was resulted in better selectivity and flux values about 8500 and 1.2 kg/m^{2}h, respectively.

Using of gel in continuous system has also some disadvantages. Gel is composed of two phases; liquid and solid. In order to obtain homogenous solution, gel should be mixed continuously otherwise phases can be separated. Liquid phase stays at the top while solid phase going down because of gravity. This causes loss of homogeneity in the solution which can cause to obtain non homogenous membranes. Moreover in order to pump the gel within the system, high pressures are generally required [5, 28]. However, any kind of pump can be used to circulate the clear solution without using high pressures.

Clear solutions have also been used for zeolite A membrane synthesis in batch systems. Generally they contain organic templates like TMA^+. Templates work as a directing agent and occupy the zeolitic pores. Boudreau and Tsapatsis [3] studied synthesis of oriented zeolite A films on glass substrates by using clear synthesis solution with template. In this study solution having the composition of $4.1(TMA)_2O$: $0.3Na_2O$: $1Al_2O_3$: $4.4SiO_2$: $706.2H_2O$ was used for zeolite A membrane synthesis in which tetramethylammonium (TMA) was used as template. They obtained oriented zeolite A membranes after crystallization at 90°C for 72 h under rotation. After membrane synthesis they calcined the membrane to remove the template. In order to use the membrane in separation processes templates should be removed. The temperature of calcination should be determined carefully since membrane can be damaged because of the different thermal expansion coefficients of the support and membrane [24].

Recently, clear synthesis solutions without template have been used for synthesis of zeolite A membrane in batch system [4, 8, 12, 23, 27, 29]. Jafar and Budd [12] synthesized zeolite A membranes from the clear solution without using any template. They used clear solutions having the composition of $55.12Na_2O$: $1Al_2O_3$: $5SiO_2$: $1004.66H_2O$ for synthesis at 50°C for 48 h. Pure zeolite A membranes having high selectivities in pervaporation of water/ethanol mixtures were obtained.

Xu et al. [23] studied clear solutions having the composition of $50Na_2O$: $1Al_2O_3$: $5SiO_2$: $1000H_2O$ in order to synthesize zeolite A membrane on seeded and unseeded supports. Continuous zeolite A membranes could not be synthesized on unseeded supports. When synthesis was carried out on seeded support zeolite A membranes were formed but extension of synthesis time caused the formation of other types of zeolites like X and sodalite.

Zah et al. [29-31] synthesized zeolite A membranes from the similar composition ($49Na_2O$: $1Al_2O_3$: $5SiO_2$: $980H_2O$) at 85°C for 1-4h. Fully crystalline zeolite A membranes were obtained after 4h synthesis. Moreover, they performed two stage syntheses to improve membrane intergrowth. These membranes were characterized by pervaporation. Membranes synthesized in two stages in 4h showed selectivity 8500 and flux 0.23 kg/m^{2}h in pervaporation of 95%ethanol / 5%water mixture.

Although different results were obtained in these studies, they all used similar clear solution compositions for synthesis of zeolite A membranes in batch system.

In literature, there was only one study using clear solution without template for synthesis of zeolite A membrane in continuous system. Tsutsumi and Yamazaki [14] studied zeolite A membrane synthesis in circulated solution. In this study liquid phase was separated from the hydrogel and this liquid solution was used for membrane synthesis on PTFE substrates. Liquid solution was circulated through the substrate which was heated only. The synthesis conditions changed in the range of 353-403 K for 24 and 48 h. In the static synthesis other zeolite types such as gmelinite, chabazite and faujasite were also formed in addition to zeolite A. However, when the synthesis was performed in circulating system, pure zeolite A membranes were obtained.

As mentioned, there have been studies for synthesis of zeolite A membranes in batch and continuous systems. Mainly gel was used for synthesis in these systems. Studies in which clear solution was used mainly performed in batch systems. However in this study, different from in literature, zeolite A membranes were synthesized from clear solutions in a flow system.

2.3. Characterization of zeolite A membranes by Pervaporation

Pervaporation is a membrane based separation process used for separation of liquid mixtures. In this process liquid mixture is fed to the one side of the membrane and vacuum is applied at the other side. The stream passed through the membrane is called permeate and the stream rejected by the membrane is called as retentate, as shown in Figure 2.2.

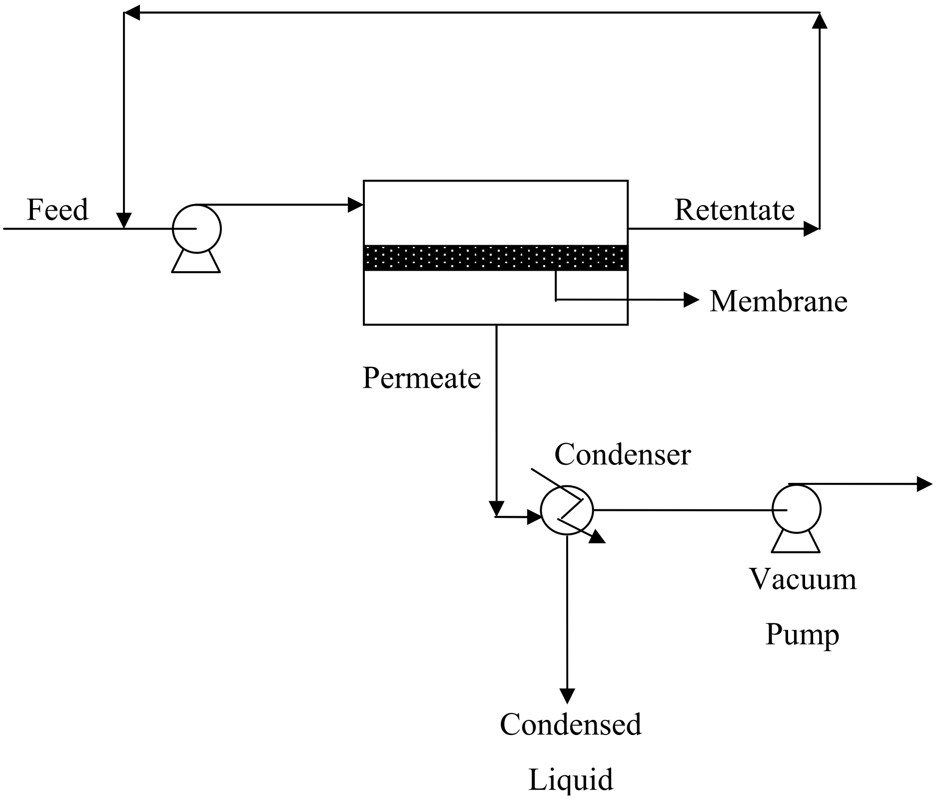


Figure 2.2: Typical setup for pervaporation (redrawn based on [24]).

The performance of a membrane in the pervaporation process is determined by flux and separation factor. Flux is defined as the amount of liquid permeated through the membrane per unit time per unit area. Flux is usually reported in terms of kg/m^{2}h or mol/m^{2}h. The separation factor for a binary component mixture is calculated from Equation 2.1.

$$\alpha_{a/b} = \frac{(y_a / y_b)_{Permeate}}{(x_a / x_b)_{Feed}} \tag{2.1}$$

where permeate and feed compositions are shown as y and x, respectively.

In pervaporation, molecules that are adsorbed onto the zeolite at the feed side diffuse through the zeolitic pores because of chemical potential gradient across the membrane. When molecules reach the permeate side of the membrane, they desorbed from the zeolite surface.

Water/organic separations mainly achieved based on the adsorption affinity of zeolites to the components in the mixture. Hydrophobic or organophilic membranes have tend to adsorb organics more than water. Therefore these membranes are ideal to separate organics from aqueous solutions [24]. Silicalite-1 and ZSM-5 membranes, which are organophilic membranes, are used to remove organics from solutions [32]. However, hydrophilic membranes which have high affinity to water are used for removal of water from organic solutions [24]. These membranes preferentially adsorb water from water/organic mixtures.

Zeolite A membranes are hydrophilic membranes and they are used to separate water from organic/water mixtures. Many researchers have synthesized zeolite A membranes with high selectivity by performing different synthesis methods [7, 13, 18-21, 30].

Kita et al. [7] synthesized zeolite A membranes on seeded alumina tubes in batch system and performed pervaporation tests for the separation of 90% ethanol / 10% water mixtures at 75°C. They obtained separation factor over 10000 and flux 2.15 kg/m^{2}h. High separation factors indicated that membranes have few defects.

Okamoto et al. [13] synthesized zeolite A membranes on seeded tubes in batch system and characterized them by single gas permeation measurements and pervaporation tests. Membranes showed Knudsen selectivity (8.54) for H_2/SF_6, suggesting that there were some non zeolitic pores larger than the pores of zeolite A. Same membranes, however, exhibited separation factors larger than 10000 in the pervaporation tests performed with 10:90 (wt.%) water/ethanol mixtures at 75°C. These results suggested that existence of non zeolitic pores did not significantly affect the membrane performance in pervaporation.

In a semi continuous system, Pina et al. [5] synthesized zeolite A membranes on outer surface of seeded tubular supports. Membranes having 10 μm thickness showed pervaporation separation factors of 94-3603 and fluxes of 2.2-3.8 kg/m^{2}h at 125°C for 10%water / 90%ethanol liquid mixtures. Semi-batch system provided better control of synthesis conditions.

Pera-Titus et al. [28] used same system to synthesize zeolite A membranes. Synthesis was carried out at 90-100°C for 5 h on the inner side of the seeded tubular supports. In order to obtain significant results two cycles were performed for zeolite A membrane synthesis. Selectivity and flux of these membranes were reported as 16000 and 0.5 kg/m^{2}h, respectively, for pervaporation separation of 90:10 (wt.%) ethanol/water mixture at 50°C. Repeated synthesis cycles resulted in higher selectivity.

Recently, synthesis of zeolite A membrane was performed in a continuous flow system in which solution was flow by the action of gravity [17] . Membranes having thickness about 10-20 μm was formed on tubular titania supports. For pervaporation separation of ethanol/water (92:8 wt %) mixtures at 50°C, seeded synthesis was resulted in better selectivity and flux values about 8500 and 1.2 kg/m^{2}h, respectively. Seeding of the support increased the performance of the membranes in pervaporation.

Pervaporation performances of several zeolite A membranes for ethanol/water separation in literature were shown in Table 2.1. Best pervaporation results were obtained from the membranes synthesized on seeded supports and in multi-stage. Membranes synthesized in semi-continuous and continuous flow systems resulted similar selectivities with the ones in batch system.

Table 2.1: Pervaporation results for the zeolite A membranes studied in literature for separation of ethanol/water mixtures

Thickness (µm)	Support Type	Synthesis Method	Temperature (°C)	X water (wt. %)	Selectivity $\alpha_{W/E}$	Flux (kg/m^{2}h)	Ref.
20-30	Seeded Alumina Tube	Semi-cont., 2 cycles	50	10	>10000	0.5	[28]
10	Seeded Alumina Tube	Semi-cont.	125	10	3600	3.8	[5]
10-20	Seeded TiO_2 Tube	Cont. Flow	50	8	8500	0.9	[17]
3.5	TiO_2 Disc	Batch	45	5	>10000	0.9	[8]
10	Seeded Mullite tube	Batch	50	10	>10000	0.8	[20]
30	Seeded Alumina Tube	Batch	75	10	10000	2.2	[7]
10	Alumina Disc	Batch, microwave	60	10	>10000	0.6	[33]
4	Seeded Alumina Disc	Batch, multi layers	30	10	10000	0.7	[27]
7	Seeded Alumina tube	Batch	93	9	130	2.5	[34]
30	Mullite tube	Batch	60	10	1000	1.2	[35]
6	Seeded Alumina Tube	Batch, two layers	45	5	8300	0.2	[30]
5-6	Seeded Alumina Tube	Batch	50	5	>10000	1.5	[18]

CHAPTER 3

EXPERIMENTAL METHODS

3.1. Synthesis of Zeolite A Powder for Composition Selection

In the preparation of the synthesis solution; water glass, sodium hydroxide (NaOH), aluminum hydroxide ($Al(OH)_3$) and distilled water were used. Synthesis solution was composed of aluminate and silicate solutions which were prepared separately. Silicate solution had water glass and half amount of the distilled water. Remaining water, NaOH and $AlOH_3$ were formed the aluminate solution (details are included in Appendix A1 and A2). Mixing of aluminate solution was carried out on by heating and the amount of evaporated water was added after clear solution was obtained. Aluminate solution was mixed with the silicate solution to obtain synthesis solution and powder synthesis was carried out at 80-95°C for 24 h. Tested compositions are shown in Table 4.1.

For the powder synthesis in flow system under atmospheric pressure, system was designed as shown in Figure 3.1. Synthesis solution was put into a reservoir and it was inserted into silicone oil bath to keep the temperature of solution at desired temperature. Synthesis solution was circulated within the system with a flow rate of 6 ml/min and condenser was used to prevent the loss of the solution. Powders were washed with distilled water until pH of the powder reduced to 8.

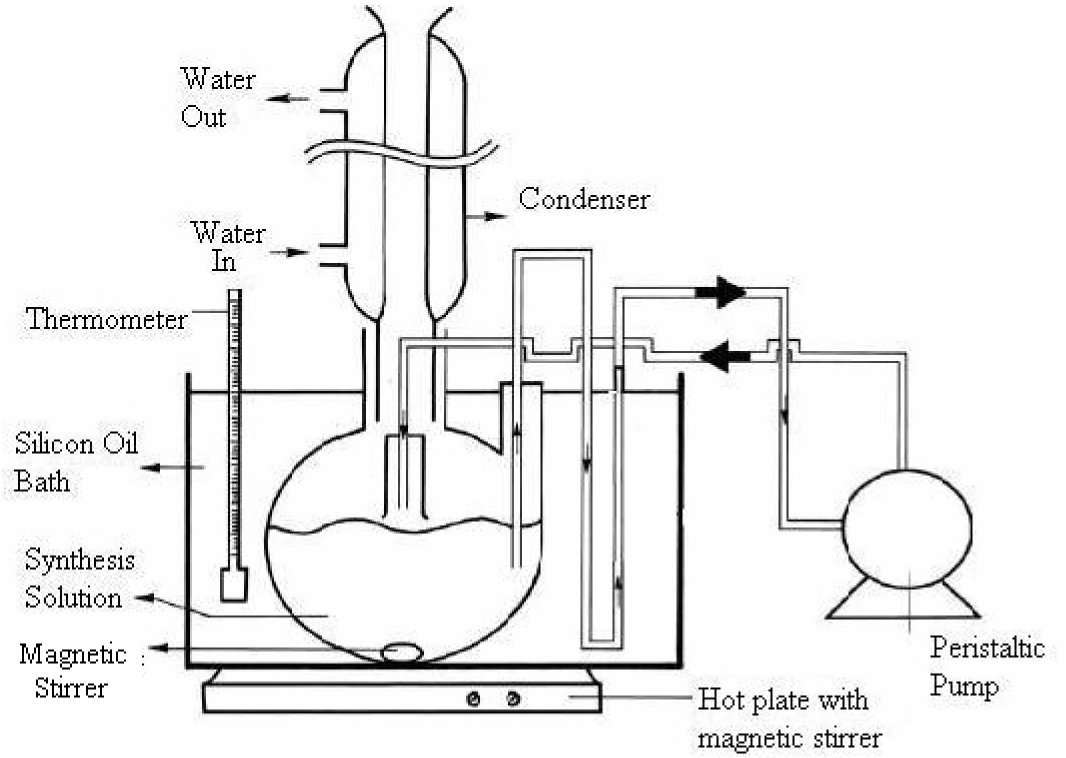


Figure 3.1: Schematic view of flow system used in powder synthesis (redrawn from [36]).

3.2. Supports Used For Membrane Synthesis

Tubular and disc shape α-alumina supports were used in this study. Discs purchased from Inocermic were asymmetric with a thin layer 200 nm pores (mesoporous layer) on top of a thick bulk having larger pores (macroporous bulk) (SEM image of disc support is shown in Appendix C). The discs had a diameter of 20 mm and a thickness of 1 mm with an area of 3.14 cm^2.

As tubular support, α-alumina tubes were purchased from Pall Exekia. Tubes, which were originally 25-cm long, were cut into 4.5 cm pieces. They had an inner diameter of 0.7 cm with a wall thickness of 0.15 cm. Tubes were also asymmetric, inside of the tubes had α-alumina layer with pores 200 nm in size and outside of the tubes had larger macropores. Tubes were cleaned in water by keeping in ultrasonic bath for 10 min and then they were kept in 0.1 M HNO_3 solution. They were finally rinsed with distilled water and dried. Approximately 1 cm from each side of a tube was glazed with Duncan IN1001 Envision Glaze so that impermeable zones were obtained at both sides. For glazing, tubes were dipped into the glaze suspension two or three times. Tubes were then dried at room temperature for a few minutes and put into the furnace to mature the glaze. The furnace was heated to 900°C with a heating rate of 1.5°C/min, kept at 900°C for one hour and then cooled with an average cooling rate of 1.5°C/min. After glazing, a tube had an effective membrane length and area of 2.5 cm and 5.5 cm^2, respectively [16].

3.3. Seeding of the Supports

Two different methods were used for seeding of the supports. In the first method seeding was performed by rubbing. In this method, zeolite A powder was rubbed to the inside of the tubes by the help of a brush to seed the inside of the tubular support. Solution with $10Na_2O$: $1Al_2O_3$: $2SiO_2$: $500H_2O$ molar composition was used for the synthesis of zeolite A powder. Synthesis of this powder was performed by mixing aluminate solution with silicate solution. For 40 g batch 3.06 g of NaOH, 34.45 g of deionized water, 0.63 g of $Al(OH)_3$ and 1.81 g waterglass were used. Silicate solution was prepared by mixing 1.81 g waterglass and 17 g of deionized water. For aluminate solution, firstly, NaOH and the remaining amount of deionized water were mixed. After dissolving sodium hydroxide, aluminum hydroxide was added and solution was stirred and heated to provide dissolution of alumina. Then lost amount of water because of evaporation was added. Finally aluminate and silicate solutions were mixed to obtain synthesis gel. Synthesis was carried out in batch system where solution was poured into 30 ml Teflon autoclave and crystallization was performed at 80°C for 72 h.

On the other hand, disc shape supports were seeded by vacuum seeding method. In this method seed crystals were synthesized from a solution having the composition of $15Na_2O$: $1Al_2O_3$: $2.2SiO_2$: $500H_2O$. In the synthesis of seed, sodium silicate solution, sodium hydroxide pellets, aluminum hydroxide powder and deionized water were used. For a 40 g batch, silicate solution was prepared by mixing 1.93 g waterglass and 16.50 g deionized water and aluminate solution was prepared by mixing 4.52 g of NaOH, 8.22 g of deionized water and 0.61 g of $Al(OH)_3$. (Sample calculation to determine batch composition was shown in Appendix A) Aluminate solution was heated and continuously stirred on a hot plate until clear solution was obtained. Evaporated water during this mixing stage was added after aluminate solution was cooled to room temperature. Then aluminate and silicate solutions were mixed and poured into Teflon autoclaves and synthesis was carried out at 80°C for 24 h. After synthesis autoclaves were taken from the oven and cooled in water. Then the product in the autoclave was filtered and washed with water until pH became less than 8. The dried powder was analyzed with XRD for phase identification.

Then the powder was used to prepare seed suspension in which 35 mg of zeolite A powder was mixed with 100 mL of deionized water. To increase dispersion and homogeneity and to prevent the settling of the seed crystals in the seed suspension, it was stirred for 1 h, kept in ultrasonic bath for 10 min and then stirred again for 30 min.

Vacuum seeding set-up was shown in Figure 3.2. In this system, disc was sealed inside the rubber gasket and then placed between two polyamide dies and screws were used to hold disc. Then seed suspension was poured on the disc and vacuum pump is used to get water in the suspension. Since the size of the seed crystals were larger than the pore sizes of disc, they could not penetrate into pores of disc.

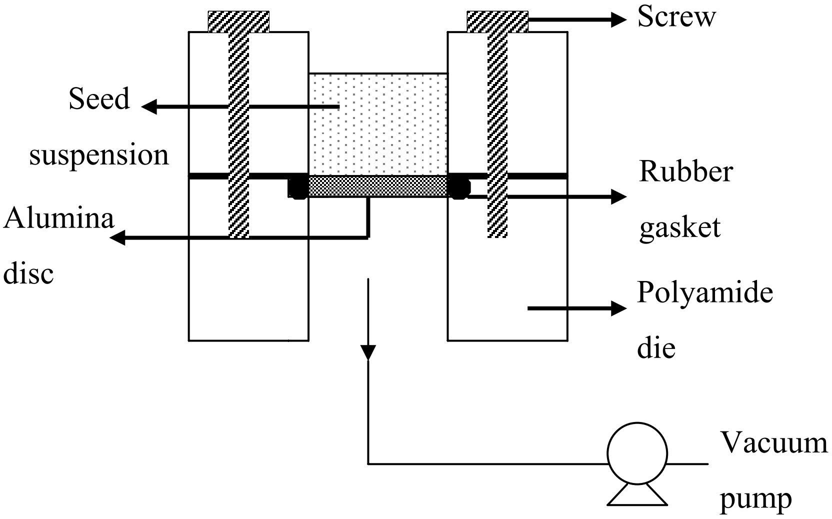


Figure 3.2: Vacuum seeding set-up.

In this method, 4 ml of this suspension was used to deposit 1.4 mg of seed crystals on to the disc surface. After seeding, discs were kept at 120°C for 2 hours to adhere the seed crystal on the support.

3.4. Preparation of Membrane Synthesis Solution

In the preparation of membrane synthesis solution, sodium metasilicate pentahydrate ($Na_2SiO_35H_2O$) as silica source, anhydrous sodium aluminate ($1.322Na_2O$: $1Al_2O_3$, Riedel-de Haen) as alumina source, sodium hydroxide pellets as sodium source and deionized water as water source were used. For the membrane synthesis clear solution with a molar composition of $49Na_2O$: $1Al_2O_3$: $5SiO_2$: $980H_2O$ was used. For 100 g of batch, the amounts of raw materials were 0.880 g sodium aluminate, 5.083 g sodium metasilicate pentahydrate, 16.194 g sodium hydroxide pellets and 77.843 g deionized water. Silicate solution and aluminate solution were prepared separately. 5.083 g of sodium metasilicate pentahydrate, 6.804 g of the sodium hydroxide and 38.922 g of deionized water were mixed to prepare the silicate solution. Aluminate solution was prepared from 0.880 g of sodium aluminate, 9.390 g of the sodium hydroxide and 38.921 g of deionized water. These aluminate and silicate solutions were mixed for one hour separately.

Then aluminate solution was added to the silicate solution slowly and the final clear synthesis solution was mixed for one hour (Zah et al [29]).

3.5. Membrane Synthesis in Batch System

Zeolite A membranes were synthesized in autoclaves on alumina discs from the clear solution with a molar composition of $49Na_2O$: $1Al_2O_3$: $5SiO_2$: $980H_2O$. Synthesis solution was prepared as described in Section 3.4 poured into 30 ml Teflon autoclaves for the synthesis under autogenous pressure. In each synthesis, one unseeded disc was put vertically into the autoclave with a Teflon holder and the synthesis solution was poured into the autoclave. The synthesis conditions of the membranes for batch system are given in Table 3.1. Synthesized membranes were washed with distilled water until pH was around 8 and they were dried for 2 days at 100°C. Also powder synthesized during membrane formation was filtered and washed with distilled water.

Table 3.1: Membrane synthesis conditions

Membrane	Synthesis Method	Support Shape	Seeding Type	Synthesis Temperature (°C)	Synthesis Time (h)	Flow rate ml/min
M1	Batch	Disc	-	95	3	-
M2	Batch	Disc	-	80	4	-
M3	Batch	Disc	-	80	8	-
M4	Batch	Disc	-	60	8	-
M5	Batch	Disc	-	60	24	-
M6	Batch	Disc	-	50	24	-
M7	Batch	Disc	-	50	48	-
F1	Flow	Disc	-	60	24	6
F2	Flow	Disc	-	80	8	6
F3	Flow	Disc	-	95	3	6
F4	Flow	Disc	-	80	8	24
F5	Flow	Disc	-	80	8	48
F6	Flow	Disc	Vacuum	80	8	6
F7	Flow	Tubular	Rubbing	80	8	6
F8	Flow	Tubular	Rubbing	80	8 + 8	6

3.6. Membrane Synthesis in Flow System

In the flow system, zeolite A membranes were synthesized on seeded and unseeded alumina discs and tubes from the clear solution with a molar composition of $49Na_2O$: $1Al_2O_3$: $5SiO_2$: $980H_2O$ (Table 3.1). Synthesis was carried out under atmospheric pressure by recirculating the synthesis solution. The schematic drawing of the system was shown in Figure 3.3. In this system, synthesis solution which was about 120 g was pumped through the support by the help of a peristaltic pump. Temperature of the synthesis solution was kept constant by using silicone oil bath which was put on magnetic stirrer-heater. Support was held vertically in the membrane module having about 30 ml volume and the module was also kept in oil bath. Tube module or disc module was used in membrane synthesis. For disc support a Teflon holder was used to keep the support in vertical position but for tubes no holder was needed (Figure 3.4). The detailed information for the flow system has been reported in the study of Çulfaz et al. [16, 36]. The synthesis conditions of the membranes for flow systems are also given in Table 3.1. All membranes were washed with distilled water after the synthesis until pH was around 8 and they were dried for 2 days at 100°C.

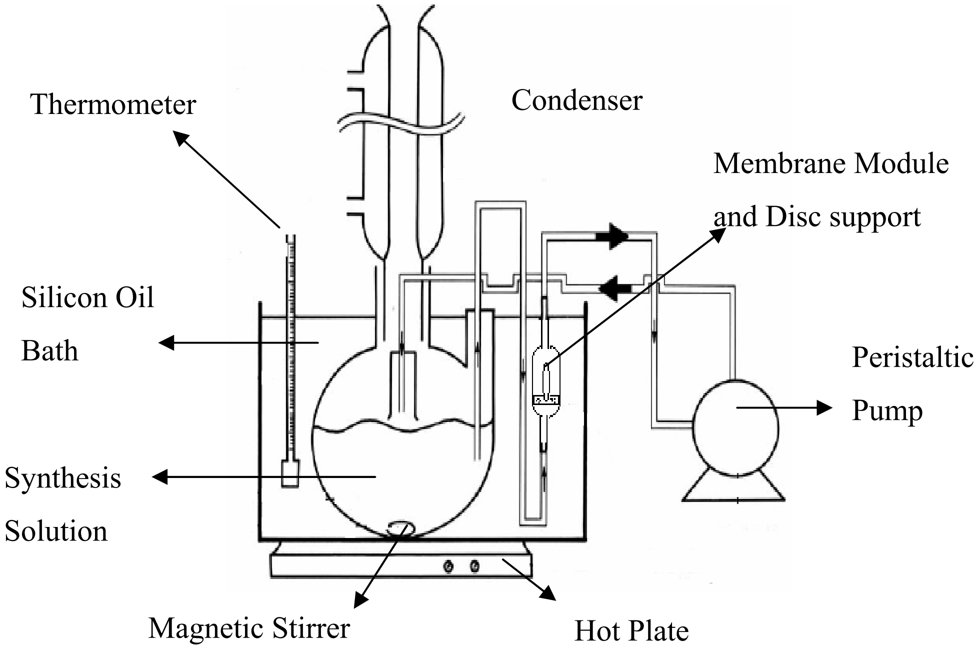


Figure 3.3: Schematic drawing of the flow system for synthesis of disc membranes (redrawn from [36]).

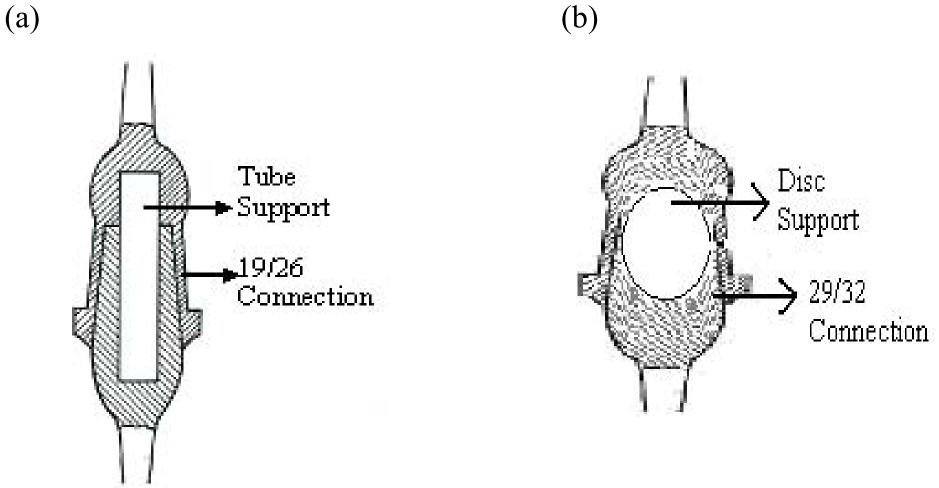


Figure 3.4: Membrane modules used in flow system (a: tubular module, b: disc module).

3.7. Characterization of the membranes

X-ray diffractometer (XRD, Philips PW 1729) with Ni filtered Cu-Kα radiation was used for identification of crystalline structures. The powder samples were analyzed by using depression mounts. However when the powder amount was not enough to fill the depression mount, powders were analyzed by preparing smear slides. Both of the surfaces of the discs were analyzed by mounting the membranes on glass slides without breaking. Operating conditions of the X-ray diffractometer was tabulated in Table 3.2.

Table 3.2: Conditions for XRD analysis

Tube	Cu
Filter	Ni
Radiation	CuKα
Voltage (kV)	30
Current (mA)	24
Speed (°2θ/s)	0.1
Time constant (s)	1
Slit (mm)	0.2

Morphology of the membranes was analyzed by JEOL JSM-6400 scanning electron microscopy (SEM). Before analysis samples were coated with gold.

3.8. Single Gas Permeation Test

For the single gas permeation tests, membranes were placed inside the membrane modules as shown in Figure 3.5. In this module, membrane was inserted between two o-rings which were used to prevent leakage from retentate to permeate side.

After placing the membrane in this module gas permeation tests were carried out by using the set-up shown schematically in Figure 3.6. In this system, a dead end module was used and the measurement was performed by constant pressure-variable volume method. Permeate side was at atmospheric pressure (0.91atm) and feed side had an absolute pressure of 1.91 atm. All measurements were performed at room temperature. Bubble flow meter was used to measure the flow rate of the permeate. Permeance was calculated assuming ideal gas behavior from Equation 3.1.

$$\text{Permeance} = \frac{\text{Molar Flux}}{\text{Trans membrane Pressure Difference}} \tag{3.1}$$

Ideal selectivities of the gases were determined by ratio of the single gas permeances by using Equation 3.2.

$$\text{Ideal Selectivity, A/B} = \frac{\text{Permeance of A}}{\text{Permeance of B}} \tag{3.2}$$

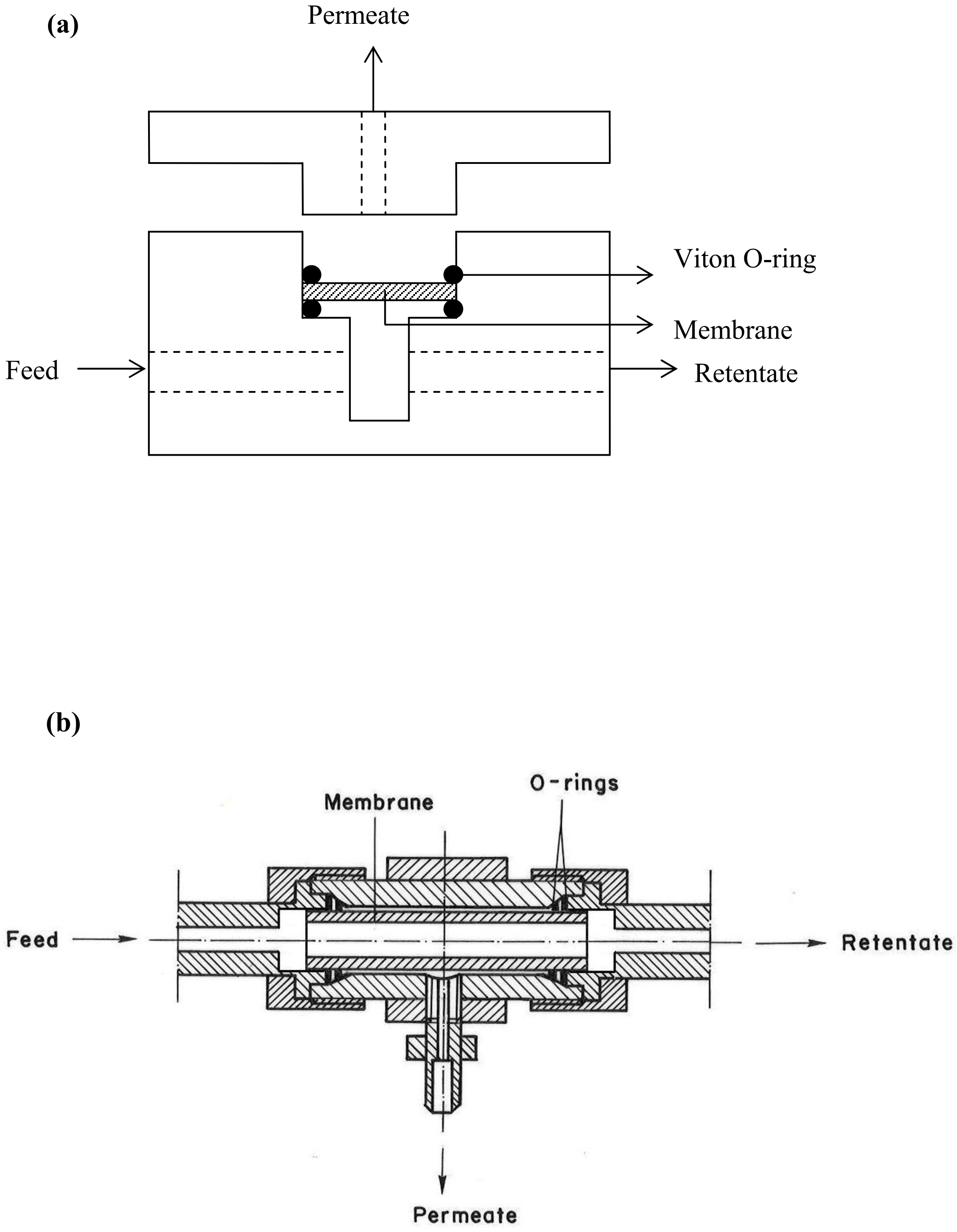


Figure 3.5: Membrane modules used in single gas permeation set-up [36] (**a**: Disc module, **b**: tubular module).

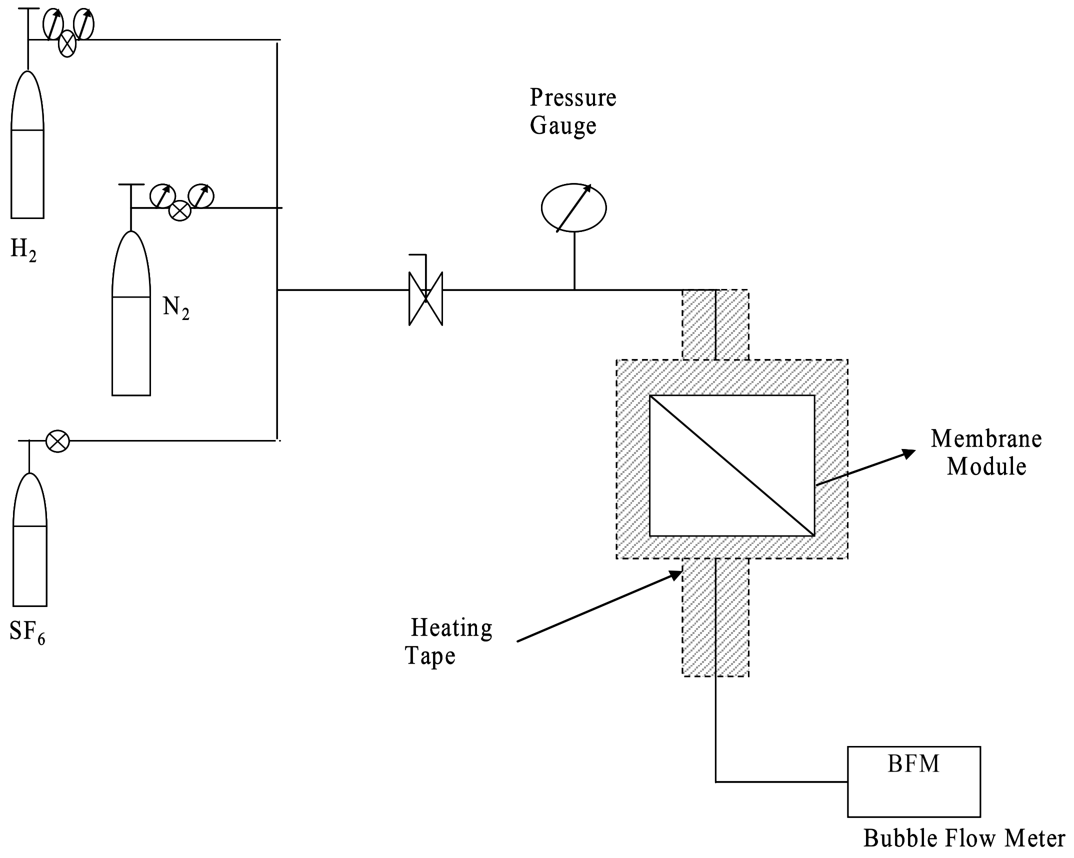


Figure 3.6: Single gas permeation setup [36].

Membranes were dried at 100°C for 2 days prior to gas permeation. Membranes that were synthesized in the batch system were tested with N_2 gas only. However, for the membranes synthesized in flow system, H_2, N_2 and SF_6 gases were used in permeation tests.

3.9. Pervaporation Test

Tubular membranes were also qualified in the pervaporation system by using 7-10 (wt.%) water / 93-90 (wt.%) ethanol feed mixtures at temperatures of 25°C, 50°C and 75°C. Figure 3.7 shows the experimental setup for pervaporation.

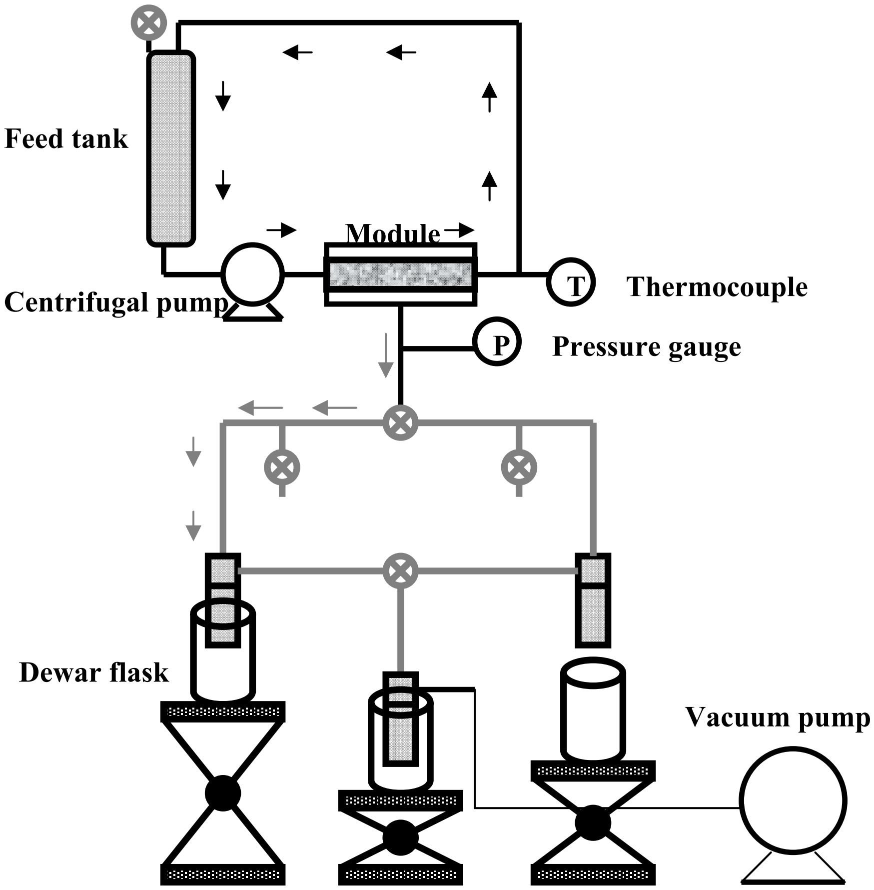


Figure 3.7: Pervaporation setup [37].

In this setup ethanol-water mixture was put into feed tank and circulation of the mixture was provided by the help of pump. Tubular membrane inserted in the membrane module by using o-rings and these rings prevent the leakage of mixture. The permeate side of the system was kept under vacuum by using vacuum pump and two liquid nitrogen traps were used to condense the samples.

Permeate samples were weighed and analyzed by using gas chromatograph Varian CP-3800. Thermal conductivity detector with a Porapak T Column with a carrier gas as helium was used. Operating conditions were tabulated in Table 3.3.

Table 3.3: GC operating Conditions

Column	Porapak T
Column oven temperature	120°C
Mid 1041	180°C
Rear valve	50
Detector Temperature	225°C
Pressure	10
Sample Flow Rate	20 ml/min
Reference Flow Rate	27 ml/min

In this analysis calibration curve was plotted. Manual injections of 1 μl sample were performed and calculated peak areas were compared with the areas in the calibration curve to determine percentage of ethanol and water in the sample. H_2O/EtOH (W/E) selectivity was calculated as:

$$\alpha_{\mathrm{W/E}} = \frac{P_W / P_E}{F_W / F_E} \tag{3.3}$$

where F_w , and P_w represent the composition of water in feed and permeate respectively. Composition of ethanol in feed and permeate is shown as F_E, and $P_{E,}$ respectively.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Synthesis in Batch System

Membranes were synthesized in batch system on unseeded alumina discs from the clear solution having the composition of 49Na_2O: 1Al_2O_3: 5SiO_2: 980H_2O. The aim for the batch synthesis was to find out the conditions to be used in flow system. In batch system, membrane syntheses were performed at 50, 60, 80 and 95°C with various times (Table 3.1). Nucleation rate and crystal growth rate decreases as temperature decreases, longer times can be needed for crystallization of the zeolite A at low temperatures [23]. Therefore synthesis time changed depending on the synthesis temperature. XRD patterns of the membranes showed that zeolite A was the only crystalline phase formed on the supports during membrane synthesis except membrane M1, which was synthesized at 95^{o}C (Figure 4.1). The peaks of alumina support were labeled with asterisks on the patterns. The membrane M1 consisted of other crystalline phase(s) as well as zeolite A, however, the other phase(s) cannot be identified (peaks that not correspond to zeolite A was shown by arrows).

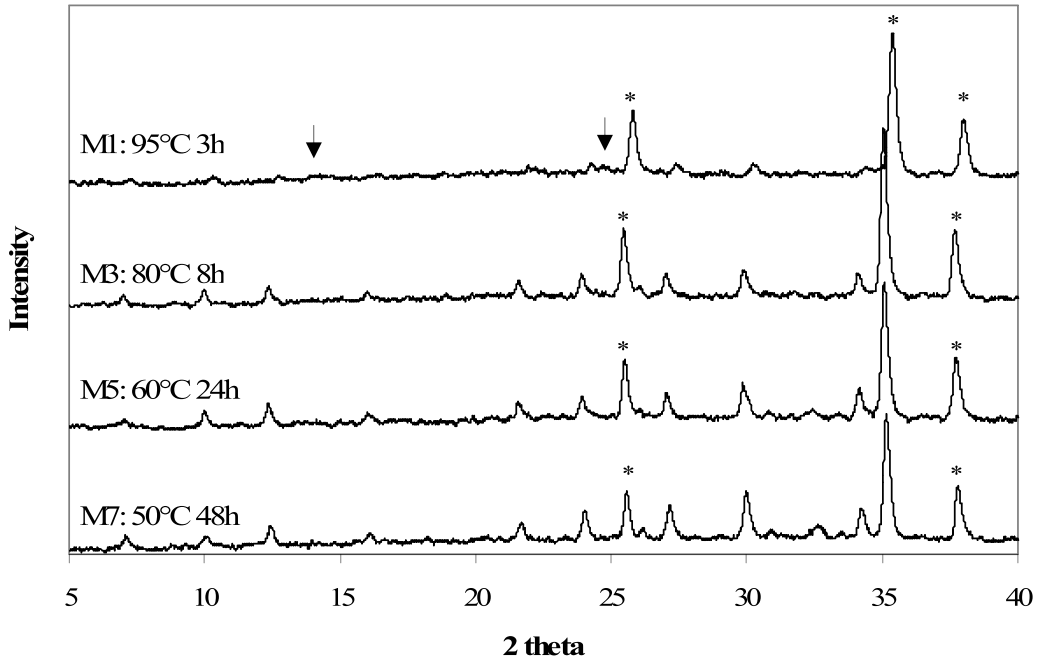


Figure 4.1: XRD patterns of the membranes synthesized in batch system.

For quantitative comparison of membranes, a peak ratio was defined as shown in Equation 4.1.

$$\text{Peak Ratio} = \frac{\text{Sum of peak intensities of zeolite A at } 21.7, 24, 27.2 \text{ and } 30^{o}}{\text{Intensity of alumina support at } 35^{o}} \cdot 100\% \qquad (4.1)$$

Peak ratio is proportional to the crystallinity and amount of zeolite layer forming the membrane. If there is a large amount of zeolite A on the surface, the peaks of zeolite A would be stronger than the peaks of alumina so that peak ratio will be high. Therefore the peak ratio changes between 0, indicating no zeolite A on the support, and infinity, indicating very thick zeolite A layer such that alumina cannot be seen. Therefore the peak ratio resembles the weight change of membrane after crystallization. However, the weight change indicates the amount of zeolite A deposited in the support and on both sides of the alumina disk, although the peak ratio shows the amount of zeolite on one side of the alumina disk. Table 4.1 shows the peak ratios and change of weight of membranes after synthesis of zeolite A layer.

Table 4.1: Synthesis conditions, weight change and peak ratio values for membranes synthesized in batch system.

Membrane	Synthesis Conditions	Weight change of disc (mg)	Weight Increase (%)	Peak Ratio (%)
M1	95°C, 3 h	+10	1.0	19
M2	80°C, 4 h	+18	2.3	40
M3	80°C, 8 h	+17	2.2	69
M4	60°C, 8 h	+26	3.5	11
M5	60°C, 24 h	+29	3.8	85
M6	50°C, 24 h	+38	5.4	24
M7	50°C, 48 h	+42	5.5	70

Percent weight change of the membranes increased with decreasing synthesis temperature; it was 2.3 and 5.5% for membranes synthesized at 80°C and 50°C, respectively. Besides no difference was observed between the percent weight changes of membranes prepared with different synthesis times for a particular temperature, for instance the weight changes of membranes were 3.5 and 3.8% after synthesis for 8 and 24 h at 60^{o}C, respectively. Since the synthesis solutions with the same composition were used for synthesis at all temperatures, it can be concluded that low temperatures favor the deposition from the bulk solution on to the support surface.

On the other hand, the peak ratio increased with time for a given temperature. For example, the peak ratio of M7 was almost twice higher than that of M6 although the weight change of those membranes was almost the same. Apparently crystallinity of membrane layer increases with time although there was no significant change in the weight of the discs. Okamoto et al. [13] suggested that in the membrane formation, an amorphous gel firstly covers the support and the zeolite crystals form in this gel layer so that a continuous membrane layer is eventually obtained. Besides, Kalıpçılar and Çulfaz [38] suggested that a similar gel layer may form during the formation of silicalite membranes even if a clear synthesis solution is used. Similarly, a gel layer may form on the support during the synthesis of zeolite A membranes from clear solutions. As synthesis proceeds, the gel layer turns to zeolite A so that the peak ratio increases although the weight change remains almost the same. The XRD pattern of all membranes can be seen in Appendix B.

Although XRD patterns and weight changes were helpful to identify the crystalline phases grown and their amounts on the supports, they are not sufficient to determine whether or not a continuous zeolite layer formed. Therefore, the surfaces of membranes were analyzed with SEM to see the morphology of the membranes.

Figure 4.2 shows the SEM images of fractured cross-section of membranes. Cross section SEM image of M1 showed that membrane had discontinues zeolite layer with a thickness of about 1 μm as expected from weight change and peak ratio values. When cross section views of membranes M2 and M3 were analyzed continuous and uniform layers were observed on both membranes. Both of them consisted of significant amount of zeolite A as suggested by XRD peak ratios. However, the zeolite A content of membrane M3 was much higher than that of membrane M2, indeed, the surface SEM images of membrane M2 suggested the presence of amorphous layer as shown in Figure 4.3. According to SEM image of M4 no layer was observed as expected from low peak ratio (11%). However extension of synthesis time to 24 h was resulted in peak ratio of 85% showing that higher amount of zeolite A was collected on M5 than M4. From cross section view of M5, continuous and uniform zeolite A layer which bonded directly to the support with a thickness of 3 μm was observed. Both of the membranes synthesized at 50°C (M6 and M7) had continuous zeolite A layer. M7 had almost two times higher peak ratio than M6 suggesting that thicker layer was formed on M7. Cross section view of M6 showed that continuous layer was formed on the support with a thickness of only 1.2 μm, but thickness of M7 was 3.8 μm as expected from peak ratios. However, it was observed that there was deposited material attached to the membrane layer M7. Since no other zeolite phase was obtained from the XRD analysis the deposited material could not have other type of zeolites but it could have zeolite A crystals as well as amorphous particles.

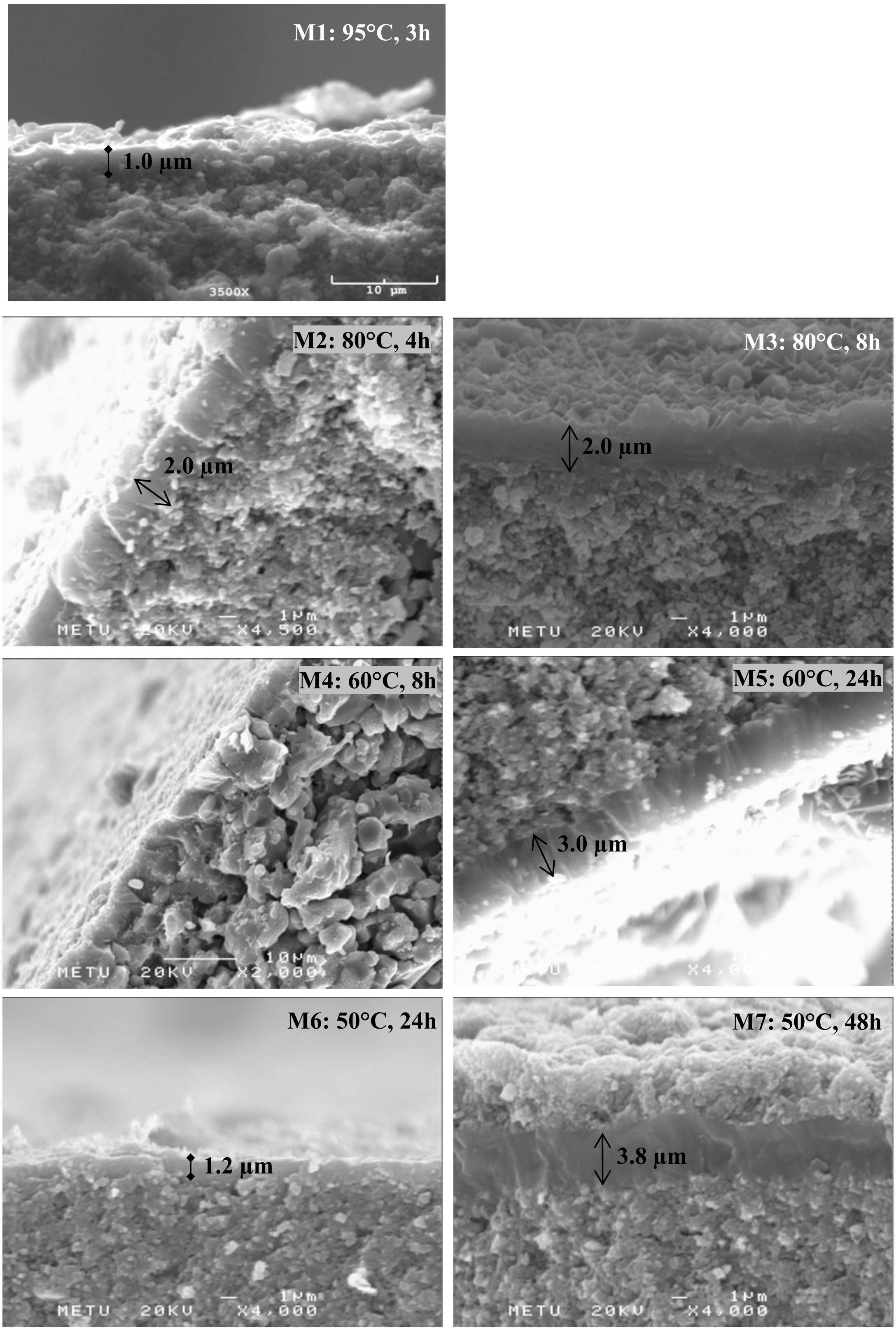


Figure 4.2: Cross sectional images of the batch synthesized membranes.

Figure 4.3 shows the surface SEM images of membranes. The surface of membrane M1 consists of zeolite A crystals with their typical cubic shape in addition to the crystals of unidentified phase. These crystals have a shape of cabbage like morphology. Yamazaki et al. [14] who studied zeolite A formation on plate heater observed that chabazite and gmelinite type of crystals formed cabbage like crystals as in our case (Figure 4.3). The number of these crystals was less than the number of zeolite A crystals. The membranes M2 and M3 are composed of cubic zeolite A crystals with a size of 1-2 μm as shown in Figure 4.3. The surface view of membrane M2 also showed that there was an amorphous layer attached to the membrane layer, suggesting that the synthesis time was not sufficient for complete crystallization. SEM image and XRD pattern of membrane M4 showed that no membrane formed on the alumina disk at 60°C after 8 h of synthesis. However membrane M5 had a continuous zeolite A layer with typical cubic form of zeolite A crystals. Sizes of cubes changed between 1 and 3 μm. From the top view SEM image of M6, it was seen that zeolite A crystals was surrounded by the amorphous layer and crystals were in the spherical shape. Zah et al. [29] studied the growth of the zeolite A in membrane synthesis with respect to time and they claimed that before fully crystallization of zeolite A, spherical form of A embedded in the gel like structure was seen on the support. Moreover low peak ratio also showed that crystallization of zeolite A was not completed for M6. On the other hand impurities on M7 prevented the view of membrane layer.

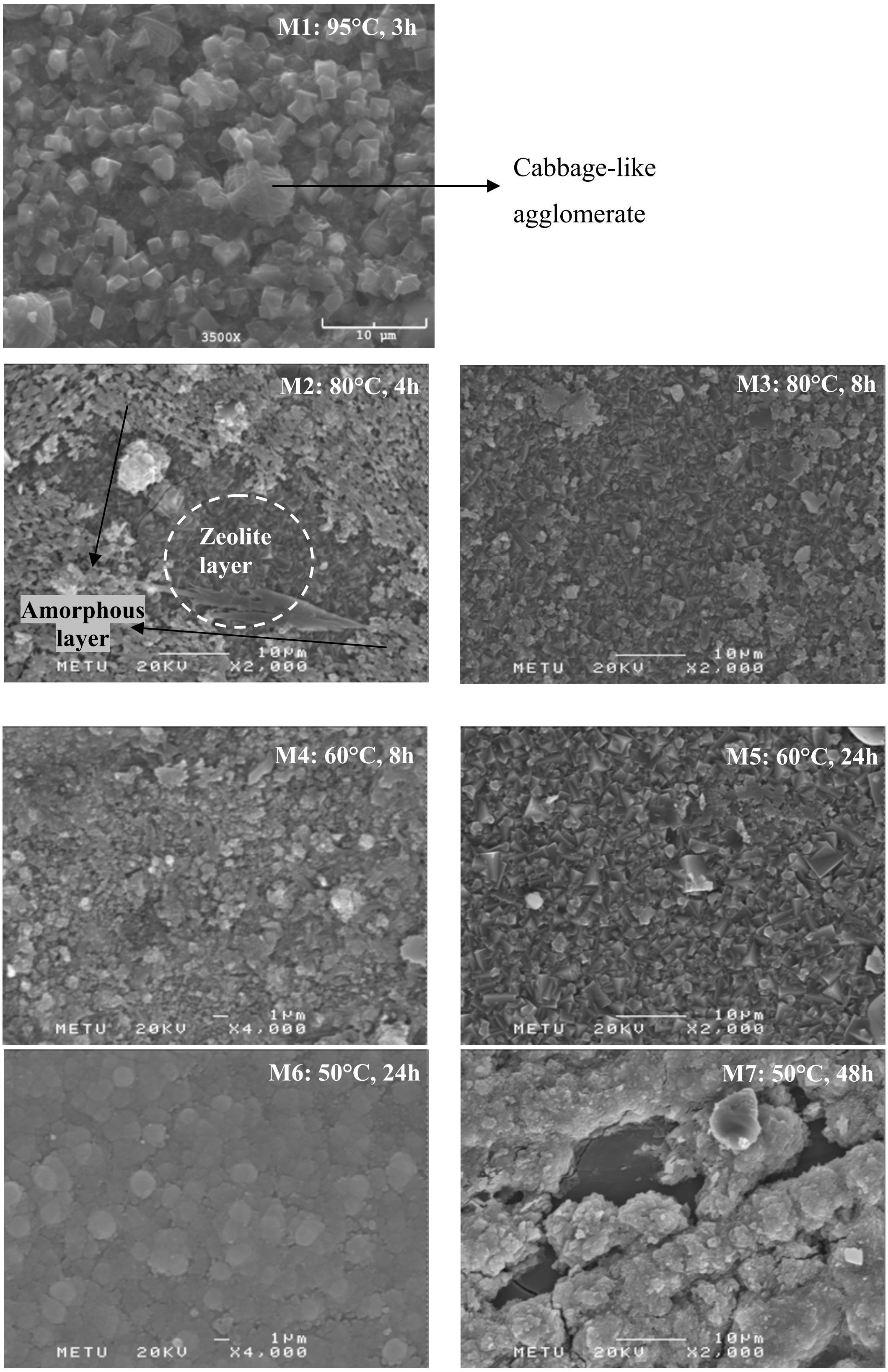


Figure 4.3: Surface SEM images of batch synthesized membranes (For larger views see appendix C).

Table 4.2: Thickness and peak ratio results for batch synthesized membranes.

Membrane	Synthesis Conditions	Peak Ratio (%)	Thickness µm
M1	95°C, 3 h	19	1.0
M2	80°C, 4 h	40	2.0
M3	80°C, 8 h	69	2.0
M4	60°C, 8 h	11	0.0
M5	60°C, 24 h	85	3.0
M6	50°C, 24 h	24	1.2
M7	50°C, 48 h	70	3.8

Calculated peak ratios and thicknesses are tabulated in Table 4.2. The membrane thickness increased with decreasing temperature, indicating that more crystals, as shown from high peak ratio values, deposited onto the surface as temperature decreased. For the synthesis in low temperatures longer synthesis times are required for complete crystallization. At low temperatures large amount of nuclei are formed on the support and these large amount causes thicker membrane layer as they grow.

The integrity of membranes and their defect density was determined by measuring N_2 permeation rates. For N_2 permeation, membranes were kept at 100°C for 2 days. Although this temperature is not enough to completely remove water from zeolite A crystals, it is sufficient to remove water from large non-zeolitic pores. Therefore, the rate of N_2 permeation gives information about the existence of non-zeolitic pores in the membrane so that a good quality membrane is expected to have low N_2 permeance.

Table 4.3: Thickness and N_2 permeation results of the membranes.

Membrane	N_2 Permeance (mol/m^{2}Pas x10^{-8})	Thickness μm
M1	20	1.0
M2	4.0	2.0
M3	8.1	2.0
M4	---	0.0
M5	1.8	3.0
M6	2.9	1.2
M7	<0.01	3.8

According to N_2 permeation results that tabulated in Table 4.4, M7 showed very low permeation for N_2. However the low N_2 permeance is probably not due to the defect-free structure of the membrane but due to the material deposited on the membrane M7 as shown in Figure 4.2. Membranes M2 and M3, which had similar thicknesses, showed almost the same N_2 permeation that could be the evidence for similar membrane quality. The membrane M5, which was thicker than the membranes M2 and M3, showed lower N_2 permeation rates than the other two membranes. This could be caused from two reasons; Membrane M5 could be better membrane which means that membrane M5 had less defects or the thickness of membrane M5 decreased the permeance. High N_2 permeance was observed for M1 since it did not have a continuous zeolite layer.

Zeolite A membranes studied in literature showed N_2 permeances in the range of 10^{-8} to 10^{-9} mol/m^{2}Pas. These membranes are generally expected to have zeolite layers of good quality and they generally showed higher separation performances in pervaporation tests. Therefore, membranes having nitrogen permeances in this range are assumed as high quality membranes.

From these results, the synthesis conditions for membranes M3 and M5 seemed to be the best choice to perform synthesis in flow system because of their high peak ratio, crystallinity, and low N_2 permeation results. Even N_2 permeation of M7 was the smallest, condition of M7 was not preferred because of the impurities on the membrane layer and long synthesis time.

4.2. Synthesis in Flow System

Batch syntheses at various temperatures were carried out in order to define the synthesis conditions for use in flow system. Based on batch syntheses, in flow system synthesis was carried out at the conditions of 60°C for 24 h, 80°C for 8 h and 95°C for 3 h. In addition, membranes were synthesized at 80°C on seeded supports and with different flow rates and effect of the seeding and flow rate were investigated.

Membranes were analyzed by XRD and SEM, for phase identification and morphology, respectively. From XRD patterns, the peak ratios were also calculated to estimate the amount of zeolite and thickness of the membrane layer as done in batch synthesis. The membranes were also characterized by single gas permeation measurements of H_2, N_2 and SF_6.

As described in Section 3.2, discs were composed of two parts; thin mesoporous layer and thick macroporous layer as shown in Figure 4.4. Since both of the parts were in contact with the synthesis solution, membrane formation could occur on both sides. Zeolite layer formed on mesoporous part of the support was called as “layer-a” whereas zeolite layer formed on macroporous part was called as “layer-b”. In flow system syntheses, XRD and SEM analysis were performed for both layers to observe the effect of support surface.

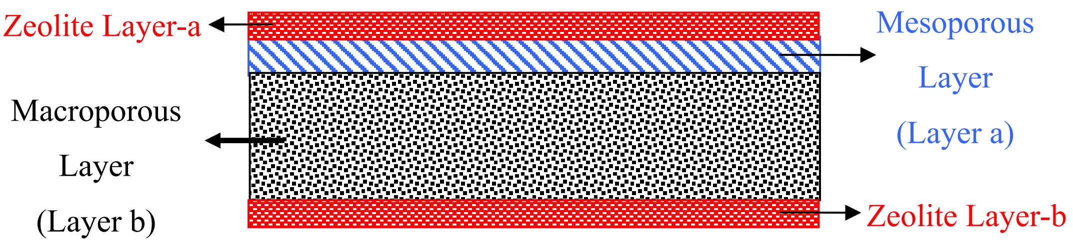


Figure 4.4: Schematic view of the disc support and the membrane layers on the disc.

4.2.1. Effect of synthesis temperature on membrane morphology

In flow system, zeolite A membranes were synthesized at 80°C for 8h, 60°C for 24h and 95°C for 3h on unseeded discs with a flow rate of 6 ml/min. X-ray results of the membranes were shown in Figure 4.5. The peaks related with alumina were signed with asterisks. When peaks of membranes were compared with those of powder zeolite A, no other phases were observed in the membranes. When literature is considered, these membranes are only zeolite A membranes synthesized in flow system.

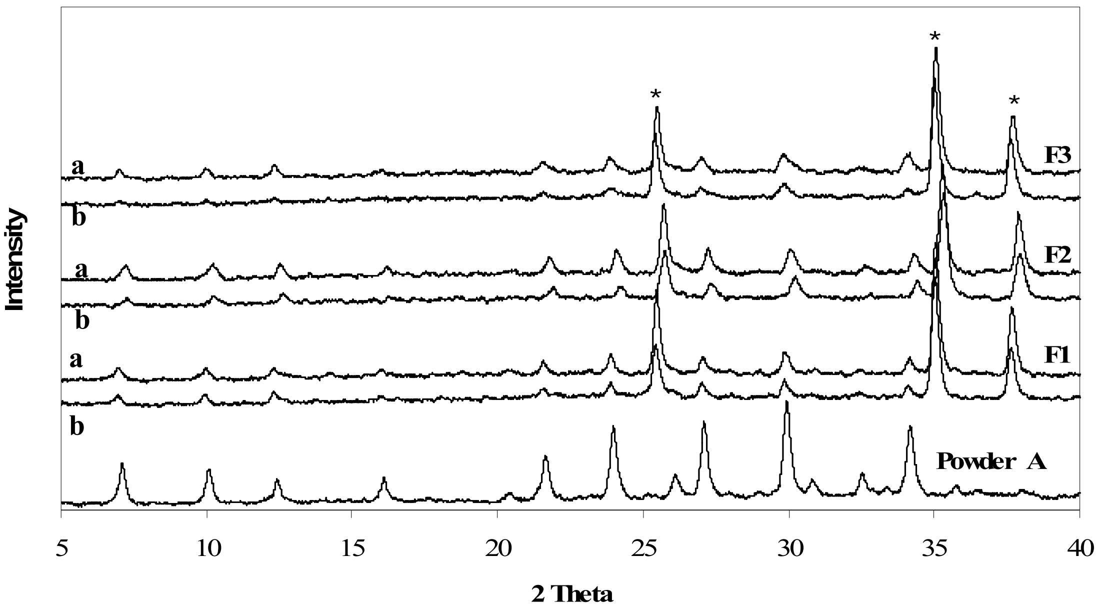


Figure 4.5: XRD patterns of the membranes synthesized in flow system, F1: 95°C for 3h, F2: 80°C for 8h, F3: 60°C for 24h (*: Alumina Peaks, a: mesoporous layer, b: macroporous layer).

Surface SEM images of the membranes are shown in Figure 4.6. From these images, it was obvious that morphology of the membranes formed on two surfaces was almost same. For F1 which was synthesized at 95°C for 3h, no other types of crystals were observed on the surface of F1, cubic form of zeolite A was easily identified having about 2-4 μm sizes on both of the surfaces. Synthesis at 80°C for 8h yielded membranes with a morphology similar to membranes prepared at 95°C. Regardless of the temperature, zeolite A layer was composed of highly intergrown crystals. On the other hand, the membrane F3, which was synthesized at 60°C, consisted of spherical particles. The particles are possibly agglomerates of smaller and cubic zeolite A crystals. Besides the mesoporous surface of the membrane is likely to be coated with a gel layer, indicating incomplete crystallization due to short period of synthesis time.

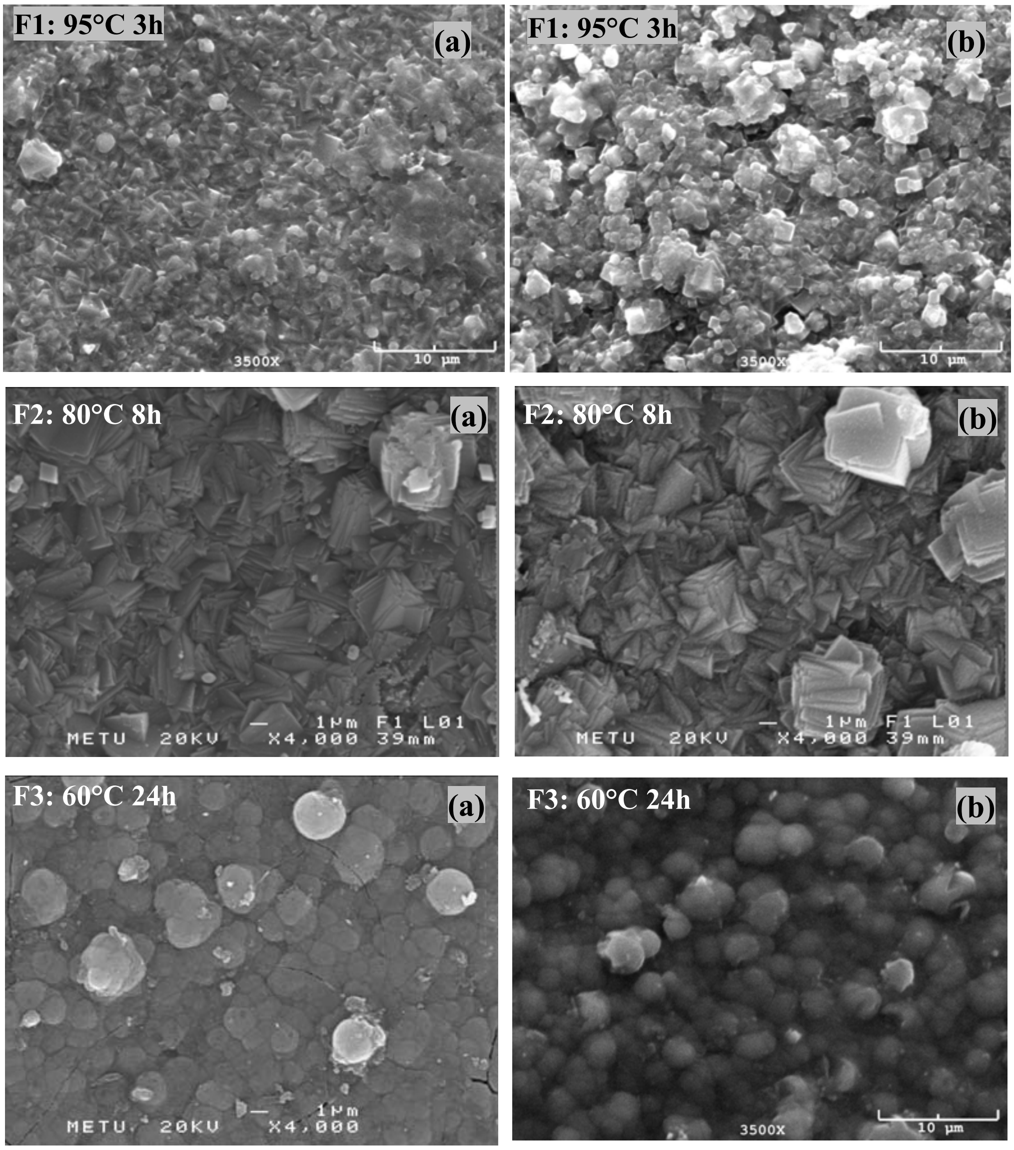


Figure 4.6: Top views of membranes synthesized in flow system (a: mesoporous surface, b: macroporous surface) (Larger views shown in Appendix C).

Figure 4.7 shows the cross section SEM images of the membranes synthesized in the flow system. From the cross section view, it was seen that uniform and continuous layers were formed on both surfaces of membrane F1. The zeolite A layer-b is slightly thicker than the layer-a, which were 1.7 and 2.0 µm, respectively. Synthesis at 80°C resulted in uniform and continuous zeolite A layers, however, the layers a and b have significantly different thicknesses; 2.5 and 3.8 µm for layer a and b, respectively. For synthesis at 60°C for 24h, continuous zeolite A layer with a thickness of 1. 5 μm could be seen easily on layer-a but no membrane was seen on layer-b.

Weight increase and peak ratio values are tabulated in Table 4.4. Percent weight increase values increased with decreasing temperature. It was 1.3% for 95°C synthesis whereas it increased to 3.2% for 60°C synthesis. Although membrane F3 had higher weight increase than membranes F1 and F2; lower peak ratio suggested that amount and crystallinity of zeolite crystals were lower on membrane F3. Peak ratio values were calculated for two surfaces of the support to estimate the distribution of weight to the surfaces. Peak ratios for layer-b were larger than those for layer-a for all membranes. This showed that amount of zeolite collected on layer-b was higher than layer-a so thicker membranes could be prepared on the layer-b, which was the macroporous side of the support.

Table 4.4 also shows the thicknesses of the membranes, which were determined from SEM images. Thickness of the membrane on layer-b was larger than that on layer-a, which is parallel to the results obtained from XRD analysis. At high alkalinity since the leaching of alumina support is inevitable, synthesis compositions on the support and in the bulk are different; the alumina concentration is higher around the support and in the pores. Since it is easier for synthesis solution to penetrate into the macroporous surface the interaction between the support and solution is higher for this side. It is known that the crystal size and surface coverage increases with increasing alumina concentration which may cause thicker zeolite layer on macroporous surface.

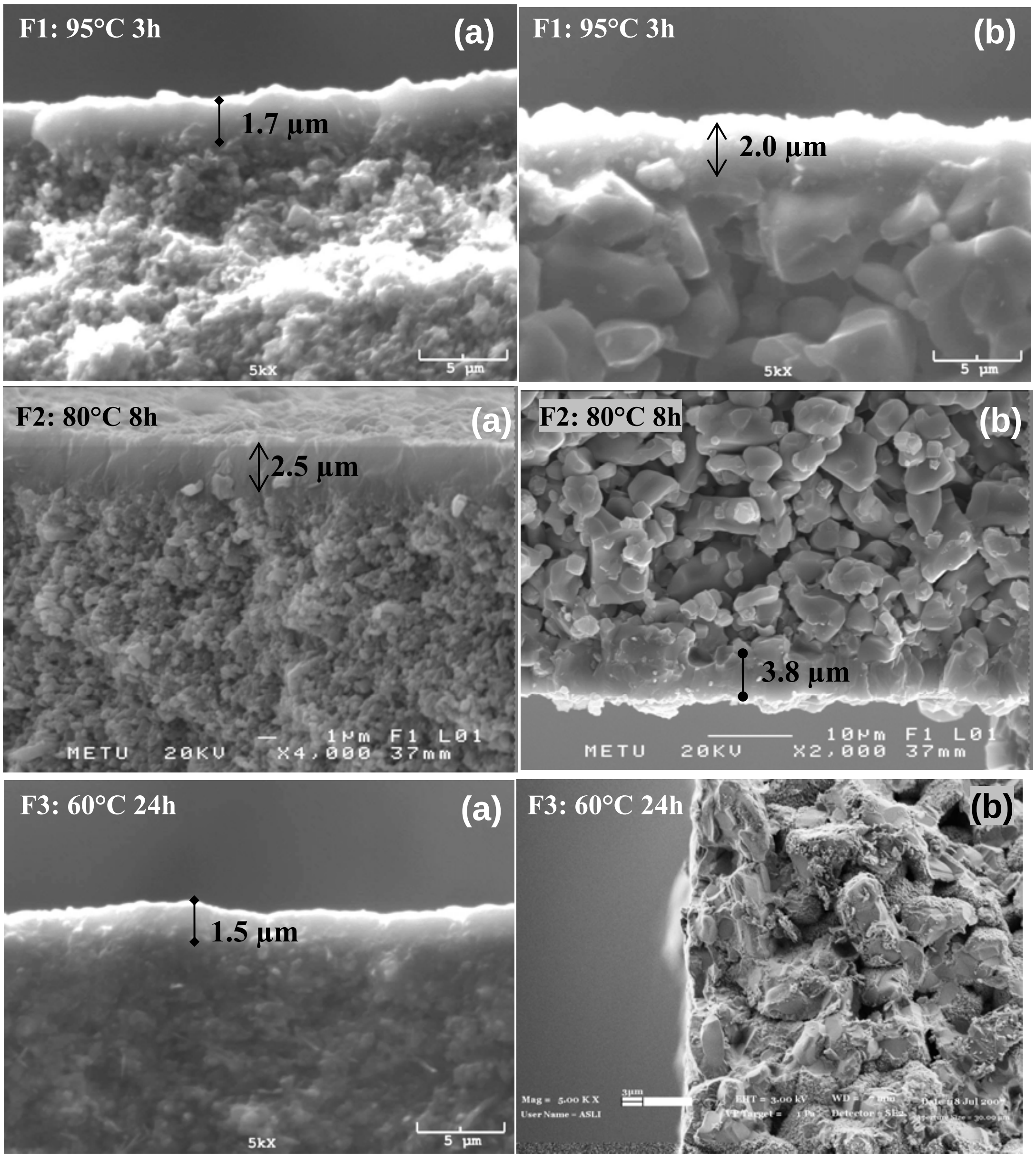


Figure 4.7: Cross section views of membranes synthesized in flow system (a: mesoporous layer, b: macroporous layer)

Table 4.4: Results for the membranes synthesized in flow system.

Membrane	Synthesis Conditions	Weight Increase (%)	Peak Ratio (%)		Thickness (μm)	
			Layer-a	Layer-b	Layer-a	Layer-b
F1	95°C, 3h	1.3	36	39	1.7	2.0
F2	80°C, 8h	2.6	57	87	2.5	3.8
F3	60°C, 24h	3.2	30	40	1.5	--

In flow system synthesis, during the drying stage, a film detached from the mesoporous surface of some membranes that were prepared at 80°C for 8h. The synthesis solution used for membrane preparation was highly alkaline, which probably dissolved some alumina and caused detachment of mesoporous layer from macroporous layer as shown in Figure 4.8. Essentially, high alkalinity of the synthesis solution is expected to cause detachment of mesoporous layer, however, the temperature of the system and the flow of solution over the support may also contribute to the detachment of the mesoporous layer. No damage was observed on the membranes synthesized at 95°C for 3h and 60°C for 24h. Although the conditions at 95°C are even harsher than the conditions at 80°C, the support preserved its structure probably due to the short synthesis time at 95°C.

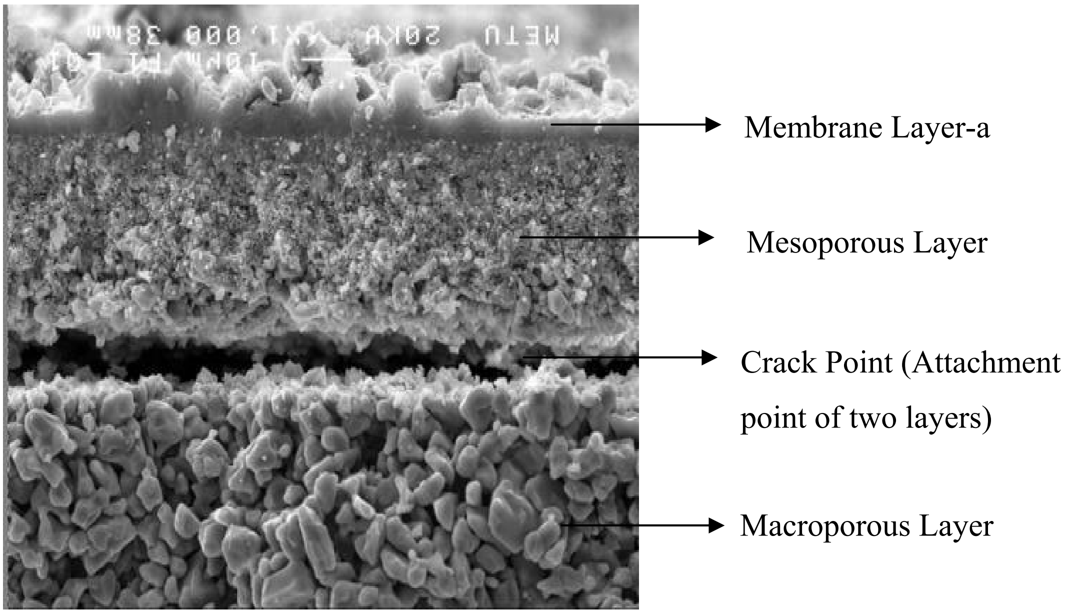


Figure 4.8: SEM image of the cracked disc (F2).

In order to compare the membranes synthesized in flow system with those in batch system, values of weight changes, peak ratios and thicknesses were used (Table 4.5).

The weight change and the thickness of the membranes synthesized in batch and flow systems were comparable, however, it should be noted that the flow rate was quite low in this set of experiments, at higher flow rates the weight change can be influenced from the flow of synthesis solution. However peak ratios obtained from membranes synthesized in flow system are lower than those in batch system, except at 95°C. In zeolite membrane synthesis, zeolites can grow directly on the support surface or they can deposit from the bulk solution. In a batch system both route can play role in membrane formation however in flow system synthesis flow can sweep away the deposited crystals which may cause fewer zeolite crystals on the support.

Table 4.5: Peak ratio and thickness values for the membranes synthesized in batch and flow systems.

Membrane	Synthesis Conditions		Weight Increase (%)	Peak Ratio (%)	Thickness of layer-a (µm)
M1	Batch	95°C, 3 h	1.0	19	1.0
M3		80°C, 8 h	2.2	69	2.0
M5		60°C, 24 h	3.8	85	3.0
F1	Flow	95°C, 3 h	1.3	36	1.7
F2		80°C, 8 h	2.6	57	2.5
F3		60°C, 24 h	3.2	30	1.5

4.2.2. Effect of flow rate on membrane formation

Syntheses were carried out at 80°C and 8 h by using three different flow rates (6, 24, 48 ml/min) to investigate the effect of flow rate on the membrane formation. XRD patterns of the surfaces of the membranes were shown in the Figure 4.9. In this Figure, “a” and “b” represent the mesoporous and macroporous layer of the disc, respectively. It was observed that pure zeolite A membranes were obtained for all flow rate syntheses.

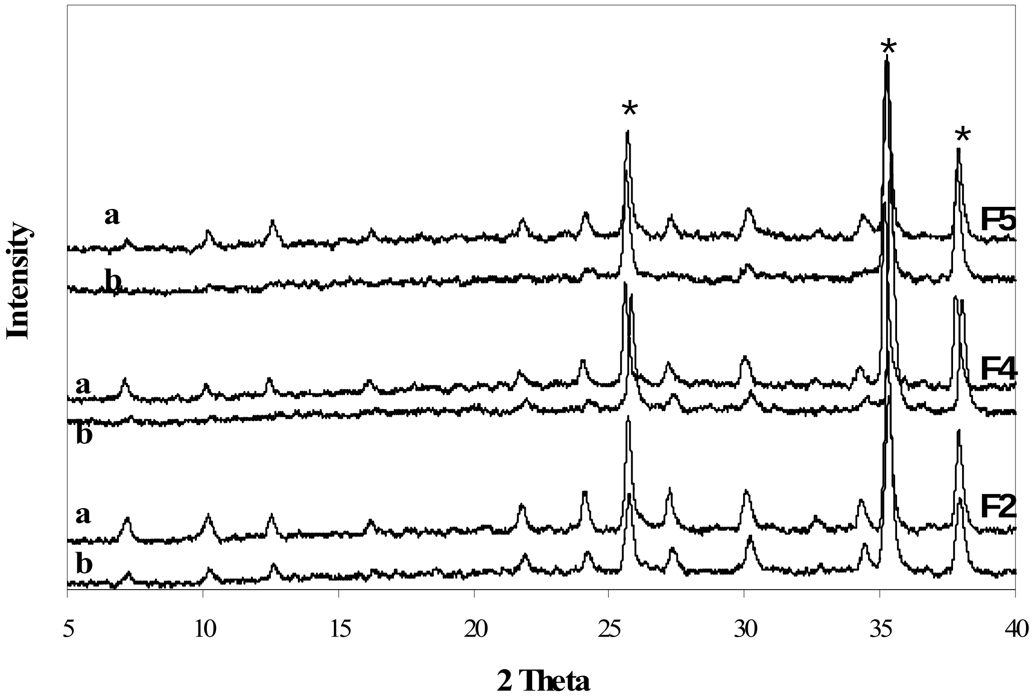


Figure 4.9: XRD patterns of the membranes that synthesized at 80°C for 8h with different flow rates F2: 6ml/min, F4: 24 ml/min, F5: 48 ml/min.

Table 4.6: Results for the membranes synthesized with different flow rates.

Sample #	Flow Rate mL/min	Weight change of disc, mg	Peak Ratio		Thickness µm	
			Layer-a	Layer-b	Layer-a	Layer-b
F2	6	20	57	87	2.5	3.8
F4	24	12	23	47	2.7	4.0
F5	48	4	11	45	--	--

Peak ratios were calculated by using Equation 4.1 and they were tabulated in Table 4.6. From this table, it was seen that value of peak ratio decreased with increasing flow rate. Note that small pieces detached and fell from the mesoporous side of the support after crystallization. As the amount of the broken layer increased with flow rate, the weight change decreased, in addition, as the amount of zeolite A decreased on layer-a, the peak ratio also decreased. The reason for that was not the crystallization of zeolite but the detachment of the membrane layer caused decrease in intensities of the zeolite A peaks. It could be concluded that high flow rates causes more damage on the support and the thickness and crystallinity of the zeolite A membrane depends on the stability of the support at high flow rates.

Since no damage occurred on the layer-b, higher peak ratio values than peak ratio of layer-a were obtained. For layer-b similar peak ratios were calculated for the membranes synthesized at medium and high flow rates (F4 and F5). With the minimum flow rate, deposition of zeolite crystals to the surface became easier causing peak ratio as high as 80%. These peak ratios also helped in the estimation of the distribution of the weight increase. Since peak ratio of layer-b is more than of layer-a, it can be concluded that more zeolite formed on layer-b causing thicker membrane on this layer. This was also proved from the cross section SEM images of these membranes. SEM analysis was performed on both surfaces for these membranes.

Cross section views of both of the layers were shown in Figure 4.10. For the synthesis with a flow rate of 6 ml/min (F2), uniform and continuous zeolite A layer was formed on both sides. As expected from peak ratios thicker membrane was obtained on layer b. When flow rate increased to 24 ml/min, similar membrane was observed on layer as the one in F2 even lower peak ratio was observed. Membranes on F2 and F4 were attached to the support tightly. Thicknesses of the membranes on F4 were 2.7 and 4.0 μm for layer a and b, respectively. When synthesis was carried out at maximum flow rate (F5), damage on the support was maximized so no membrane layer could be observed on mesoporous part of the membrane since the entire layer was broken out during drying stage. Membrane layer on macroporous surface could not be easily identified. It can be concluded that because of high flow rate the deposition of the zeolite crystals to the support would be difficult.

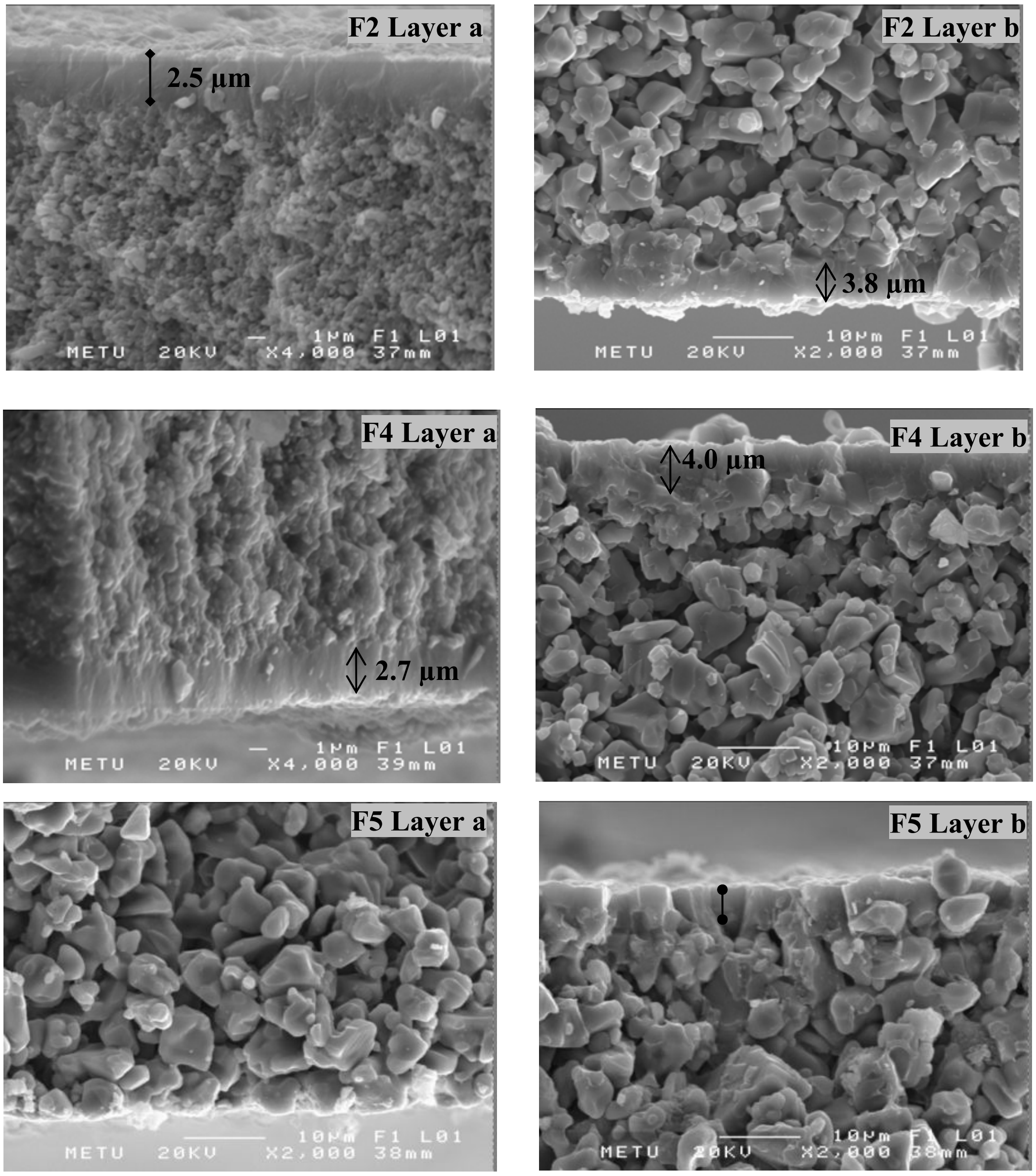


Figure 4.10: Cross section SEM images of the membranes synthesized in flow system with different flow rates.

Top view SEM images are shown in Figure 4.11. It was observed for minimum flow rate (F2) there was no morphological change within the surfaces; well inter-grown cubic form of zeolite A was occurred on both of the surfaces forming a continuous membrane layer. As seen from the top view of SEM images there were zeolite crystals, some of which had 4 µm sizes, attached to the membrane on layer-

b. The appearance of the big crystals and thicker membrane explained the higher peak ratio for layer b. When top view SEM images of F4 was analyzed, cubic zeolite A crystals were seen on layer-b, but on layer “a” the crystals were embedded in the amorphous gel. Maximum flow rate synthesis (F5) caused broken of entire membrane on layer-a therefore no crystals were observed on the surface of layer-a. Top view of layer-b showed that there were some crystals but the gel like structure on them prevented the appearance of these crystals.

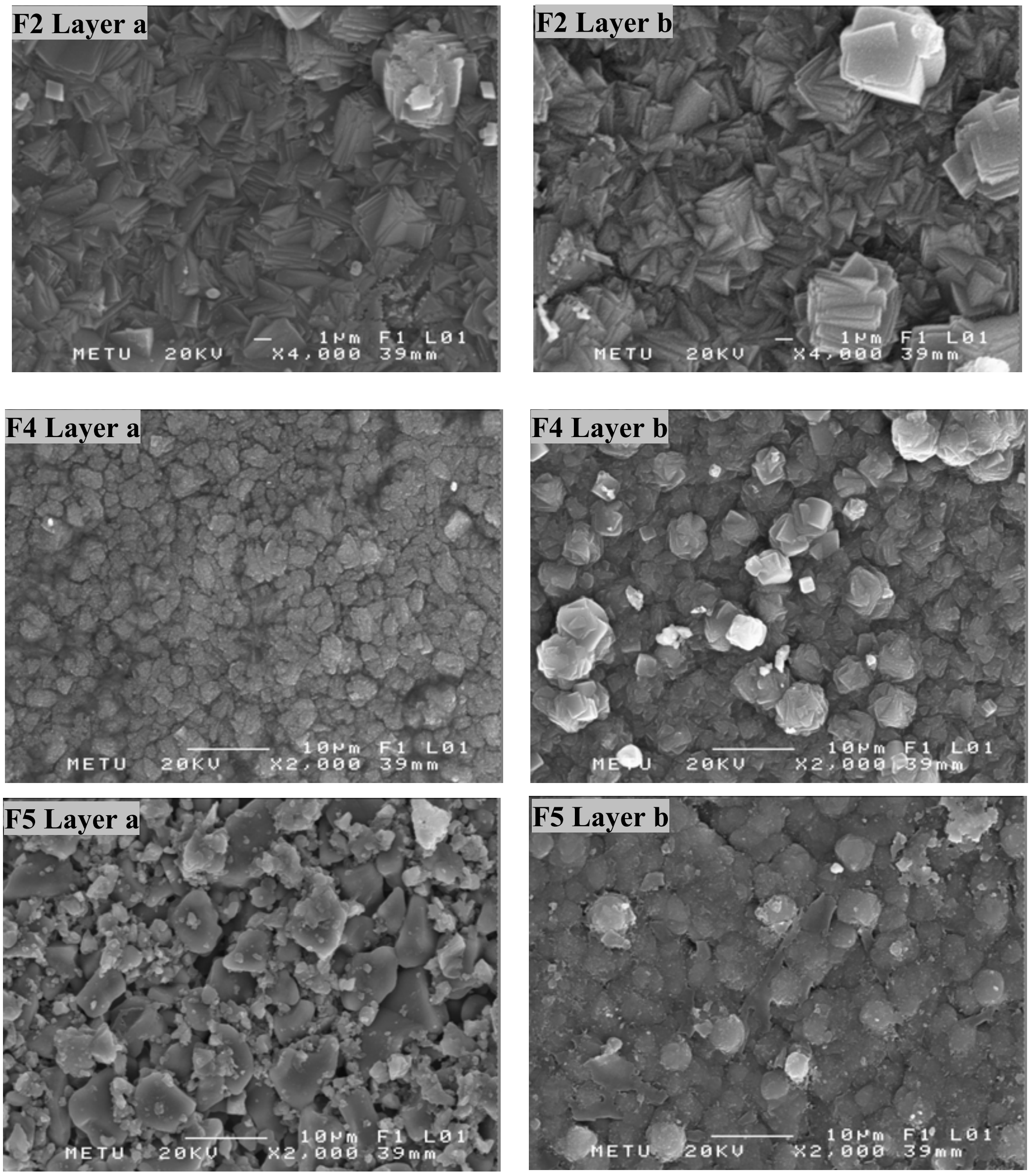


Figure 4.11: Top view SEM images of the membranes synthesized in flow system with different flow rates (For larger views see appendix C).

In this study high alkaline synthesis solution damaged the support by causing detachment of mesoporous layer from macroporous layer and this detachment increased with flow rate increase. It should be noticed that different results can be obtained when synthesis is carried out by using different solutions of supports.

4.3. Seeding of the supports

Seeding improves the quality of zeolite A membranes [25].In literature, seeding have been performed by various methods such as dip-coating [16, 29], vacuum seeding [39] and rubbing [23]. According to the study of Huang et al. [19] more uniform and effective seeding can be made by vacuum seeding method. Therefore, in this study vacuum seeding method was used to coat the support surface with seed crystals. For this purpose, about 1 mg of zeolite A crystals having 1-2 µm sizes was deposited onto the mesoporous surface of the disc.

In the study of Huang et al. [19] after vacuum seeding, supports were kept at 100°C for 3 h to adhere the zeolite A crystals to the support. In this study this was done at 120°C for 2 h.

The support surface was analyzed with XRD to verify the existence of seeds on the support (Figure 4.12). Weak zeolite A peaks were obtained from the seeded disc since the seed amount was small. Also SEM analysis was performed to understand whether a seed layer was formed (Figure 4.13). Seeds coated most of the support but some parts of the support remained uncoated, probably because of non-uniform settling of particles.

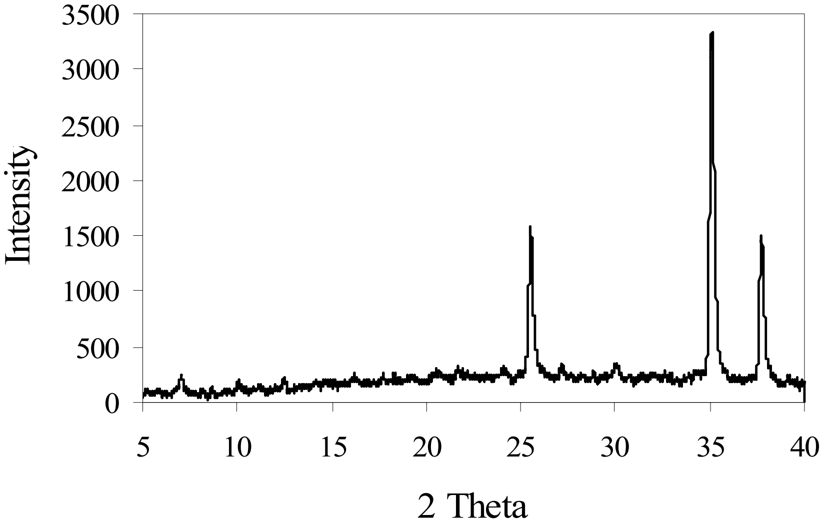
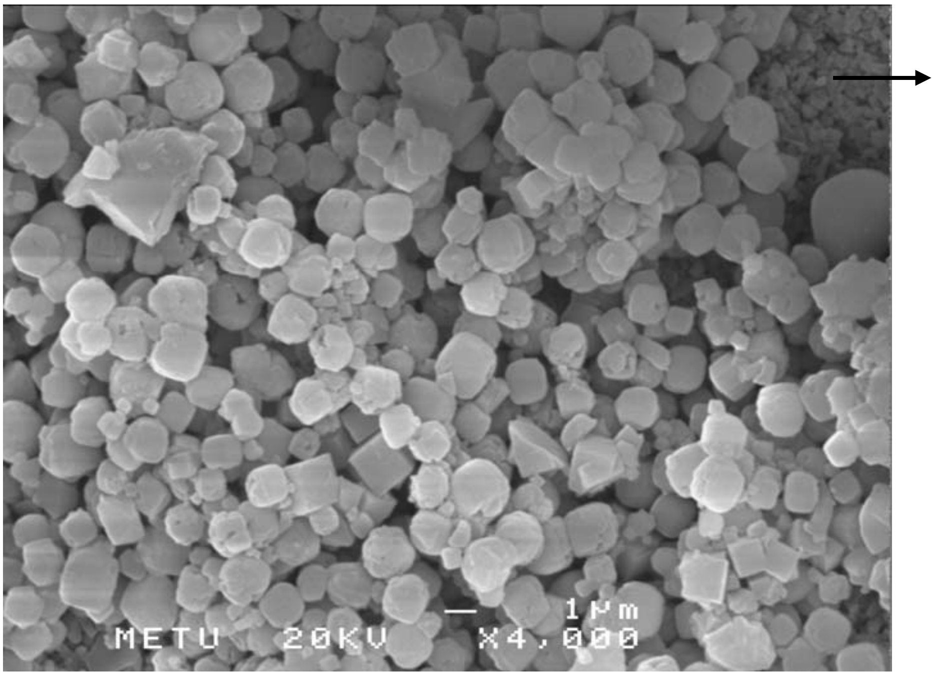


Figure 4.12: XRD pattern of seeded disc.



Unseeded Area

Figure 4.13: SEM image of the seeded support.

4.4. Effect of seeding on the membrane synthesis

Discs were seeded by vacuum seeding and the membrane formation on these discs was investigated. By providing sites for zeolite growth seeding increases the membrane formation on the support [23, 24, 40]. After seeding peak ratio of disc was calculated and the change in peak ratio was investigated to compare the membrane formation.

XRD pattern of membrane F6 after seeding and after membrane formation was shown in Figure 4.14. In this figure, membrane F2 which was synthesized under the same conditions on unseeded disc was also shown.

Peak ratio values were inserted into the figure to get an idea about the membrane growth on the support. When the XRD figures of seeded and unseeded membranes were compared, it was concluded that seeding increased the growth rate of the membrane. Peak ratio of seeded disc was about 9% but after membrane synthesis by peak ratio increased up to 102%. This peak ratio was almost twice higher than the peak ratio of the membrane F2. Therefore there was a significant increase in the peak ratio when seeded support was used.

When XRD pattern of layer-b (Appendix B) was analyzed it was seen that no change in peak ratio was observed for seeded and unseeded synthesis because there were no seeds on layer-b.

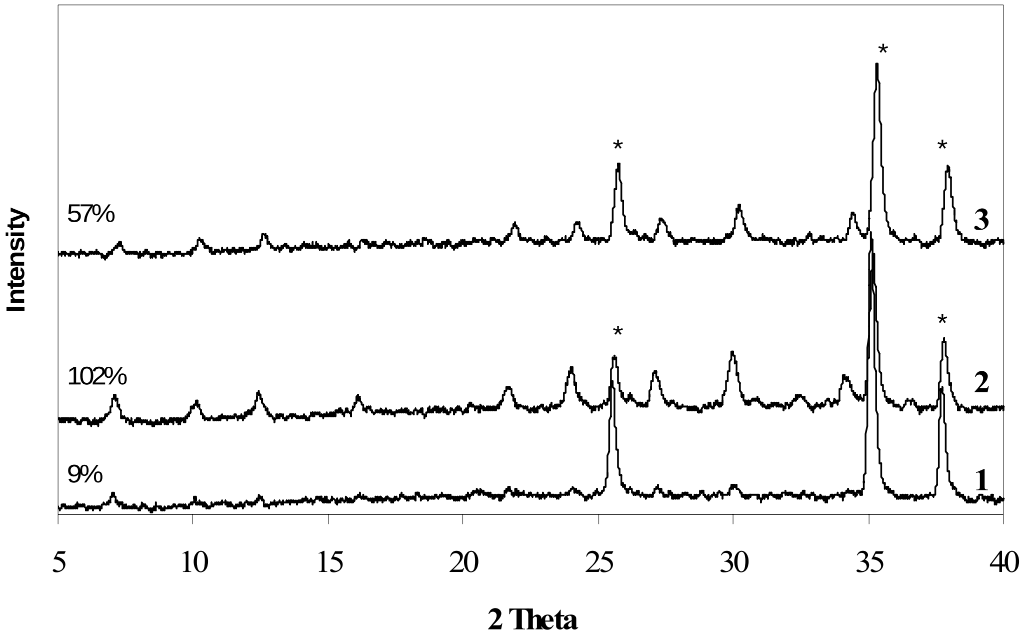


Figure 4.14: XRD pattern seeded disc with vacuum method before and after synthesis (1: seeded disc, 2: after membrane synthesis (F6), 3: pattern of F2 which was synthesized under same conditions on unseeded disc, *: alumina peaks).

SEM images of F6 showed that pure and continuous zeolite A membrane was formed on the disc (Figure 4.15). Well inter-grown of zeolite A crystals was easily seen from the top-view SEM images. No significant thickness change was observed but crystal size of zeolite A increased from 3 to 5 μm.

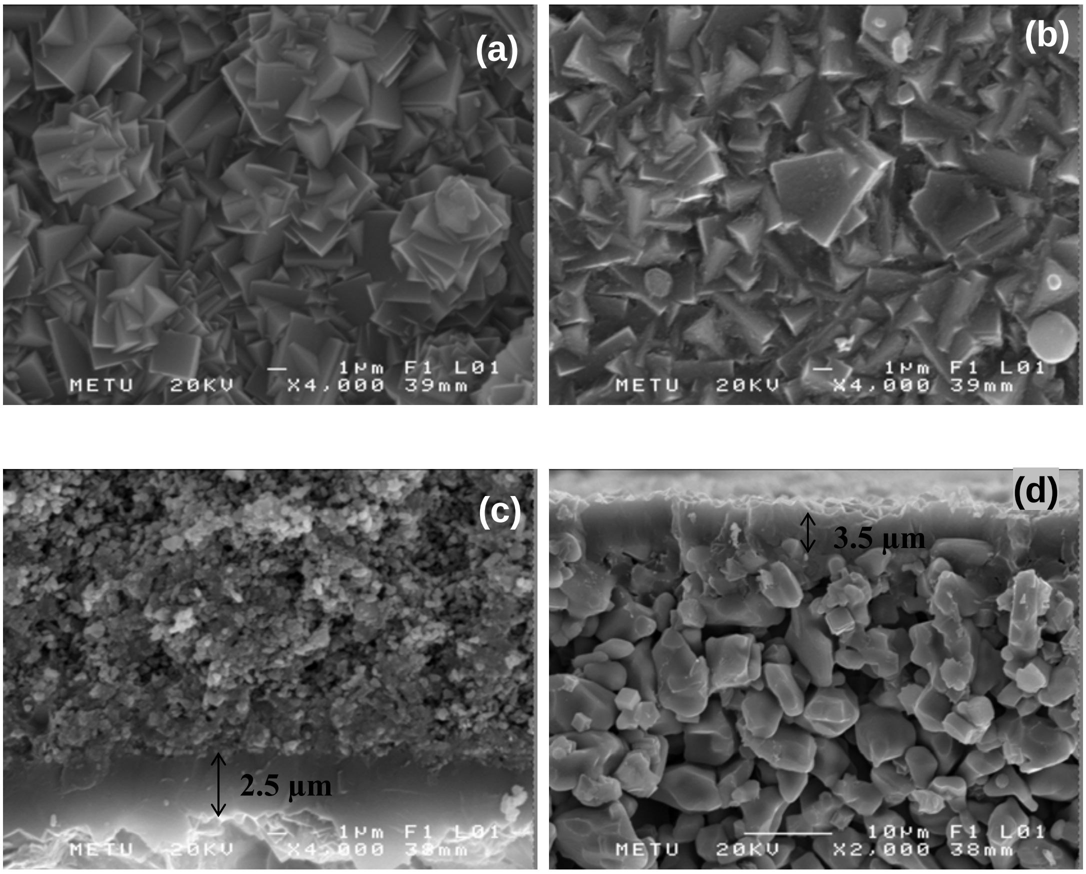


Figure 4.15: SEM images of the membrane F6 (a and c: mesoporous part, b and d: macroporous part).

4.5. Single gas permeation

Membrane quality was tested by single gas permeation measurements of H_2, N_2 and SF_6 at 25°C. Before tests, membranes were kept at 100°C for two days. At this temperature removal of water in the zeolitic pores is not possible but it is expected that water in the non zeolitic pores can be vaporized. Breck [1] reported that zeolite A is likely to be heated up to 430°C for complete removal of water in the pores. Nevertheless, uneven thermal expansion coefficients of crystallographic axes in zeolite A may cause microcracks or defects on the membrane surface, which significantly reduces the membrane quality [41].

Since kinetic diameter of H_2 and N_2 are about 0.29 nm and 0.36 nm, respectively, they can easily permeate through the pores of zeolite A which are about 0.4 nm [1]. However, SF_6 should not permeate since its diameter (0.54 nm) was larger than pore size of zeolite A. Therefore SF_6 is a control gas to detect the existence of defects. High permeation of SF_6 shows that membrane has very large defects. Membranes having less or no defects (high quality) will have high permselectivity of H_2/SF_6 which should be higher than Knudsen diffusivities.

The results that tabulated in Table 4.7 were the performances of the membranes synthesized in this study and the results that obtained in literature. All membranes showed higher permeances for H_2 than N_2 and SF_6 as expected from the kinetic diameters. Permeation of SF_6 indicated that there were some defects on all of the membranes. Since the kinetic diameter of SF_6 is larger than zeolite A pores, defect pore size was larger than size of zeolitic pores. Moreover ideal selectivity of H_2/SF_6 for membranes F2, F3 and F6 were larger than Knudsen diffusivity which showed that fewer defects existed for these membranes.

The amorphous content of the membranes increased with increasing the flow rate during the synthesis and the membranes with more amorphous content (F4 and F5) exhibited lower permeances. Zah et al. [31], who studied single gas permeation through zeolite A membranes, compared the performance of semi-crystalline zeolite A layer with a crystalline A membrane using H_2, N_2 and SF_6 gases. They obtained lower permeances for the semi-crystalline membrane than the crystalline membrane at low temperature (23°C). They concluded that amorphous layer closed the boundaries and prevented the passage of the gas.

When the performances of the membranes were compared with the membranes in literature it was obvious that the membranes synthesized in this study showed almost similar and somewhat better ideal selectivities although membranes reported in the literature were mostly seeded and had double layers. Besides it should be noted that drying conditions have strong effect on membrane performance and the membranes reported in literature have different drying conditions.

One the other hand, the highest quality membranes in the literature, for example membranes of Aoki et al [26] which has a H_2/N_2 selectivity of 10 consisted defects so that this membrane showed permeation of C_3H_8 which should not permeate for a defect free membrane. Okamoto et al. [13] synthesized zeolite A membranes which showed high selectivity in the pervaporation of ethanol/water mixtures. However these membranes showed selectivity about Knudsen diffusion for gas separation. This result indicated that there were non zeolitic pores in the membranes. The membranes having asterisk were the membranes that showed high selectivities in pervaporation tests therefore it can be concluded that small defects does not affect significantly the membrane performance in pervaporation.

It can be concluded that synthesis in the flow system may yield better quality membranes; however, the membrane needs some further developments.

Table 4.7: Single gas permeation results (TS: This study)

Membrane Code	Synthesis	Thickness (µm)	Permeation Temperature	Permeance x10^{-8} mol/m^2sPa			Permselectivity		Ref.
				H_2	N_2	SF_6	H_2/N_2	H_2/SF_6	
F3	Flow, 60°C,24h, 6ml/min	1.5	298	1.52	0.28	0.15	5.43	10.13	TS
F2	Flow,80°C,8h, 6ml/min	2.5	298	20	6.5	3	3.26	9.22	TS
F4	Flow, 80°C,8h, 24ml/min	2.7	298	2.35	0.82	0.66	2.87	3.56	TS
F5	Flow, 80°C,8h, 48ml/min	--	298	0.65	0.11	0.08	5.91	8.13	TS
F1	Flow, 95°C, 3h, 6ml/min	1.7	298	1.85	0.58	0.31	3.19	5.97	TS
F6	Flow, 80°C,8h, 6ml/min, seeded	2.6	298	1.66	0.48	0.18	3.46	9.22	TS
*	Batch two layer	6	296	4.57	0.96	0.41	4.76	11.15	[31]
*	Batch , multi layer	30	308	0.3	0.08	0.03	3.75	10	[13]
*	Batch, multi layer	3.8	308	0.64	0.14	-	4.57	-	[11]
-	Batch, seeded, multi layer	--	308	0.8	0.15	-	5.33	-	[42]
-	Batch, seeded, multi layer	16	298	28.6	1.2	-	23.83	-	[43]
-	Batch, seeded, two layer	10	298	10.2	1.52	-	6.71	-	[23]
*	Batch , seeded	1.7	308	10	1	-	10	-	[26]
							3.74	8.54	Knud

4.6. Pervaporation test

Because of the hydrophilic nature of zeolite A membranes they were characterized by pervaporation separation of water from water/ethanol mixtures. Pure zeolite A membrane having less defects should yield high separation factor in pervaporation.

Membranes prepared on disc shaped supports were tried for pervaporation separation; however, all disc shaped membranes were broken under vacuum. The harsh synthesis conditions probably weakened the discs and caused them to lose their mechanical stability. Therefore, pervaporation experiments were performed using tubular membranes instead of disk shaped membranes. Tubular membranes were synthesized in flow system with a flow rate of 6 ml/min at 80°C for 8h. Before synthesis, tubes were seeded by rubbing of zeolite A powder inside of the tube.

Pervaporation tests were performed at temperatures of 25, 45 and 75°C by using feed composition of 7-9 wt.% water / 93-91wt.% ethanol. Multi stage synthesis was also performed to increase the membrane quality. Pervaporation conditions and results were shown in Table 4.8.

Table 4.8: Conditions and results for pervaporation tests (W: water, E: ethanol)

Membrane	**Temp (°C)**	**Feed % wt**		**Permeate % wt**		**Separation Factor**	**Flux kg/m^{2}h**
		W	**E**	**W**	**E**		
F7	25	9.1	90.9	99.1	0.9	1100	0.3
	45	9.1	90.9	9.1	90.9	1	1.1
F8	25	7.2	92.8	99.6	0.4	3250	0.09
	45	7.9	92.1	99.7	0.3	3750	0.14
	75	7.2	92.8	85.4	14.6	75	0.5

Membrane F7 showed a selectivity of 1100 and flux of 0.3 kg/m^{2}h in the separation of 9%water/91%ethanol. Membrane showed no selectivity with a significant increase in flux when temperature was increased, indicating crack formation on membrane surface. Therefore it was decided to perform a second synthesis on the same membrane to repair the membrane. It was expected that the cracks on the zeolite layer could be patched by forming a second layer of zeolite A on the membrane. This membrane was called as membrane F8. Membrane F8 exhibited very high selectivity as expected. Nevertheless flux decreased significantly since repeated synthesis increased the thickness of the membrane.

The increase of pervaporation temperature did not significantly influence the separation factor; the separation factor was 3250 at 25°C and 3750 at 45°C. No significant change in selectivity was observed as temperature increased from 25 to 45°C. However, when the temperature was further increased to 75°C, selectivity decreased from 3750 to 75, showing that again some cracks formed on the membrane. Small amount of amorphous material remained on the membrane surface can be detached and carried away by ethanol/water mixture, remaining defects on the membrane surface.

Despite unstable structure of membranes, this study is the first one performed in the literature synthesizing zeolite A membranes from clear solutions in a recirculating flow system. When compared with literature thinner membranes were obtained by using this method. Pina et al. studied zeolite A membrane synthesis in a semi continuous system. They obtained separation factor about 3600 for pervaporation separation of ethanol/water mixture at 125°C for the membrane having thickness about 10µm. On the other hand Pera-Titus et al. used same system for zeolite A membrane synthesis and obtained separation factor about 16000 for pervaporation at 50°C after carrying two synthesis cycles. Recently Pera-Titus studied zeolite A membrane synthesis in a continuous flow system. They characterized the membranes by pervaporation for dehydration of ethanol/water mixture at 50°C. Membrane synthesized in that method had thickness about 10-20 µm and showed separation factor about 8500. When compared with literature the membranes synthesis in our method was thinner than those but separation factor as high as in the literature could be obtained.

CHAPTER 5

CONCLUSION

In this study, zeolite A membranes were synthesized on disc and tubular alumina supports at temperatures of 60-95°C under atmospheric pressure in a flow system by circulating the synthesis solution through the support during synthesis.

- For the first time syntheses of zeolite A membranes were performed in flow system by using clear solution. Pure and comparable membranes with those in literature were obtained in this study. However, because of the high alkalinity of the solution, stability of the membranes was poor.
- Thinner membranes having cubic zeolite A crystals were synthesized in a flow system at 95°C for 3 h and 80°C for 8 h.
- Synthesis of zeolite A membranes was carried out at three different flow rates and no morphological change on the membrane layer was observed.
- Synthesis carried out at by using seeded supports yielded highly crystalline membranes having larger crystals.
- In single gas permeation test with H_2, N_2 and SF_6 gases at 25°C all of the membranes synthesized in flow system showed comparable performances with the ones in literature in single gas permeation tests.
- Tubular membranes synthesized at 80°C for 8 h showed pervaporation separation about 1100 with a flux of 0.3 kg/m^2h at 25°C. However double layer membrane had separation factor about 3600 for 25°C and 45°C.

CHAPTER 6

RECOMMENDATIONS

Thin and continuous zeolite A membranes were synthesized on alumina supports in a flow system. Further improvements can be done in membrane synthesis therefore followings can be recommended.

- Synthesis can be performed on symmetric supports to eliminate the possible damage on the support. Moreover supports in different shapes can be used for membrane synthesis. More resistive supports like titania or glass can be preferred for membrane synthesis.
- Parallel or serial connected membrane modules can be inserted into the system. Therefore multiple membrane synthesis can be performed in one step.
- Less alkaline solution and different clear solution compositions can be used for synthesis of zeolite A and also other types of membranes can also be synthesized in this system.
- Different seeding techniques like dip-coating can be used to obtain seeded supports.
- By analyzing all synthesis steps with SEM, morphology can be followed and different synthesis conditions can be used to obtain membranes with higher separation factors.

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APPENDIX A

CALCULATIONS OF COMPOSITIONS

A1. Calculation of Batch Compositions

Table A.1: Composition of raw materials used in this study.

Raw Material	Formula Weight (g/mol)	Reactant			
		Na_2O	SiO_2	Al_2O_3	H_2O
Sodium Silicate (waterglass)	222.44	0.287 (mole)	1 (mole)	-	8.036 (mole)
Aluminum hydroxide	78	-	-	0.5 (mole)	1.5 (mole)
Sodium hydroxide	40	0.5 (mole)	-	-	0.5 (mole)
Sodium Aluminate	183.89	44 (wt%)	-	55 (wt%)	1 (wt%)
Sodium metasilicate pentahydrate	212.14	29 (wt%)	28 wt(%)	-	43 (wt%)

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Table A.2: Molecular weight of the reactants.

Reactant	Molecular Weight (g/mol)
Na_2O	62
Al_2O_3	102
SiO_2	60
H_2O	18

Batch composition: $10Na_2O: 1Al_2O_3: 2SiO_2: 500H_2O$

Formula weight of the batch: 10*62 + 1*102 + 2*60 + 500*18 = 9842 g

Raw materials:	Waterglass
	Aluminum hydroxide
	Sodium hydroxide
	Water

For 100 g batch;

<u>Amount of waterglass needed</u>:

$$100g\ \text{batch}\cdot\frac{1\,\text{mol batch}}{9842\,\text{g batch}}\cdot\frac{2mol\ \text{SiO}_2}{1\,\text{mol batch}}\cdot\frac{1\,\text{mol waterglass}}{1\,\text{mol SiO}_2}\cdot\frac{222.44\text{g waterglass}}{1\,\text{mol waterglass}}=$$
$$4.52g\ waterglass$$

<u>Amount of aluminum hydroxide, $Al(OH)_3$, needed</u>:

$$100g\ \text{batch}\cdot\frac{1\,\text{mol batch}}{9842\,\text{g batch}}\cdot\frac{1mol\ \text{Al}_2\text{O}_3}{1\,\text{mol batch}}\cdot\frac{1\,\text{mol Al(OH)}_3}{0.5\,\text{mol Al}_2\text{O}_3}\cdot\frac{78\text{g Al(OH)}_3}{1\,\text{mol Al(OH)}_3}=$$
$$1.59g\ \text{Al(OH)}_3$$

<u>Amount of sodium hydroxide, NaOH, needed</u>:

$$100g\ \text{batch}\cdot\frac{1\,\text{mol batch}}{9842\,\text{g batch}}\cdot\frac{10\,\text{mol Na}_2\text{O}}{1\,\text{mol batch}}\cdot\frac{1\,\text{mol NaOH}}{0.5\,\text{mol Na}_2\text{O}}\cdot\frac{40\text{g NaOH}}{1\,\text{mol NaOH}}=8.13g\ \text{NaOH}$$

$$100g\ \text{batch}\cdot\frac{1\,\text{mol batch}}{9842\,\text{g batch}}\cdot\frac{1.7\,\text{mol SiO}_2}{1\,\text{mol batch}}\cdot\frac{1\,\text{mol waterglass}}{1\,\text{mol SiO}_2}\cdot\frac{0.287\,\text{mol Na}_2\text{O}}{1\,\text{mol waterglass}}\cdot$$
$$\frac{1\,\text{mol NaOH}}{0.5\,\text{mol Na}_2\text{O}}\cdot\frac{40\text{g NaOH}}{1\,\text{mol NaOH}}=0.47g\ \text{NaOH}$$

8.13 – 0.47 = 7.66 g NaOH

<u>Amount of water, H_2O, needed</u>:

$$100g\ \text{batch}\cdot\frac{1\,\text{mol batch}}{9842\,\text{g batch}}\cdot\frac{500\,\text{mol H}_2\text{O}}{1\,\text{mol batch}}\cdot\frac{18\text{g H}_2\text{O}}{1\,\text{mol H}_2\text{O}}=91.44g\ \text{H}_2\text{O}$$

$$100g\ \mathrm{batch}\cdot\frac{1\,\mathrm{mol\,batch}}{9842\,\mathrm{g\,batch}}\cdot\frac{1mol\,\mathrm{Al_2O_3}}{1\,\mathrm{mol\,batch}}\cdot\frac{1\,\mathrm{mol\,Al(OH)_3}}{0.5\,\mathrm{mol\,Al_2O_3}}\cdot\frac{1.5\mathrm{mol\,H_2O}}{1\,\mathrm{mol\,Al(OH)_3}}\cdot\frac{18\mathrm{g\,H_2O}}{1\,\mathrm{mol\,H_2O}}=$$
$$0.55g\ \mathrm{H_2O}$$

$$100g\ \mathrm{batch}\cdot\frac{1\,\mathrm{mol\,batch}}{9842\,\mathrm{g\,batch}}\cdot\frac{10\,\mathrm{mol\,Na_2O}}{1\,\mathrm{mol\,batch}}\cdot\frac{1\,\mathrm{mol\,NaOH}}{0.5\,\mathrm{mol\,Na_2O}}\cdot\frac{0.5\mathrm{mol\,H_2O}}{1\,\mathrm{mol\,NaOH}}\cdot\frac{18\mathrm{g\,H_2O}}{1\,\mathrm{mol\,H_2O}}=$$
$$1.83g\ \mathrm{H_2O}$$

$$100g\ \mathrm{batch}\cdot\frac{1\,\mathrm{mol\,batch}}{9842\,\mathrm{g\,batch}}\cdot\frac{2\mathrm{molSiO_2}}{1\,\mathrm{mol\,batch}}\cdot\frac{1\,\mathrm{mol\,waterglass}}{1\,\mathrm{molSiO_2}}\cdot\frac{8.036\,\mathrm{mol\,H_2O}}{1\,\mathrm{mol\,waterglass}}\cdot\frac{18\mathrm{g\,H_2O}}{1\,\mathrm{mol\,H_2O}}=$$
$$2.94g\ \mathrm{H_2O}$$

91.44 – 0.55 - 1.83 - 2.94 = 86.12 g H_2O

Therefore for 100 g batch of $10Na_2O$: $1Al_2O_3$: $2SiO_2$: $500H_2O$ amount of raw materials are;
4.52 g Waterglass
1.59 g Aluminum hydroxide
7.66 g Sodium hydroxide
86.12 g Water

Batch composition: $49Na_2O$: $1Al_2O_3$: $5SiO_2$: $980H_2O$
Formula weight of the batch: 49*62 + 1*102 + 5*60 + 980*18 = 21080 g

Raw materials:	Sodium Aluminate
	Sodium Metasilicate pentahydrate
	Sodium hydroxide
	Water

For 100 g batch;

<u>Amount of sodium aluminate needed:</u>

$$100g\ \mathrm{batch}\cdot\frac{1\,\mathrm{mol\,batch}}{21080\,\mathrm{g\,batch}}\cdot\frac{1\,\mathrm{mol\,Al_2O_3}}{1\,\mathrm{mol\,batch}}\cdot\frac{102\,\mathrm{g\,Al_2O_3}}{1\,\mathrm{mol\,Al_2O_3}}\cdot\frac{100\,\mathrm{g\,Sodium\,Aluminate}}{55\,\mathrm{g\,Al_2O}}=$$
$$0.88g\ \mathrm{Sodium\,Aluminate}$$

Amount of sodium metasilicate pentahydrate needed:

$$100g \text{ batch} \cdot \frac{1\,\text{mol batch}}{21080\,\text{g batch}} \cdot \frac{5\,\text{mol SiO}_2}{1\,\text{mol batch}} \cdot \frac{60\,\text{g SiO}_2}{1\,\text{mol SiO}_2} \cdot \frac{100\,\text{g Sodium metasilicate}}{28\,\text{g Al}_2\text{O}} =$$

$$5.083g \text{ Sodium metasilicate}$$

Amount of sodium hydroxide needed:

$$100g \text{ batch} \cdot \frac{1\,\text{mol batch}}{21080\,\text{g batch}} \cdot \frac{49\,\text{mol Na}_2\text{O}}{1\,\text{mol batch}} \cdot \frac{1\,\text{mol NaOH}}{0.5\,\text{mol Na}_2\text{O}} \cdot \frac{40g\ \text{NaOH}}{1\,\text{mol NaOH}} =$$

$$18.596g\ \text{NaOH}$$

$$0.88g \text{ Sodium Aluminate} \cdot \frac{44\text{g Na}_2\text{O}}{100g \text{ Sodium Aluminate}} \cdot \frac{1\text{mol Na}_2\text{O}}{62\text{g Na}_2\text{O}} \cdot \frac{1\,\text{mol NaOH}}{0.5\text{mol Na}_2\text{O}} \cdot$$

$$\frac{40g\ \text{NaOH}}{1\text{mol NaOH}} = 0.500g\ \text{NaOH}$$

$$5.083g \text{ Sodium metasilicate} \cdot \frac{29\text{g Na}_2\text{O}}{100g \text{ Sodium metasilicate}} \cdot \frac{1\text{mol Na}_2\text{O}}{62\text{g Na}_2\text{O}} \cdot \frac{1\,\text{mol NaOH}}{0.5\text{mol Na}_2\text{O}} \cdot$$

$$\frac{40g\ \text{NaOH}}{1\text{mol NaOH}} = 1.902g\ \text{NaOH}$$

18.596 – 0.500 – 1.902 = 16.194 g NaOH

Amount of water needed:

$$100g \text{ batch} \cdot \frac{1\,\text{mol batch}}{21080\,\text{g batch}} \cdot \frac{980\,\text{mol H}_2\text{O}}{1\,\text{mol batch}} \cdot \frac{18g\ \text{H}_2\text{O}}{1\,\text{mol H}_2\text{O}} = 83.681g\ \text{H}_2\text{O}$$

$$0.88g \text{ Sodium Aluminate} \cdot \frac{1\text{g H}_2\text{O}}{100g \text{ Sodium Aluminate}} = 0.009g\ \text{H}_2\text{O}$$

$$5.083g \text{ Sodium metasilicate} \cdot \frac{43\text{g H}_2\text{O}}{100g \text{ Sodium metasilicate}} = 2.186g\ \text{H}_2\text{O}$$

$$16.194\text{g NaOH} \cdot \frac{1\,\text{mol NaOH}}{40\text{g NaOH}} \cdot \frac{0.5\,\text{mol H}_2\text{O}}{1\,\text{mol NaOH}} \cdot \frac{18\text{g H}_2\text{O}}{1\,\text{mol H}_2\text{O}} = 3.644g\ \text{H}_2\text{O}$$

83.681 - 2.186 - 3.644 - 0.009 = 77.842 g H_2O

Therefore for 100 g batch of $49Na_2O$: $1Al_2O_3$: $5SiO_2$: $980H_2O$ amount of raw materials are;

0.880 g Sodium Aluminate
5.083 g Sodium Metasilicate pentahydrate
16.194 g Sodium hydroxide
77.842 g Water

A2. Selection of Batch Composition

Batch composition to be used in the flow system for synthesis of zeolite A membranes were determined after performing a set of trials. There were two important criteria for composition selection. One of them is to obtain pure zeolite A with high crystallinity at low temperatures, mainly below 100˚C. The second one is that synthesis solution should be appropriate to be used in flow system which means that the solution can be pumped easily and keep the suspension homogenous throughout the synthesis.

Since pumping of the clear solution was easier than gel, studies using clear solutions were analyzed. Moreover compositions without template were preferred to get rid of calcination process. It was observed that clear solution having the composition of 49-55Na_2O: $1Al_2O_3$: 4-5SiO_2: 980-1000H_2O was studied for the synthesis of zeolite A membranes. However, in some of these studies other types of zeolites like sodalite, losod and X were also obtained from this composition [22, 23]. It was a risky composition since other types of zeolites could be formed easily and high alkalinity of the solution could cause high dissolution of alumina supports. Therefore it was decided to find out the new composition by performing some trials. For this reason, synthesis of powder zeolite A in flow system was studied by using the compositions shown in Table 4.1.

Table A.3: List of compositions used for selection.

Trial	Composition				Solution Type
	Na_2O	Al_2O_3	SiO_2	H_2O	
1	10	1	2	500	Milky
2	20	1	2	500	Milky
3	30	1	5	1000	Clear
4	49	1	5	980	Clear

The first trial was performed by using the solution having the composition of $10Na_2O$: $1Al_2O_3$: $2SiO_2$: $500H_2O$. According to XRD analysis, pure zeolite A was obtained (Figure 4.1). However, it was observed that milky gel like solution caused the blocking of the lines during synthesis. Therefore, as a second trial, higher amount of sodium hydroxide was used in the solution (Table 4.1) to increase the solubility and to lower the solid amount in the gel. By this was it was aimed to make solution easily pumped. Even the milky solution was pumped easily, sodalite was also observed in the powder as seen from the XRD pattern (Figure 4.1). Since these did not satisfy the criteria new compositions were studied.

In the third case; sodium, water and also silica amount was increased and clear solution was obtained. The new composition became as $30Na_2O$: $1Al_2O_3$: $5SiO_2$: $1000H_2O$. The solution was pumped easily in the flow system without causing any blocking, but XRD analysis of the powder showed that pure zeolite A could not be synthesized (Figure 4.1), zeolite X was also formed.

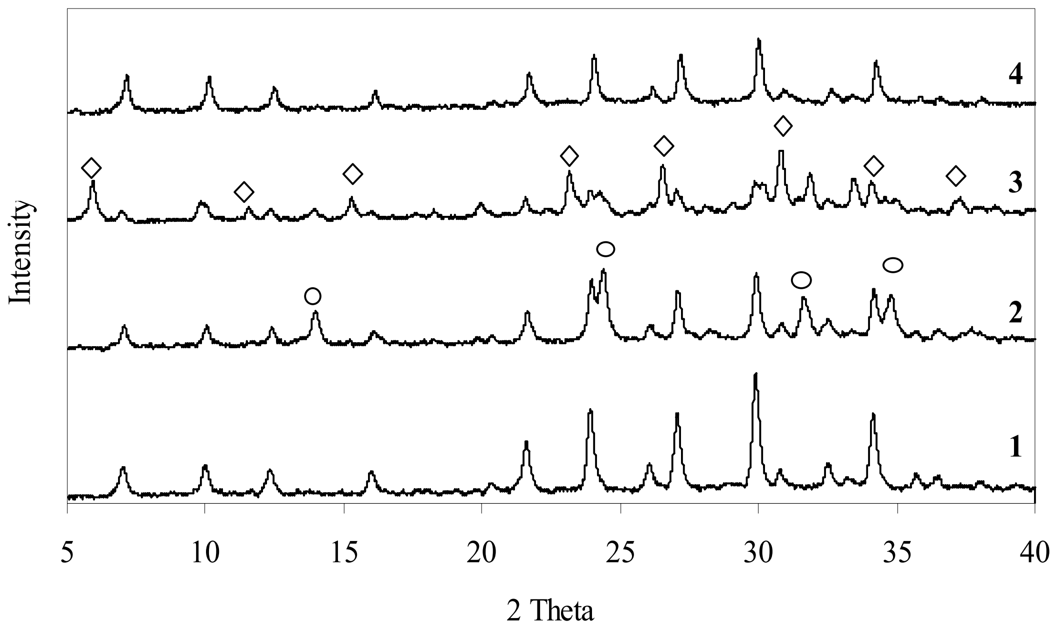


Figure A.1: XRD patterns of the powder obtained (1: $10Na_2O$: $1Al_2O3$: $2SiO_2$: $500H_2O$, 2: $20Na_2O$: $1Al_2O_3$: $2SiO_2$: $500H_2O$, 3: $30Na_2O$: $1Al_2O_3$: $5SiO_2$: $1000H_2O$, 4: $49Na_2O$: $1Al_2O_3$: $5SiO_2$: $980H_2O$, ◊: zeolite X, o: sodalite).

By increasing the sodium amount one more time, the composition used at the beginning of the study was obtained (Table 4.1). The main disadvantage of this composition was that the production of other zeolite types. According to the studies in literature, extension of synthesis time caused the transformation of zeolite A into the other types of zeolites like sodalite or X [22, 23]. Therefore in order to use this composition synthesis time should be decided with care.

Powder synthesis in flow system showed that pure zeolite A was obtained from the solution having composition of $49Na_2O$: $1Al_2O_3$: $5SiO_2$: $980H_2O$. Therefore using of this composition was throughout the study was decided.

APPENDIX B

XRD PATTERNS OF MEMBRANES

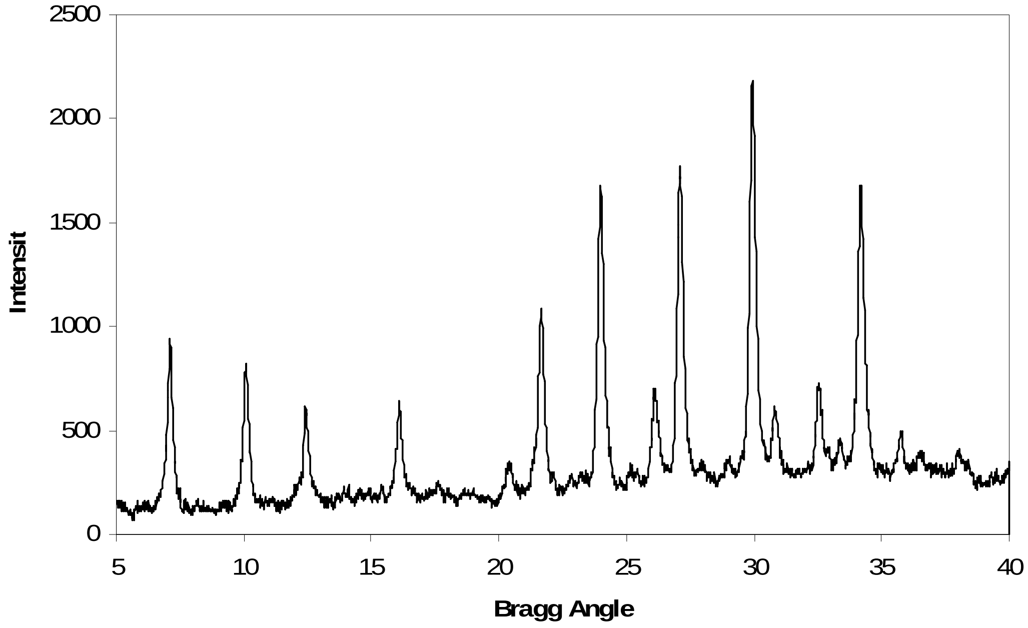


Figure B.1: XRD pattern of commercial powder zeolite A

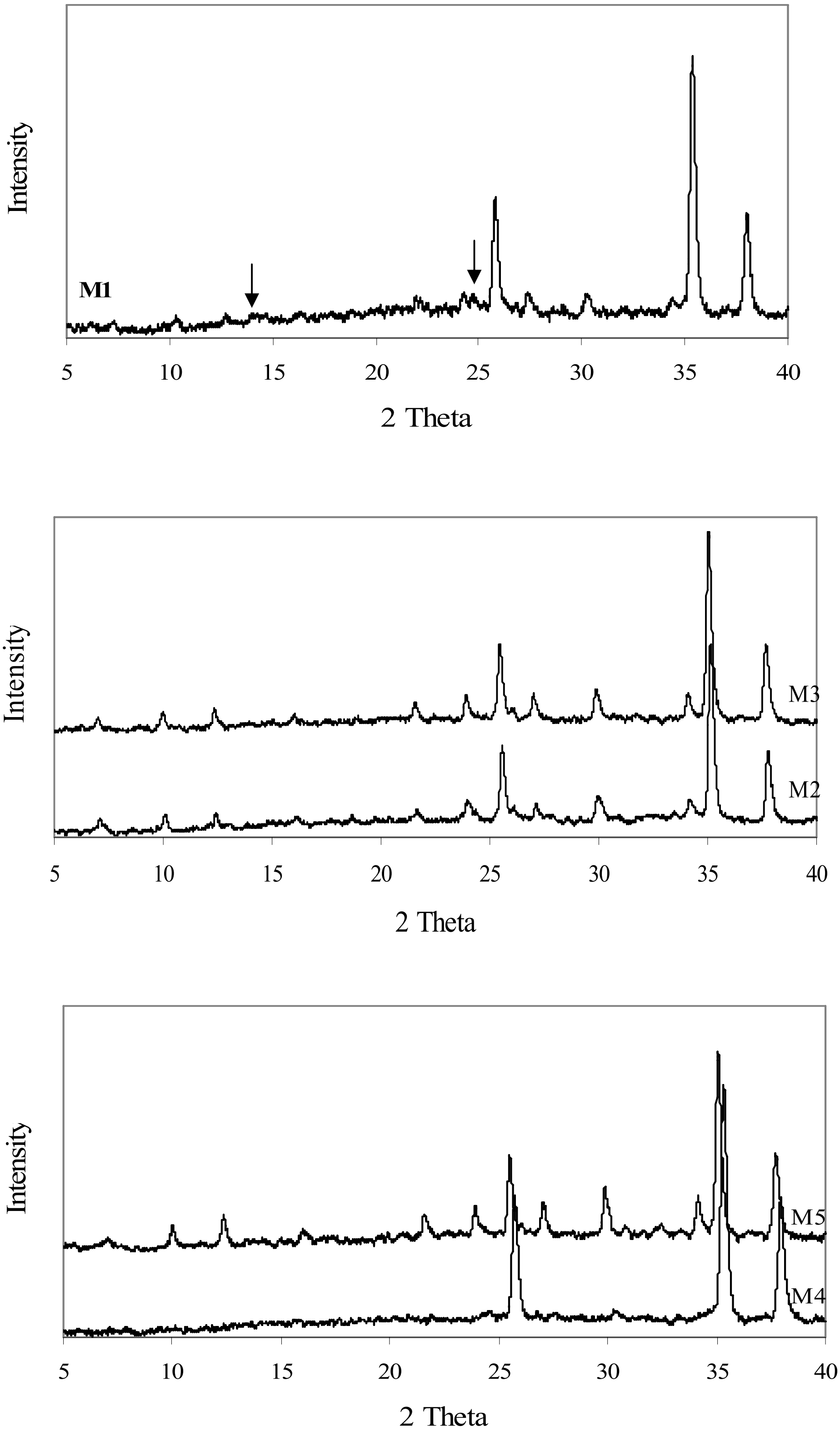


Figure B.2: XRD Patterns of the batch synthesized membranes (M1: 95°C for 3h, M2: 80°C for 4h, M3: 80°C for 8h, M4: 60°C for 8h, M5: 60°C for 24h).

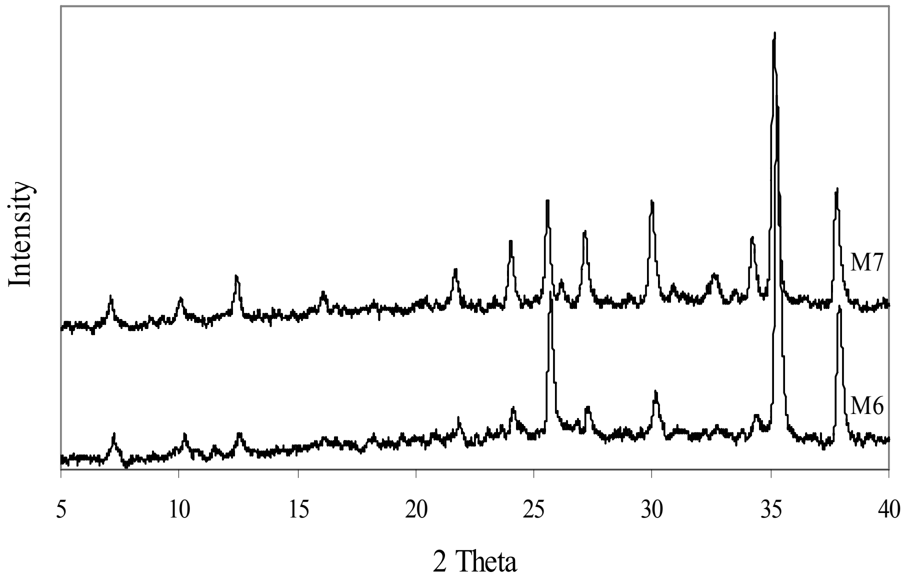


Figure B.3: XRD Patterns of the batch synthesized membranes (M6: 50°C for 24h, M7: 50°C for 48h).

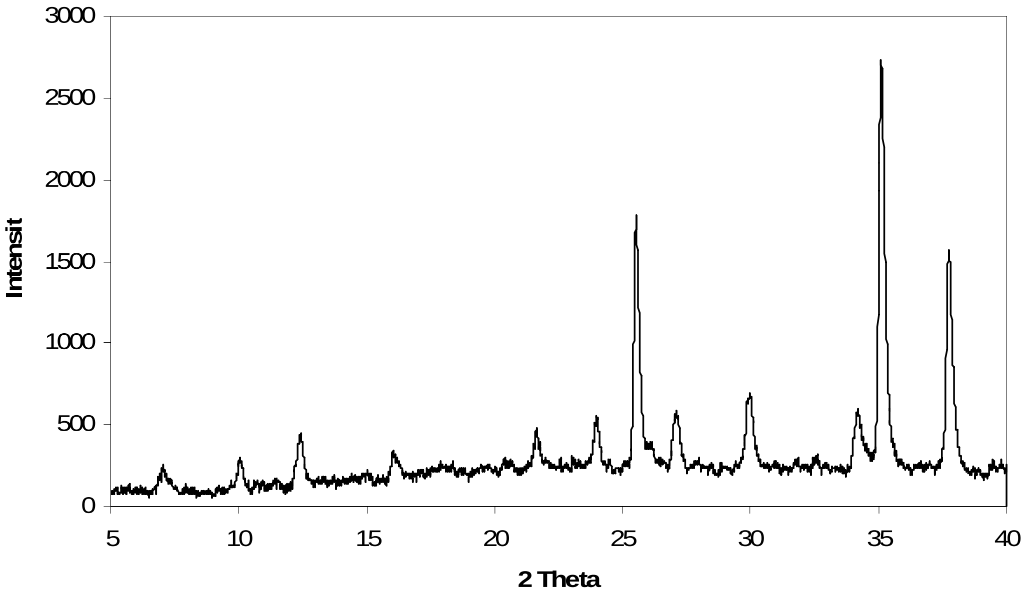
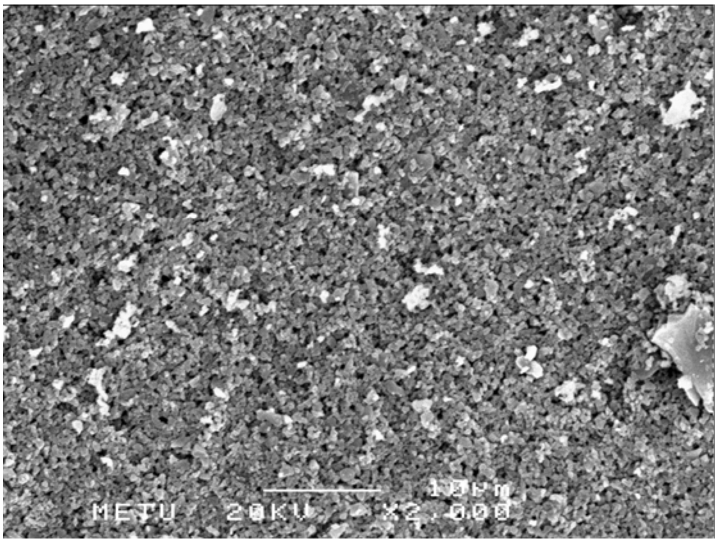


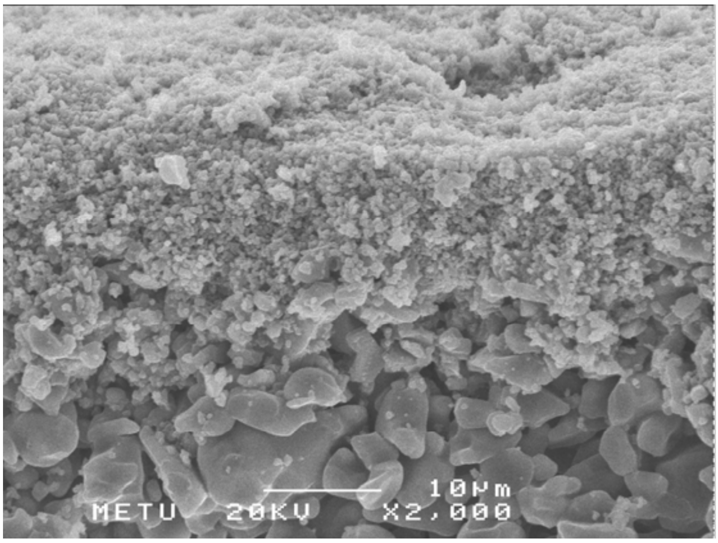
Figure B.4: XRD pattern of the macroporous layer of F6 (Layer-b).

APPENDIX C

SEM IMAGES OF THE MEMBRANES



Top view of blank disc support



Cross-section view of blank disc support

Figure C.1: SEM images of blank disc support.

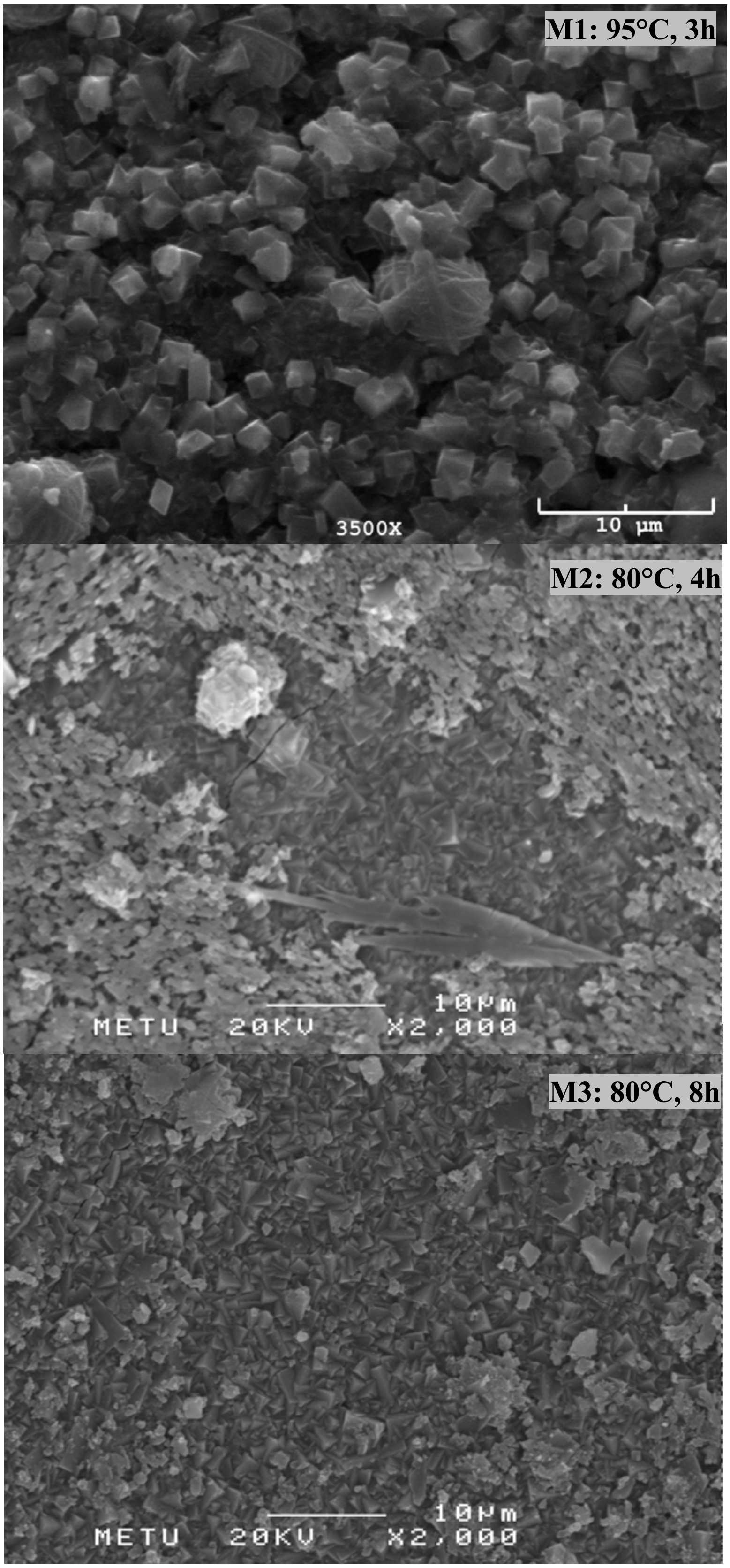


Figure C.2: Top view SEM images of the membranes synthesized in batch system.

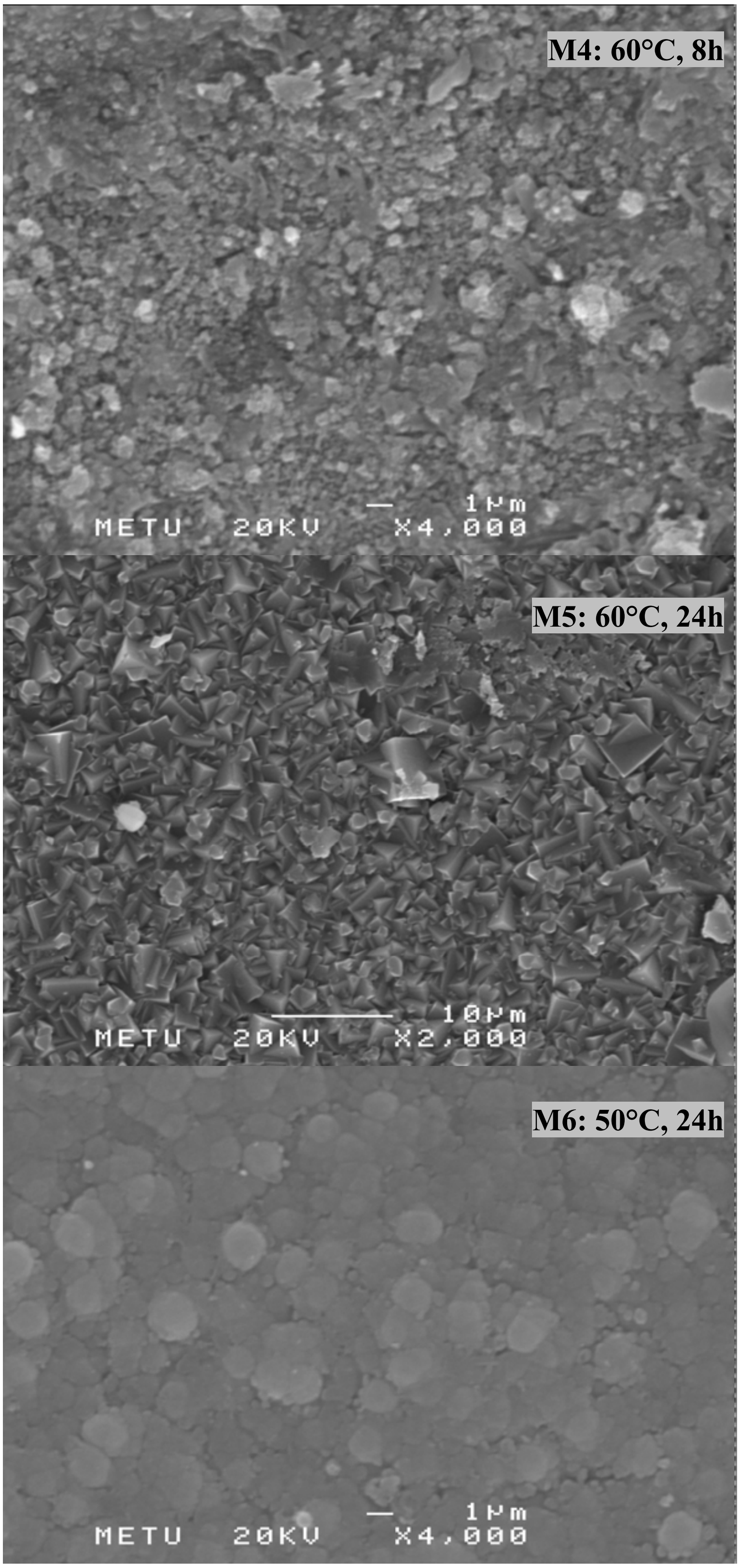


Figure C.3: SEM images of the batch synthesized membranes.

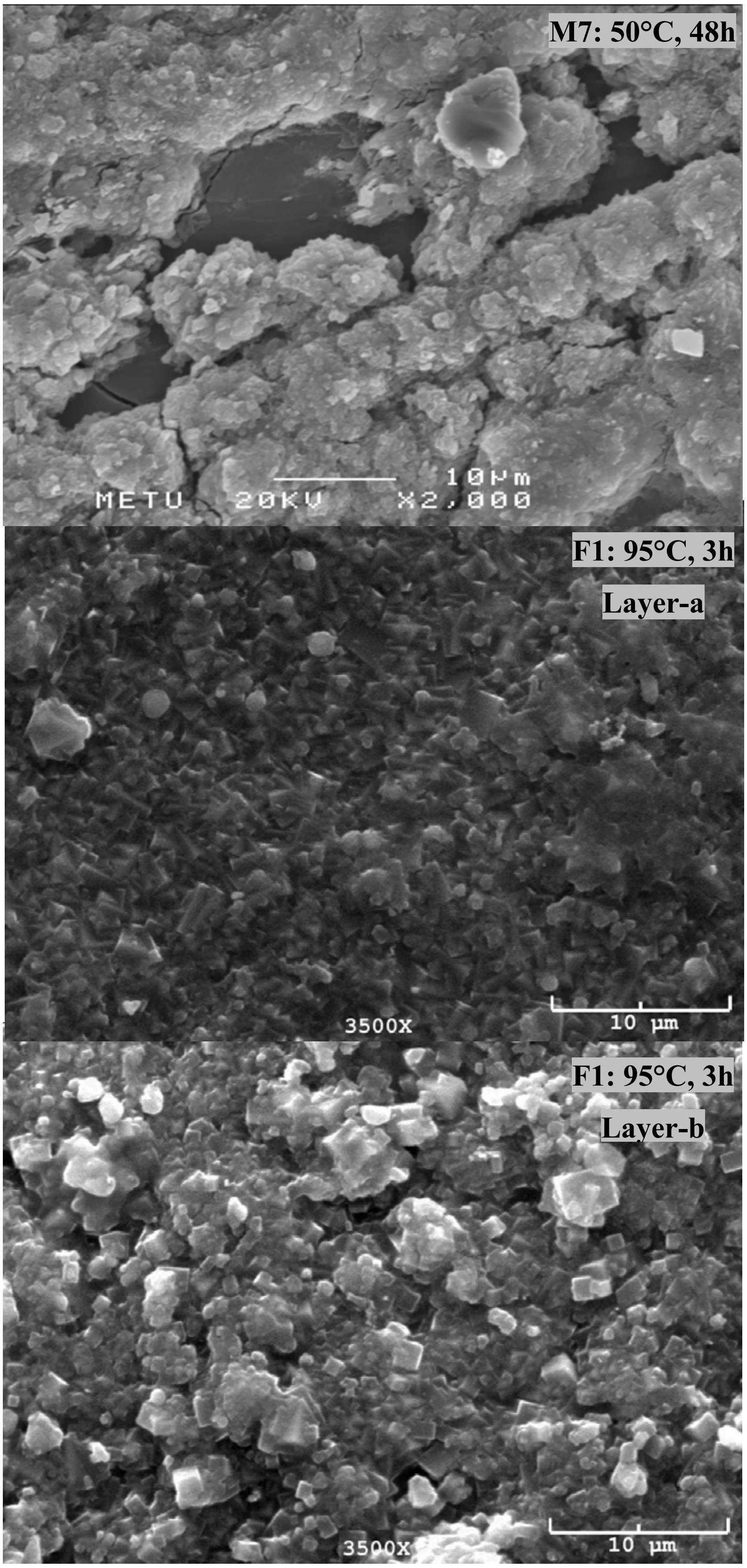


Figure C.4: Top views of M7 and F1 which synthesized in batch and flow system.

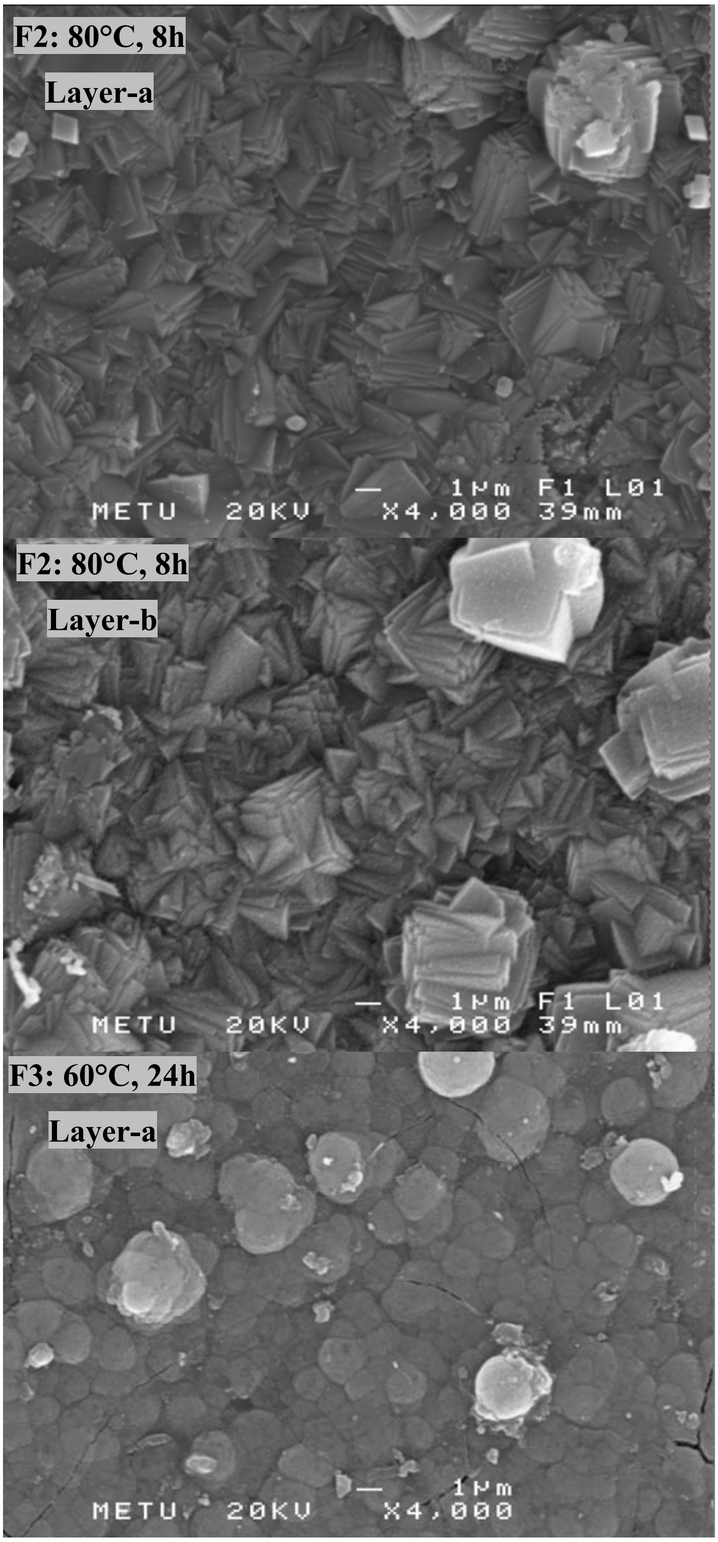


Figure C.5: Membranes F2 and F3 synthesized in flow system.

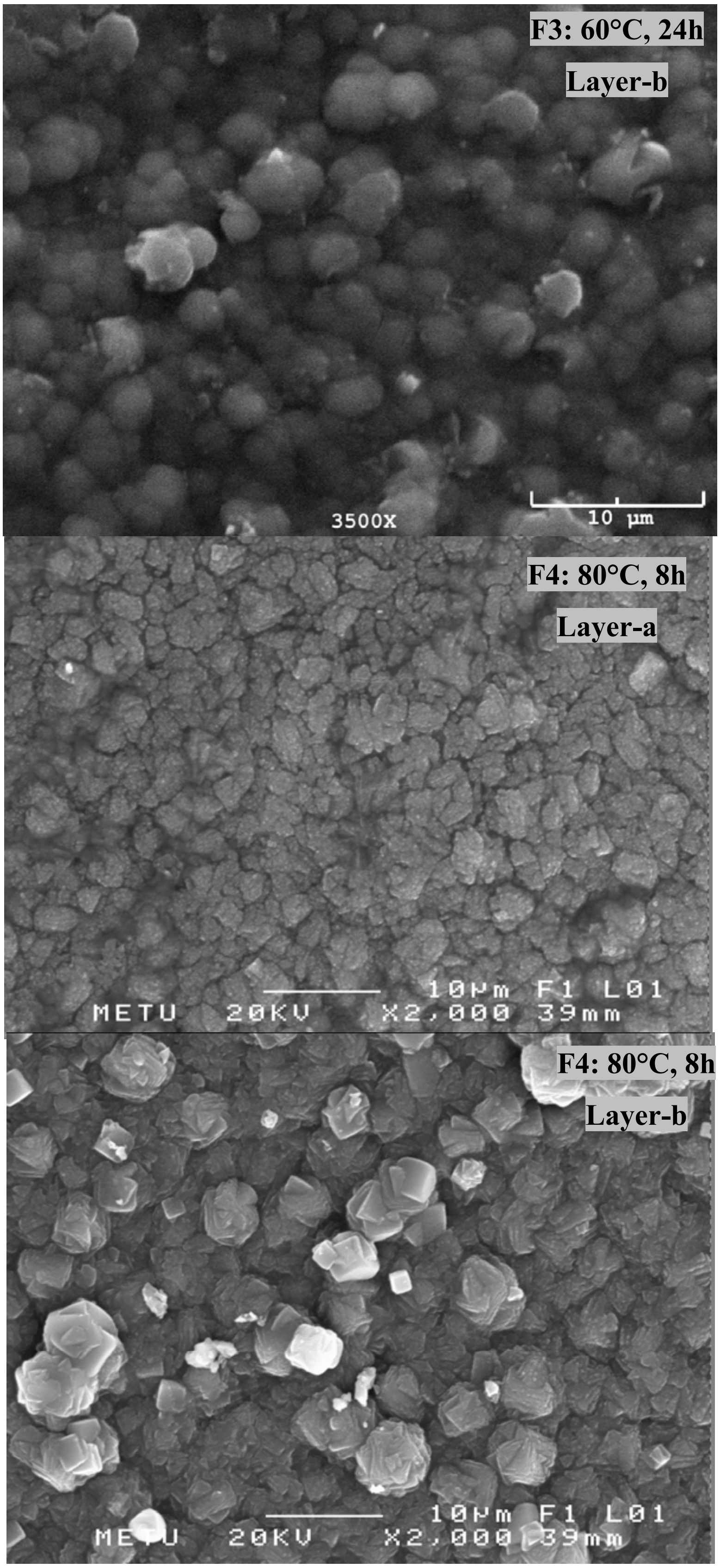


Figure C.6: Membranes synthesized in flow system.

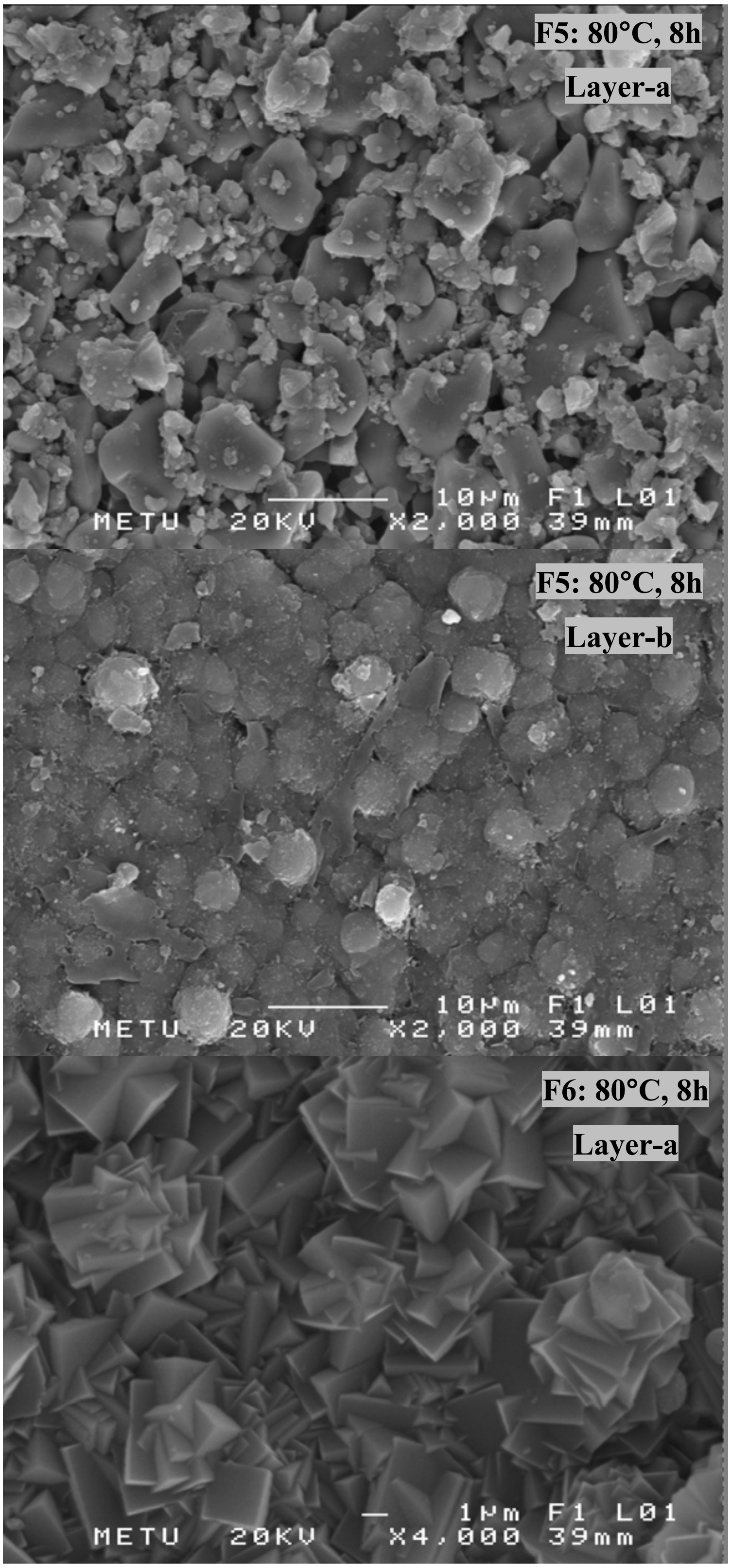


Figure C.7: Membranes F5 and F6 synthesized at 80°C for 8h in flow system.

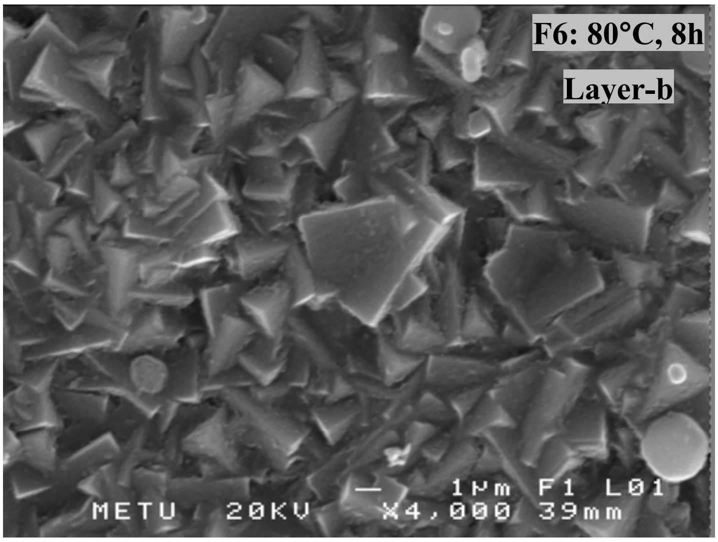


Figure C.8: SEM image of F6 layer-b.