



Optimization of conditions for the preparation of zeolite HS membrane

Mansoor Kazemimoghadam

Department of Chemical Engineering, Malek-Ashtar University of Technology, Tehran, Iran

Abstract

Effects of synthesis parameters on the membrane structure and performance have been investigated for Nano pore Hydroxysodalite (HS) zeolite membranes grown onto seeded mullite supports. Molar composition of the starting gel of HS zeolite membranes was $\text{SiO}_2/\text{Al}_2\text{O}_3=1.0-5.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=15-65$, and $\text{H}_2\text{O}/\text{Al}_2\text{O}_3=500-1500$. In addition, Effects of crystallization time and temperature on the membrane performance were studied. X-ray diffraction (XRD) patterns of the membranes exhibited peaks corresponding to the support and the zeolite. The crystal species were characterized by XRD and morphology of the supports subjected to crystallization was characterized by Scanning electron microscopy (SEM). Separation performance of HS zeolite membranes was studied for water-Ethanol mixtures using pervaporation (PV). The membranes showed good selectivity towards water in the water-Ethanol mixtures. Water permeates faster because of its preferential adsorption into the Nano-pores of the hydrophilic zeolite membrane. In PV of water-Ethanol mixtures, the membrane exhibits a hydrophilic behavior, with a high selectivity towards water and a good flux. The best Flux and separation factor of the membranes were $2.05 \text{ kg/m}^2\cdot\text{h}$ and 10000, respectively. Effects of operation condition (temperature, rate and pressure) on the membrane performance have been investigated for HS zeolite membranes grown onto seeded mullite supports.

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Keywords: Nano, hydroxysodalite, Pervaporation, Zeolite, membrane

1. Introduction

Ethanol is a very important and commonly used solvent in biopharmaceutical and chemical industries. However, it forms an azeotrope with water once it reaches 89.4 mol% at 78 °C and atmospheric pressure. This mixture is hard to be separated by using normal distillation process and but can only be done through azeotropic distillation. However, azeotropic distillation is more energy consuming than conventional distillation. Apart from high-energy consumption for azeotropic distillation, benzene, a highly carcinogenic and toxic substance, which is used as an azeotropic dehydrating agent in many plants, is a major health concern [1-4].

Pervaporation is an economical separation technique compared to conventional separation methods such as distillation especially in processes involving azeotropes, isomers and removal or recovery of trace substances. Due to its high separation efficiency and flux rates, PV results in energy cost saving and safe operation. In this regard, pervaporation eliminates the use of toxic materials and is a promising alternative for energy consuming distillation processes in separating azeotropic mixtures. Table 1 shows

energy consumptions required by different separation methods in ethanol dehydration. In terms of energy requirement, pervaporation is an obvious choice in ethanol–water separation [1, 5-7].

Table 1: Energy requirements for ethanol dehydration

Purification (Wt. %)	Energy required (kJ/kg EtOH)	Process
8.0–99.5	10376	Distillation
95.0–99.5	3305	Azeotropic distillation
95.0–99.5	423	Pervaporation

Furthermore, PV has several advantages over traditional distillation: (1) reduced energy demand because only a fraction of the liquid that needs to be separated is vaporized, (2) simple equipment since only a vacuum pump is used to create a driving force and (3) lower capital cost. Thus, relatively mild operation conditions and high effectiveness make PV an appropriate technique for such separations. As a result, most PV studies have been focused on dehydration of

organic mixtures. In PV, the feed mixture is contacted with a nonporous permselective membrane. Separation is, in general, explained by the steps of sorption into, diffusion through and desorption from the membrane. The latter is usually considered fast and taking place at equilibrium, while diffusion is kinetically controlled and the slowest step of the process. Permeation is dependent on sorption and diffusion steps. The driving force for the separation is created by maintaining a pressure lower than the saturation pressure on the permeate side of the membrane. The mechanism of separation is usually explained in terms of sorption-diffusion processes. Polymeric membranes are not generally suitable for applications involving harsh chemicals due to membrane chemical instability. However, a recent development of chemical-and-temperature resistant hydrophilic ceramic membranes has made it possible to overcome the limitations of hydrophilic polymeric membranes [8-10].

Zeolite membranes are another kind of pervaporation materials for separating water from highly concentrated ethanol aqueous solution since zeolites are most hydrophilic and have well-defined open crystal structures with a pore size of several angstroms. These unique structural characteristics and hydrophilic nature have rendered zeolite materials possessing pronounced molecular sieving effect and selective adsorption capability (i.e., appreciated separation performance). Therefore, zeolites can be extensively applied in removal of volatile organic chemicals from air streams, separation of isomers and mixtures of gases, shape-selective catalysis and ion exchange. The zeolitic membranes offer several advantages over polymeric ones: (i) they do not swell significantly compared to polymeric membranes, (ii) they have uniform molecular-sized pores that provide differential transport rates and molecular sieve effects, (iii) the zeolitic structures are more chemically stable, tolerant to harsh separation conditions such as strong solvents or low pH, (iv) zeolites are thermally stable up to high temperatures of 1000 °C [11, 12].

In this study, nanopore HS zeolite membranes were fabricated and then used to separate water/Ethanol mixtures. Zeolite HS layers were coated on external surface of porous tubular mullite supports using hydrothermal method. These membranes were successfully used for dehydration of water/Ethanol mixtures.

2. Zeolite structure and transport mechanisms

The hydrophilic membranes used in this research were composite zeolite HS membranes. The membranes were made of an active HS layer, deposited on a ceramic porous mullite support. The active HS layer is responsible for high separation factors achieved in PV of Ethanol mixtures. The structure of zeolite HS is shown in Figure 1.

As shown in Figure 1, the aluminosilicate framework of zeolite HS is generated by placing truncated octahedrons (b-cage) at eight corners of a cube and each edge of the cube is formed by joining two b-cages. Each b-cage encloses a cavity with a free diameter of 0.66 nm and each unit cell encloses a

larger cavity (a-cage). There are two interconnecting, three-dimensional channels in zeolite HS: (i) connected a-cages, separated by 0.3 nm apertures, (ii) b-cages, alternating with a-cages separated by 0.22 nm apertures. Thus, molecules smaller than 0.3 nm in diameter can diffuse easily through the nanopores of the zeolite. In addition, position of sodium ions in unit cells is important since these ions act as the sites for water sorption and transport through the membrane. For a typical zeolite, a unit cell having the composition $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{OH})_2 \cdot 1.5 \text{H}_2\text{O}$, eight (out of 12) sodium ions are located inside an a-cage and four ions are located in b-cages. Transport of solvent species (mainly water) through the zeolite matrix comprises of three steps: (i) strong adsorption of the species into a cage from feed side, (ii) surface diffusion of the species from cage to cage and (iii) vaporization of the species to permeate side. Normally, any physical adsorption process includes both Vander Waals dispersion-repulsion forces and electrostatic forces comprising of polarization, dipole and quadrupole interactions. However, since the zeolites have an ionic structure, the electrostatic forces become very large in adsorption of polar molecules like H_2O . This effect is manifested in the fact that heat of adsorption of water into zeolitic adsorbents is unusually high (25–30 kcal/mole).

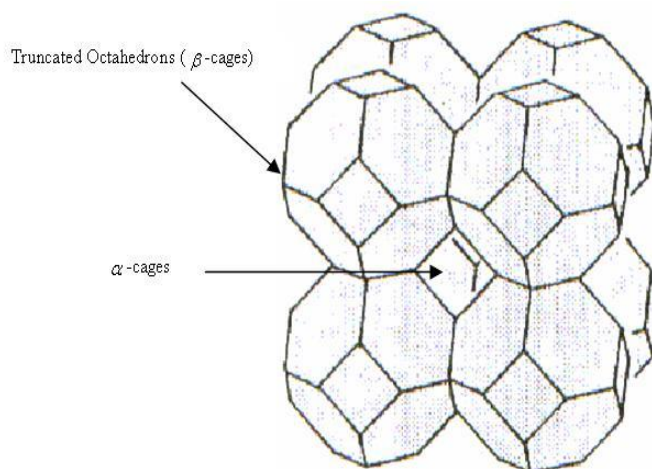


Figure 1: Repeating unit of zeolite HS

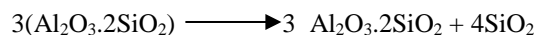
3. Experimental

3.1 Support preparation

In ceramic membranes, thin dense layers are usually deposited over porous supports. The porous supports provide mechanical strength for the thin selective layers. Porous supports can be made from alumina, cordierite, mullite, silica, spinel, zirconia, other refractory oxides and various oxide mixtures, carbon, sintered metals and silicon carbide.

In this research, mullite supports have been prepared from kaolin clay. Kaolin is thermally converted to mullite via high

temperature calcinations. The reaction takes place when kaolin is utilized as the sole source of silica and alumina. The reaction can be represented by the following equation:



Free silica (4SiO_2) is generated as a result of this conversion. The free silica has been leached out and then porous mullite bodies have been prepared. Mullite has several distinct advantages over other materials. Since kaolin is heated to high temperatures to achieve the mullite conversion reaction, strong inter-crystalline bonds between mullite crystals are formed and this results in excellent strength and attrition. Leaching time depends on several factors including:

- (1) The quantity of free silica to be removed,
- (2) The porosity of body prior to leaching,
- (3) The concentration of leaching solution.
- (4) Temperature.

Kaolin (SL-KAD grade) has been supplied by WBB cooperation, England. Analysis of the kaolin is listed in Table 2. Cylindrical shaped (tubular) bodies (ID: 10 mm, OD: 14 mm and L: 15 cm) have been conveniently made by extruding a mixture of about 75-67% kaolin and 25-33% distilled water. Suitable calcinations temperatures and periods are those at which kaolin converts to mullite and free silica. Good results have been achieved by calcining for about 3 h at temperatures of about 1250° [13, 14].

Table 2: Analysis of kaolin clay

Component	Percent (%)	Phases	Percent (%)
SiO ₂	51.9	Kaolinite	79
TiO ₂	0.1	Illite	8
Al ₂ O ₃	34.1	Quartz	10
Fe ₂ O ₃	1.4	Feldspar	3
K ₂ O	0.8	Total	100
Na ₂ O	0.1		
L.O.I	11.6		
Total	100		

Free silica has been removed from the calcined bodies after leaching by strong alkali solutions. Removal of the silica causes mesoporous tubular supports to be made with very high porosity. Free silica removal has been carried out using aqueous solutions containing 20% by weight NaOH at a temperature of 80°C for 5 h. Supports have been rinsed using a lot of hot distilled water for a long time in order to remove the all remaining NaOH. Porosity of the supports before leaching is 24.3%, while after treatment it increases to 49%. Flux of the supports before and after free silica removal at 1 bar and 20°C is $6 \text{ kg/m}^2\text{h}$ and $10 \text{ kg/m}^2\text{h}$, respectively. Porosity of the supports has been measured by water absorption method. Phase identification has been performed by X-ray diffractometry with CuK_α radiation.

3.2 Zeolite membrane synthesis

3.2.1 Coating of the support with seeds

Adding seed crystals to this crystallization system has resulted in increased crystallization rate. The enhanced rate might be due to simply increasing the rate at which solute is integrated into the solid phase from solution due to the increased available surface area, but also might be the result of enhanced nucleation of new crystals. The secondary nucleation mechanism referred to as initial breeding results from microcrystalline dust being washed off seed crystal surfaces in a new synthesis batch. These microcrystalline fragments grow to observable sizes, and result in greatly enhanced crystallization rates due to the significantly increased crystal surface area compared to the unseeded system. Consequently, it is to be expected that addition of seed crystals to a synthesis system will introduce sub-micron sized crystallites into the system that will serve as nuclei.

Porous mullite tubes (homemade) as describe above have been used as the support. The external surface of the supports have been polished with 600 grit-sand papers, and then the support has been washed and cleaned with distilled water in a microwave heater for 5 min to remove loose particles created during polishing. Then, supports have been dried at 100°C for 3h.

In order to form a thin and uniform zeolite membrane on the mullite support, the nucleation seeds should be small and uniform in size. In order to inhibit the formation of zeolites into the support pores, the seeds should not penetrate into the pores. The high purity nucleation seeds have been synthesized by hydrothermal method. Size of the seeds is about $2 \mu\text{m}$. The seeds should be dispersed homogeneously on the support surface and the amount of seeds on the support surface should not be too much. Otherwise, the synthesized zeolite membrane is heterogeneous or too thick.

The seeded supports have been prepared by dipping the mullite supports in an 8% NaA zeolite suspension in a single step. The 8% NaA zeolite suspension has been prepared by mixing 8 g NaA zeolite in 92 ml distilled water. After dipping procedure, the supports have been dried at 100°C for 3 h.

3.2.2 HS zeolite synthesis

Thin zeolite HS membrane layers were grown hydrothermally over the external surface of the mullite supports. The HS zeolite membranes were prepared by in situ crystallization on the outer surface of the porous mullite tubes. The is source was sodium silicate and the Al source was sodium aluminates. Synthesis solution was prepared by mixing aluminates and silicate solutions. NaOH was dissolved in distilled water. The solution was divided into two equal volumes and kept in polypropylene bottles. Aluminates solution was prepared by adding sodium aluminates to one part of the NaOH solution. It was mixed until cleared. Silicate solution was prepared by adding sodium silicate to another

part of the NaOH solution. Silicate solution was then poured into aluminates solution and well mixed until a thick homogenized gel was formed. Molar composition of the starting gel of the HS zeolite membranes was $\text{SiO}_2/\text{Al}_2\text{O}_3=1.0-5.0$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=15-65$, $\text{H}_2\text{O}/\text{Al}_2\text{O}_3=500-1500$ [15-18]. Crystallization was carried out in an oven at temperatures of 100°C for 12h. In addition, Crystallization was carried out in an oven at temperatures of 70, 100 and 130°C for 6, 12 and 24 h. Then, the samples were taken and the synthesized membranes were washed several times with distilled water. The samples were then dried at room temperature for 12 h in air. The zeolite membranes were used for dehydration of aqueous Ethanol. The Ethanol mixtures (90 wt%) were used and experiments were carried out at room temperature (25°C) within a period of 30-60 min. Permeate concentrations were measured using GC (TCD detector, Varian 3400, carrier gas: hydrogen, column is polyethylene glycol, sample size: 5 micron, column and detector temperatures: $120^\circ\text{C}-150^\circ\text{C}$, detector flow rate: 15 ml/min, carrier flow: 5 ml/min, column pressure: 1.6 kPa, GC input pressure: 20 kPa). Performance of PV was evaluated using values of total flux ($\text{kg}/\text{m}^2\cdot\text{h}$) and separation factor (dimensionless).

The phases Mullite, Cristobalite and SiO_2 identification was performed by X-ray diffractometry (Philips PW1710, Philips Co., Netherlands) with $\text{CuK}\alpha$ radiation. Morphology of the support and the membrane was examined by Scanning Electron Microscopy (JEM-1200 or JEM-5600LV equipped with an Oxford ISIS-300 X-ray disperse spectroscopy (EDS)).

4. Pervaporation Tests

The zeolite membranes have been used for long-term dehydration of Ethanol. The experiments have been carried out at a temperature of 30°C and a pressure of 1.5 mbara at the permeate side, within a period of 30-60 min.

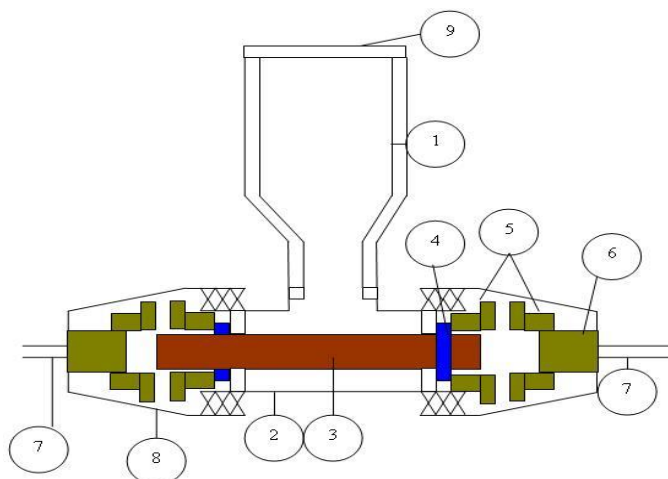


Figure 2: (a) pervaporation cell: 1- feed tank 2-membrane module 3- membrane 4- O-ring 5- Teflon fitting 6- stainless steel vacuum fitting 7- vacuum hose 8- cap 9- feed tank cap

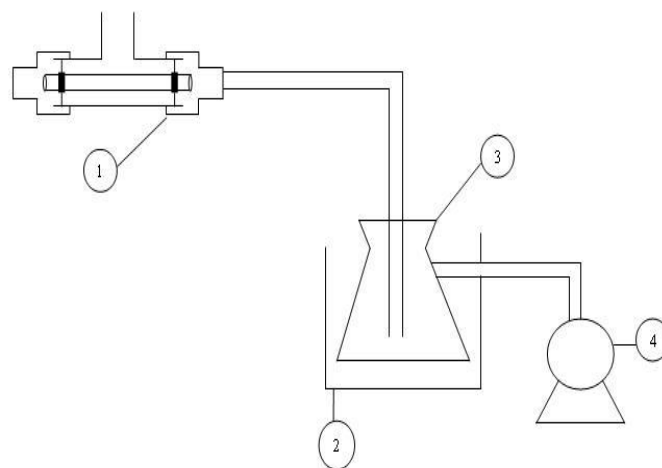


Figure 2(b) Pervaporation setup: 1- PV cell 2- liquid nitrogen trap 3- permeate container 4- three stage vacuum pump

The pervaporation setups is presented in Figure 2(a, b) and 3. Any change of feed concentration due to permeation is negligible because the amount of permeate is small (max 2 ml) compared to total feed volume in the system (0.5 lit). A three stage diaphragm vacuum pump (vacuubrand, GMBH, Germany) has been employed to evacuate the permeate side of the membrane to a pressure of approximately 1.5 mbara while the feed side has been kept at room pressure. The permeate side has been connected to a liquid nitrogen trap via a hose to condense the permeate (vapor). Permeate concentrations have been measured by a GC (TCD detector, Varian 3400).

Performance of PV is usually evaluated by total flux ($\text{kg}/\text{m}^2\cdot\text{h}$) and separation factor (dimensionless). Separation factor of any organic aqueous solution can be calculated from the following equation:

$$\text{Separation factor } (\alpha) = \frac{\left[\frac{X_{\text{H}_2\text{O}}}{X_{\text{Organic}}} \right]_{\text{permeate}}}{\left[\frac{X_{\text{H}_2\text{O}}}{X_{\text{Organic}}} \right]_{\text{feed}}}$$

Where $X_{\text{H}_2\text{O}}$ and X_{Organic} are weight fractions of water and organic compound, respectively.

5. Results and discussion

5.1 Gel Composition

As mentioned earlier, zeolites could be synthesized by the hydrothermal method. The versatility of hydrothermal chemistry owes much to the mineralizing role of water. The factors that promote reactivity in aqueous magmas include:

- Stabilization of porous lattices as zeolites by acting as space fillers, referred to above.
- Through its presence, especially at high pressures, water may be incorporated into hydrous glasses, melts, and solids. Through chemisorptions into siliceous

- Materials, Si-O-Si, and Al-O-Si, bonds hydrolyze and reform. Chemical reactivity is enhanced and magma viscosity is lowered.
- High pressures of water can modify phase equilibrium temperatures.
- Water is a good solvent, a property that assists disintegration of solid components of a mixture and facilitates their transport and mixing.

Water is important as a guest molecule in zeolite structures with relatively high Al contents and consequently, aqueous media favor their formation while salts have a parallel role in the stabilization of zeolite structure. In general, the zeolitic water can be removed leaving the unchanged hydrous zeolite. In hydrothermal systems, the good solvent powers of water promote mixing, transport of materials, and facilitate nucleation and crystal growth. Water stabilizes zeolite structures by filling the cavities and forming a type of solid solution. The stabilizing effect is such that the porous aluminosilicates will not form in the absence of a guest molecule, which may be a salt molecule as well as water. However, the water concentration or the degree of dilution is important for the synthesis of HS, which can crystallize out of gels with an extremely wide range of H₂O/Al₂O₃ ratios (from 500 to 1500).

The Na₂O or alkalinity of the media plays a vital role in crystal growth, materials synthesis/preparation, and processing, on the whole. It influences the super saturation, kinetics, morphology, shape, size, and crystallinity, of the particles or materials as the OH⁻ anions fulfill the crucial role of mineralizing agent. The Na₂O is influenced by the reactants and their concentrations/ratios, followed by temperature and time. Further, with the introduction of organics, the alkalinity changes rapidly in the system, hence, alkalinity is the key parameter in determining the crystallization rate. An increase in OH⁻ concentration will generally bring about an accelerated crystal growth and a shortened induction period before viable nuclei are formed. In zeolite synthesis, pH of the alkaline solution is usually between 8 and 12. The major role of pH is to bring the Si and Al oxides or hydroxides into solution at an adequate rate.

To study effects of gel composition on HS zeolite membrane performance, the membranes were synthesized at different compositions (SiO₂/Al₂O₃=1.0-5.0, Na₂O/Al₂O₃=15-65, H₂O/Al₂O₃=500-1500) for duration 12 h and temperature 100°C. It must be also mentioned that three samples were prepared for each condition. The results were presented on average and the maximum deviation was less than 3%.

As seen in Table 3, HS zeolite membranes have been successfully synthesized in ranges of SiO₂/Al₂O₃=1.0 to SiO₂/Al₂O₃<2.5, Na₂O/Al₂O₃=15-65, H₂O/Al₂O₃>500 to H₂O/Al₂O₃=1500.

In H₂O/Al₂O₃<500 ratio, HS zeolite membranes have not been successfully synthesized, because gel composition have not enough water for synthesis a homogenous gel. Also, in SiO₂/Al₂O₃>2.5 ratio, causes HS zeolite to transform to other zeolots. It must be mentioned that 10000 is the highest measurable value using the GC at 90 wt% Ethanol

concentration as shown in Table 3.

5.2 Temperature and Time

Temperature and time have a positive influence on the zeolite formation process, which occurs over a considerable range of temperatures. A rise in temperature will increase both the nucleation rate and the linear growth rate; hence, the crystallinity of the samples normally increases in time. As far as time is concerned, zeolite synthesis is governed by the occurrence of successive phase transformations. The thermodynamically least favorable phase will crystallize first and will be successively replaced in time by more stable phases. The best example is the crystallization sequence of amorphous → NaA → HS.

The temperature, however, can also influence the type of product that has to be crystallized. A rise in temperature leads to the crystallization of more dense products as the fraction of water in the liquid phase, which has to stabilize the porous products by filling the pores, will drop. Therefore, the existence of an upper limit for the formation of zeolites is to be expected. The use of nonvolatile pore space occupying (filling) species would, in principle, allow a high-temperature synthesis of open, porous structures. Temperature can obviously affect the rate of nucleation and crystal growth.

The linear rates of crystal growth and rates of nucleation both increase with rising temperatures.

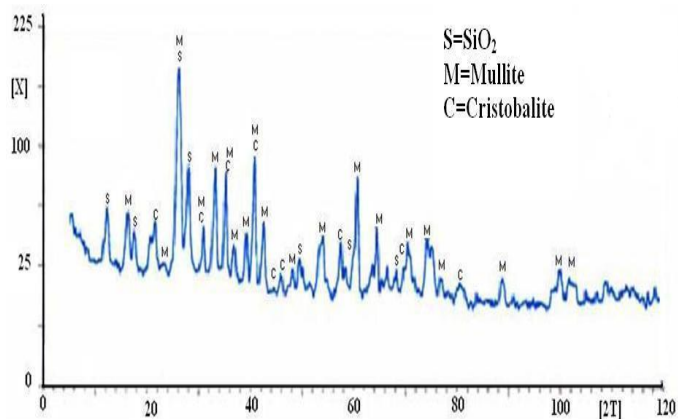


Figure 4: XRD of the support

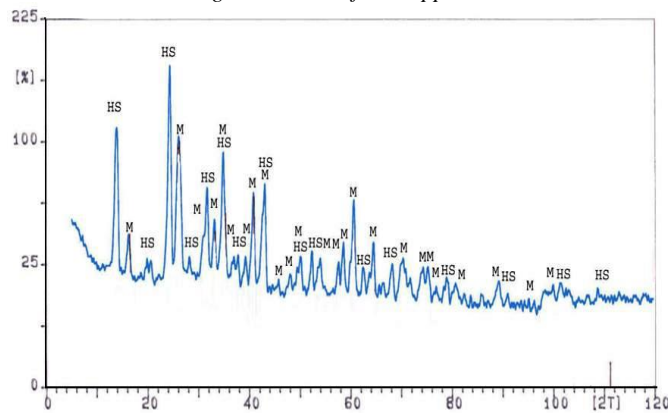


Figure 5: XRD of the HS zeolite membrane

To study the effect of crystallization time and temperature on the membrane performance, the membranes were synthesized at different temperatures (70, 100 and 130 °C) and different times (6, 12 and 24 h). As seen in Table 3, increasing crystallization time decreases water flux (samples 5 and 8). However, there is no change in separation factor. This may be due to the fact that at a longer crystallization time a thicker

membrane layer is formed. This causes water flux to decrease. This shows that the membranes behave very high selective. The results show that short crystallization time (6 h) is not enough to make an effective HS zeolite layer on the support (sample 13). This sample shows poor selectivity. The crystallization time in a range of 12-24 h was found to be very effective for making the HS zeolite layer.

Table 3: Flux and separation factor of HS zeolite membranes

Sample	Number of coating	SiO ₂ /Al ₂ O ₃	Na ₂ O/Al ₂ O ₃	H ₂ O/Al ₂ O ₃	t (h)	T (°C)	Ethanol (%)	Flux kg/m ² .h	Separation factor
1	1	1.0	65	1000	12	100	90	0.750	>10000
2	1	2.5	65	1000	12	100	90	1.140	176
3	1	5.0	65	1000	12	100	90	6.290	31
4	1	1.0	15	1000	12	100	90	0.227	>10000
5	1	1.0	40	1000	12	100	90	0.624	>10000
6	1	1.0	65	1000	12	100	90	0.750	>10000
7	1	1.0	65	500	12	100	90	3.145	88
8	1	1.0	65	1000	12	100	90	0.750	>10000
9	1	1.0	65	1500	12	100	90	1.224	>10000
10	1	1.0	65	1000	12	70	90	0.681	>10000
11	1	1.0	65	1000	12	100	90	0.750	>10000
12	1	1.0	65	1000	12	130	90	2.05	>10000
13	1	1.0	65	1000	6	100	90	1.0	26
14	1	1.0	65	1000	12	100	90	0.75	>10000
15	1	1.0	65	1000	24	100	90	0.621	>10000

Table 4: cross flow results by zeolite membrane

Run	Concentration of Ethanol in feed (wt %)	P (bar)	Q (lit/min)	T (°C)	Flux kg/m ² .h
1	80	1	0.5	20	1.1680
2	80	1	1.5	20	1.5196
3	80	1	3	20	1.905
4	80	1	0.5	20	1.1680
5	80	2	0.5	20	1.520
6	80	3	0.5	20	1.905
7	80	1	0.5	20	1.1680
8	80	1	0.5	40	2.415
9	80	1	0.5	60	2.994

As seen in Table 3, increasing crystallization temperature increases water flux (samples 10, 11 and 12). In addition, it can be observed that there is no change in separation factor. This may be due to the fact that at higher crystallization temperature, a thinner layer is formed. It is because, at higher temperatures, the synthesis solution becomes heterogeneous, and as a result, the HS zeolite layer becomes thinner. This also shows that the membranes behave very high selective. The crystallization temperature in a range of 70-130°C was found to be very effective for making the HS zeolite layer.

The results confirm that zeolite membranes synthesized at 130°C for 12 h via a single stage process can be recommended for dehydration of dilute water/ Ethanol mixtures. The membranes are uniform and defect free and as a result, their separation factors are very high. Minimum synthesis time for the HS zeolite layer was found to be 12 h for making a uniform membrane.

Figures 4 and 5 show XRD patterns of the mullite support and the HS zeolite membrane. The XRD pattern of HS zeolite membrane confirms that zeolite HS crystals were formed.

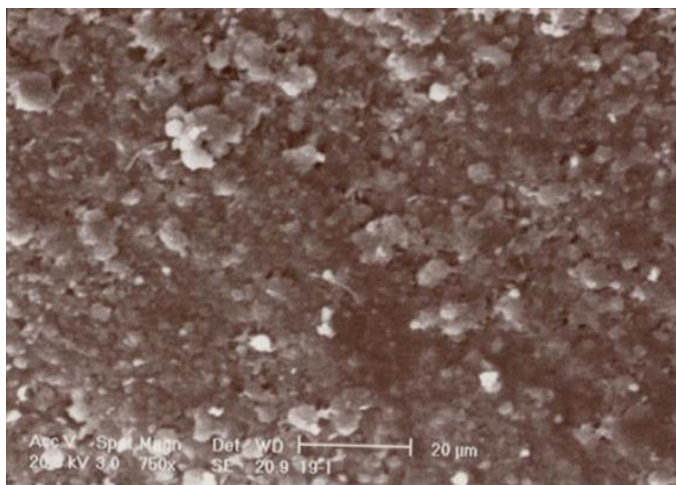


Figure 6: SEM micrograph of the support

Figures 6-8 show SEM photographs of the mullite support and the HS zeolite membrane. Porous structure of the support and thin layer of the membrane can be easily observed.

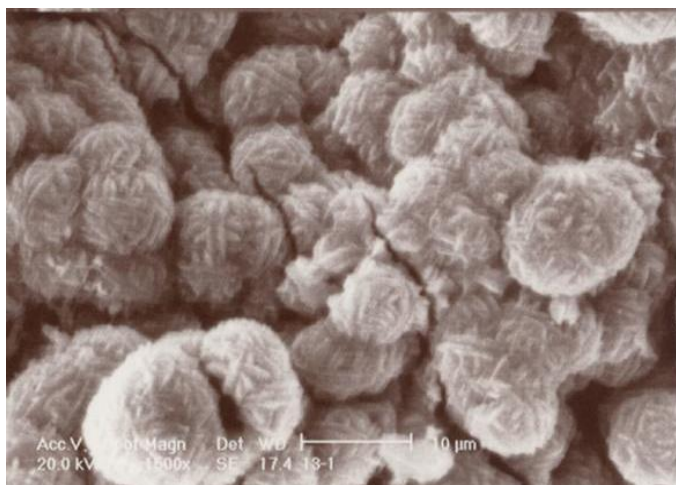


Figure 7: SEM micrograph of the membrane

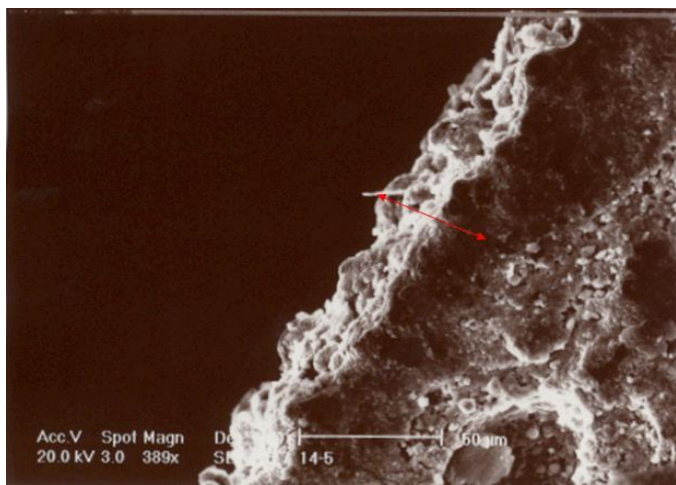


Figure 8: SEM micrograph of the thickness of membrane on support

5.3 PV Operating Conditions

Effect of operating conditions at PV process was evaluated by cross flow PV pilot. The transmembrane pressure is adjusted between 1 and 3 barg. The feed temperature is varied between 20 and 60 °C by means of a small heat exchanger employed into the feed tank. Feed rate is varied between 0.5 and 3 lit/min by means of centrifuge pumps and recycles line. Permeate collected in a sample bottle is measured. The outlet flow of the cell can be led out of the system or returned to the tank. As shown in table 4, effect of feed rate on permeate flux were measured at constant temperature (20°C) and constant pressure (1 bar). Increasing feed rate increases the permeate flux. As shown in table 4, increasing pressure increases the permeate flux. Increasing rate increases turbulence and hydrodynamic effects cause to increasing permeate flux. Temperature is known as a main parameter. Increasing temperature causes an increase in viscosity reduction. Table 4 shows the experimental data for the flux as a function of temperature. As seen, the flux increases with temperature. According to the results, it can be said the optimum operating conditions were 60°C, 3 bar and 3 lit/min.

6. Conclusion

Nano HS zeolite membrane was firstly used for dehydration of aqueous Ethanol mixtures. It was found gel compositions that nano HS zeolite membranes have been synthesized. These membranes showed very good membrane performance for separation of Ethanol /water mixtures. It is expected that PV using these membranes can be a highly interesting tool for industry, provided they can be produced cheap at a large scale. Separation factors as high as 10000 was obtained at 90 wt% Ethanol concentration. It was found gel compositions, time and temperature range that HS zeolite membranes have been synthesized. The best range operating condition (time and temperature) for hydrothermal synthesis of nanopore HS zeolite membrane were 12-24 h and 70-130°C respectively. Effect of operating condition at pervaporation process show that increasing pressure, feed rate and temperature increases the flux linearly.

References

- [1] B. Zhu, D. Myat, G. Connor, Application of robust MFI-type zeolite membrane for desalination of saline wastewater, *Journal of Membrane Science* 475 (2015) 167-174.
- [2] S. Basu, S. Mukherjee, A. Kaushik, Integrated treatment of molasses distillery wastewater using microfiltration (MF), *Journal of Environmental Management* 158 (2015) 55–60.
- [3] Sanaa Jamaly, Adewale Giwa, Shadi Wajih Hasan, Recent improvements in oily wastewater treatment: Progress, challenges, and future opportunities, *Journal of Environmental Sciences* 37 (2015) 15–37.
- [4] S. Amnuaypanich, J.Patthana, P.Phinyocheep, Mixed matrix membranes prepared from natural rubber/poly(vinyl alcohol) semi- interpenetrating polymer network (NR/PVA semi-IPN) incorporating with zeolite 4A for the pervaporation dehydration

- [5] of water–ethanol mixtures, *Chemical Engineering Science* 64 (2009) 4908–4918.
- [6] A. Almutairi, L. Weatherley, Intensification of ammonia removal from wastewater in biologically active zeolitic ion exchange columns, *Journal of Environmental Management* 160 (2015) 128–138.
- [7] H. Premakshi, K. Ramesh, M. Kariduraganavar, Modification of crosslinked chitosan membrane using NaY zeolite for pervaporation separation of water–isopropanol mixtures, *Chemical Engineering Research and Design* 94 (2015) 32–43.
- [8] Sorenson. S, E. Payzant, W. Gibbons, B. Soydas, H. Kita, R. Noble, J. Falconer, Influence of zeolite crystal expansion/contraction on NaA zeolite membrane Separations, *Journal of Membrane Science* 366 (2011) 413–420.
- [9] Kondo. M, H. Kita, Permeation mechanism through zeolite NaA and T-type membranes for practical dehydration of organic solvents, *Journal of Membrane Science* 361 (2010) 223–231.
- [10] Kresse, I., J. Springer, Z. K. Zhou, Xin-Gui Li, Effect of temperature and pressure on gas transport in ethyl cellulose membrane, *Polymer*, 42 (2001) 6801-6810.
- [11] Llorens, J., M. Pera-Titus, Description of the pervaporation dehydration performance Of A-type zeolite membranes: A modeling approach based on the Maxwell–Stefan theory, *Catalysis Today* 118 (2006) 73–84.
- [12] Pera-Titus, M., R. Mallad, Preparation of inner-side tubular zeolite NaA membranes in a semi-continuous synthesis system, *Journal of Membrane Science* 278 (2006) 401–409.
- [13] Sorenson. S, E. Payzant, W. Gibbons, B. Soydas, H. Kita, R. Noble, J. Falconer, Influence of zeolite crystal expansion/contraction on NaA zeolite membrane Separations, *Journal of Membrane Science* 366 (2011) 413–420.
- [14] K. Speronello., 1986- Porous mullite, U.S. Patent NO 4628042.
- [15] K. Speronello., 1986- Porous mullite, U.S. Patent No. 4601997.
- [16] Joaquin C., Present and future synthesis challenges for zeolites, *Chemical Engineering Journal* 156 (2010) 236–242.
- [17] Churl. H, Y. Ka, G. Jeong, K. Si, M. Young, Improvement in thermal stability of NaA zeolite composite membrane by control of intermediate layer structure, 366 (2011) 229-236.
- [18] Churl. H, Y. Ka, G. Jeong, K. Si, M. Young , Synthesis, ethanol dehydration and thermal stability of NaA zeolite/alumina composite membranes with narrow non-zeolitic pores and thin intermediate layer , *Journal of Membrane Science*,364 (2010) 138-148.
- [19] L. Ayele, J. Pariente, Y. Chebude, Synthesis of zeolite A from Ethiopian kaolin, *Microporous and Mesoporous Materials* 215 (2015) 29-36.