# Making and Evaluation of Nanopore Hydroxysodalite Zeolite Membranes for Pervaporation Applications

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## Abstract

Effects of crystallization time and temperature on the membrane structure and performance have been investigated for Nanopore Hydroxysodalite (HS) zeolite membranes grown onto seeded mullite supports. Molar composition of the starting gel of HS zeolite membranes was: $SiO_2/Al_2O_3=1.0\text{-}5.0$, $Na_2O/Al_2O_3=15\text{-}65$, and $H_2O/Al_2O_3=500\text{-}1500$. 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-Unsymmetrical Dimethylhydrazine (UDMH) mixtures using Pervaporation (PV). The membranes showed good selectivity towards water in the water-UDMH mixtures. Water permeates faster because of its preferential adsorption into the Nano-pores of the hydrophilic zeolite membrane. In PV of water-UDMH 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 2.4 kg/m2.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.

## Introduction

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).

| 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 |

**Table 1:** Energy requirements for ethanol dehydration.

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. Furthermore, PV has several advantages over traditional distillation: [1] reduced energy demand because only a fraction of the liq-

uid 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 [1-4].

In PV, the feed mixture is contacted with a nonporous perm selective membrane. Separation is, in general, explained by the steps of sorption into, diffusion through and desorption from the membrane. The latter is usually considered to be 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 [5-7].

Polymeric membranes are not generally suitable for applications involving harsh solvents like UDMH due to membrane chemical instability. However, a recent development of solvent-and-temperature resistant hydrophilic ceramic membranes made it possible to overcome the limitations of hydrophilic polymeric membranes. PV is an economical separation technique compared with conventional separation methods such as distillation especially in processes involving azeotropes, isomers and (removal or recovery of) trace substances. Due to its high separation factor and flux, PV results in energy cost saving and safe operation. In PV, feed mixture is contacted with a nonporous perm selective membrane. Separation is, in general, explained by the steps of sorption into, diffusion through and desorption from the membrane. The latter is usually considered to be fast and taking place at equilibrium, while diffusion is kinetically controlled and the slowest step of process. Permeation depends on sorption and diffusion steps. Driving force for the separation is created by maintaining a pressure lower than saturation pressure on permeate side of the membrane. The mechanism of separation is usually explained in terms of sorption-diffusion processes [8-10].

UDMH is an important liquid solvent; however, it also finds many new applications every day such as an oxygen scavenger for boiler-feed water, a starting material for drug and dye intermediates, a catalyst for polymerization reactions, etc. Polymeric membranes cannot be used to dehydrate aqueous UDMH mixtures because they are degraded rapidly. In addition, they cannot withstand the highly alkaline (pH =13-14) medium and give negligible flux so that UDMH cannot be selectively extracted from its dilute reaction liquor (their separation factor is about 2-10). However, a recent development of chemical-and-temperature resistant hydrophilic ceramic membranes has made it possible to overcome the limitations of hydrophilic polymeric membranes [11,12].

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 [13-15].

Nano and uniform pore size of these zeolites makes separation of small molecules possible via molecular sieving. Zeolite membranes were found to be extremely effective for dehydration of ethanol by PV, with separation factors of 104 or more being achieved. It was observed that it is possible to form remarkably uniform zeolite NaA and HS zeolite membranes from a homogeneous solution. This has many potential advantages in terms of reproducibility and easy control [16].

In this study, nanopore HS zeolite membranes were fabricated and then used to separate water/UDMH 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/UDMH mixtures.

## Zeolite Structure and Transport Mechanisms

The hydrophilic membranes used in this research were composite zeolite HS membranes. The membranes were basically 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 UDMH mixtures. The structure of zeolite HS is shown in (Figure 1).
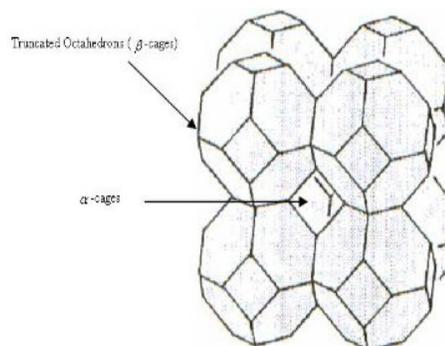


**Figure 1:** Repeating Unit of Zeolite HS.

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 $Na_6[Al_6Si_6O_{24}]$ $(OH)_2$. $(1.5\ H_2O)$, 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).

# Experimental

## 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:

$$3(Al_2O_3.2SiO_2) \rightarrow 3Al_2O_3.2SiO_2 + 4SiO_2$$

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 and

4) Temperature.

Kaolin (SL-KAD grade) has been Supplied by WBB Cooperation, England. Analysis of the Kaolin is Listed in (Table 2).

| Component | Percent (%) | Phases | Percent (%) |
|---|---|---|---|
| $SiO_2$ | 51.9 | Kaolinite | 79 |
| $TiO_2$ | 0.1 | Illite | 8 |
| $Al_2O_3$ | 34.1 | Quartz | 10 |
| $Fe_2O_3$ | 1.4 | Feldspar | 3 |
| $K_2O$ | 0.8 | | |
| $Na_2O$ | 0.1 | Total | 100 |
| L.O. I | 11.6 | | |
| Total | 100 | | |

**Table 2:** Analysis of Kaolin Clay.

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°C [17,18].

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 kg/m²h and 10 kg/m²h, respectively. Porosity of the supports has been measured by water absorption method. Phase identification has been performed by X-ray diffractometry (Philips PW1710, Philips Co., Netherlands) with $CuK_\alpha$ radiation.

## Zeolite Membrane Synthesis

**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 has 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 μm. 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.

**HS Zeolite Synthesis:** The hydrophilic membranes used in this research were composite zeolite HS membranes. The membranes were basically 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 UDMH mixtures. 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, zirconium, other refractory oxides and various oxide mixtures, carbon, sintered metals and silicon carbide. 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. This 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 $SiO_2/Al_2O_3=1.0-5.0$, $Na_2O/Al_2O_3=15-65$, $H_2O/Al_2O_3=500-1500$ [19-23].

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 UDMH. Dilute UDMH mixtures (5 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: 5micron, column and detector temperatures: 120°C- 150°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 (kg/m².h) and separation factor (dimensionless). A typical experimental setup was employed as presented in (Figure 1).

## 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 m bara at the permeate side, within a period of 30-60 min.  The pervaporation setups are presented in (Figure 2a, 2b) and (Figure 3).
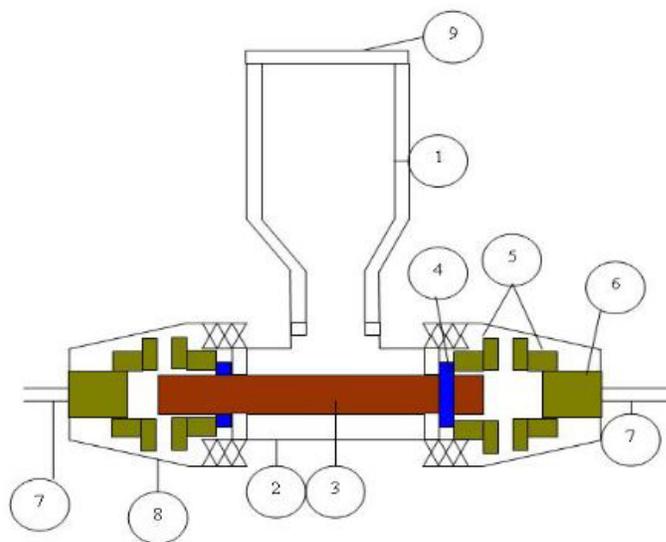


**Figure 2a:** pervaporation cell: 1- feed tank 2-membrane module 3- membrane 4- O-ring 5- Teflon fitting 6- stainless steel vacuum fitting 7- vacuum hose 8- cap 9- feed tank cap.
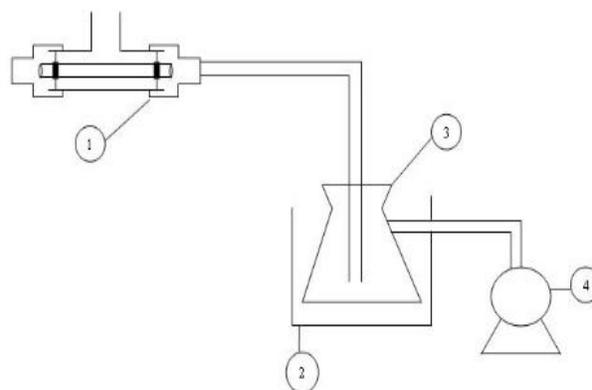


**Figure 2b:** Pervaporation Setup: 1- PV cell 2- Liquid Nitrogen Trap 3- Permeate Container 4- Three Stage Vacuum Pump.
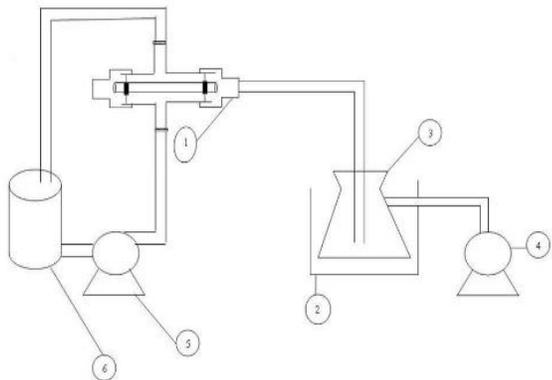
**Figure 3:** PV Setup Cross Flow; 1- Feed Container and PV Cell 2- Liquid Nitrogen Trap 3- Permeate Container 4- Three Stage Vacuum Pump 5- Centrifuge Pump 6- Tank Feed.

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 evacuated 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 (kg/m2h) and separation factor (dimensionless). Separation factor of any organic aqueous solution can be calculated from the following equation:

$$Separation\ factor\ (a) = \frac{\left[ X_{H_2O} \middle/ X_{Organic} \right]_{permeate}}{\left[ X_{H_2O} \middle/ X_{Organic} \right]_{feed}}$$

Where $X_{H_2O}$ and $X_{organic}$ are weight fractions of water and organic compound, respectively.

## Results and Discussion

### 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 re-form. 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 $H_2O/Al_2O_3$ ratios (from 500 to 1500).

The $Na_2O$ 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 $Na_2O$ 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 ($SiO_2/Al_2O_3$=1.0-5.0, $Na_2O/Al_2O_3$=15-65, $H_2O/Al_2O_3$=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).

| Sample | Number of coating | $SiO_2/Al_2O_3$ | $Na_2O/Al_2O_3$ | $H_2O/Al_2O_3$ | t (h) | T ($^{\circ}$C) | UDMH (%) | Flux kg/ $m^2$.h | Separation factor |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 1.0 | 65 | 1000 | 12 | 100 | 5 | 0.890 | >10000 |
| 2 | 1 | 2.5 | 65 | 1000 | 12 | 100 | 5 | 1.340 | 176 |
| 3 | 1 | 5.0 | 65 | 1000 | 12 | 100 | 5 | 7.400 | 31 |
| 4 | 1 | 1.0 | 15 | 1000 | 12 | 100 | 5 | 0.267 | >10000 |
| 5 | 1 | 1.0 | 40 | 1000 | 12 | 100 | 5 | 0.734 | >10000 |
| 6 | 1 | 1.0 | 65 | 1000 | 12 | 100 | 5 | 0.890 | >10000 |
| 7 | 1 | 1.0 | 65 | 500 | 12 | 100 | 5 | 3.700 | 88 |
| 8 | 1 | 1.0 | 65 | 1000 | 12 | 100 | 5 | 0.890 | >10000 |
| 9 | 1 | 1.0 | 65 | 1500 | 12 | 100 | 5 | 1.440 | >10000 |
| 10 | 1 | 1.0 | 65 | 1000 | 12 | 70 | 5 | 0.80 | >10000 |
| 11 | 1 | 1.0 | 65 | 1000 | 12 | 100 | 5 | 0.89 | >10000 |
| 12 | 1 | 1.0 | 65 | 1000 | 12 | 130 | 5 | 2.40 | >10000 |
| 13 | 1 | 1.0 | 65 | 1000 | 6 | 100 | 5 | 1.0 | 26 |
| 14 | 1 | 1.0 | 65 | 1000 | 12 | 100 | 5 | 0.89 | >10000 |
| 15 | 1 | 1.0 | 65 | 1000 | 24 | 100 | 5 | 0.73 | >10000 |

**Table 3:** Flux and Separation Factor of HS Zeolite Membranes (dead end).

HS zeolite membranes have been successfully synthesized in ranges of $SiO_2/Al_2O_3$=1.0 to $SiO_2/Al_2O_3$<2.5, $Na_2O/Al_2O_3$=15-65, $H_2O/Al_2O_3$>500 to $H_2O/Al_2O_3$=1500. In $H_2O/Al_2O_3$<500 ratio, HS zeolite membranes have not been successfully synthesized, because gel composition have not enough water for synthesis a homogenous gel. Also, in $SiO_2/Al_2O_3$>2.5 ratio, causes HS zeolite to transform to other zealots. It must be mentioned that 10000 is the highest measurable value using the GC at 5 wt% UDMH concentration as shown in (Table 3).

## 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. To study the effect of crystallization time and temperature on the membrane performance, the membranes were synthesized at different temperatures (70, 100 and 130$^{\circ}$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.

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$^{\circ}$C was found to be very effective for making the HS zeolite layer. The results confirm that zeolite membranes synthesized at 130$^{\circ}$C for 12 h via a single stage process can be recommended for dehydration of dilute water/UDMH 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. Phase identification was performed by XRD (Philips PW1710, Philips Co., Netherlands) with CuKα radiation. Also, morphological

studies were performed using SEM (JEM-1200 or JEM-5600LV equipped with an Oxford ISIS-300 X-ray disperse spectroscopy, EDS). (Figures 4) and (Figure 5) show XRD patterns of the mullite support and the HS zeolite membrane.
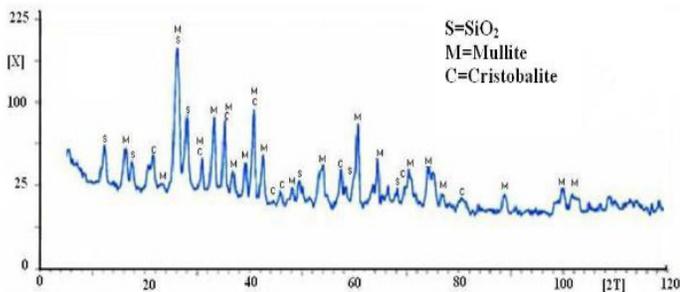


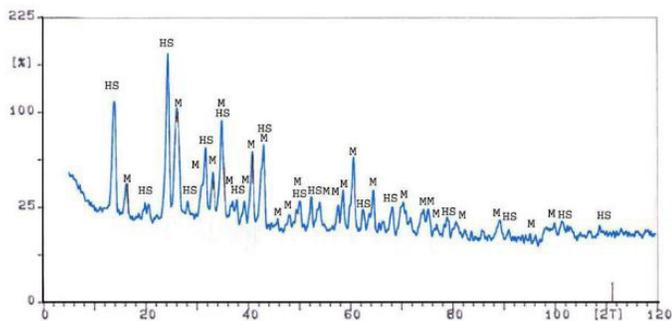**Figure 4:** XRD of the Support.



**Figure 5:** XRD of the HS Zeolite Membrane.

The XRD pattern of HS zeolite membrane confirms that zeolite HS crystals were formed. Morphology of the support subjected to crystallization was characterized by SEM. (Figure 6)
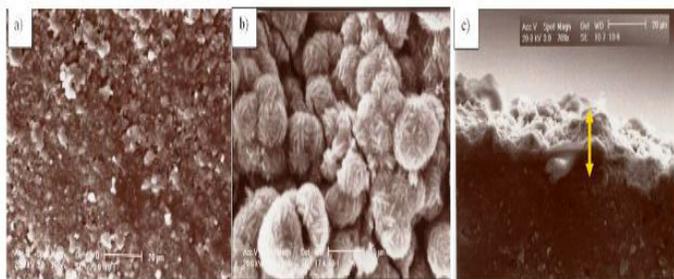


**Figure 6:** SEM Micrograph of a) The Support b) The Membrane c) Thickness of Membrane on Support.

Shows SEM photographs of the mullite support (a) and the HS zeolite membrane (b). Porous structure of the support and thin layer of the membrane can be easily observed. (Figure 6) shows morphology of the HS zeolite membranes (surface and cross section). As seen, most of the crystals lie disorderly on the surface.

The SEM photograph of the HS zeolite membranes (cross section) show that the mullite surface is completely covered by a zeolite crystal layer. The HS zeolite membrane thickness was found to be about 20-30 μm judging from the SEM observation.

## 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. A shown in (Table 4),

| Run | Concentration of UDMH in feed (wt %) | P (bar) | Q (lit/min) | T (°C) | Flux kg/m2.h |
|-----|------|------|------|------|------|
| 1 | 5 | 1 | 0.5 | 20 | 1.112 |
| 2 | 5 | 1 | 1.5 | 20 | 1.447 |
| 3 | 5 | 1 | 3 | 20 | 1.814 |
| 4 | 5 | 1 | 0.5 | 20 | 1.112 |
| 5 | 5 | 2 | 0.5 | 20 | 1.447 |
| 6 | 5 | 3 | 0.5 | 20 | 1.814 |
| 7 | 5 | 1 | 0.5 | 20 | 1.112 |
| 8 | 5 | 1 | 0.5 | 40 | 2.301 |
| 9 | 5 | 1 | 0.5 | 60 | 2.851 |

**Table 4:** Cross Flow Results by Membrane Sample 1.

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.

## Conclusion

Zeolite nanopore HS membranes were synthesized on the porous mullite tubes by hydrothermal method. It was found gel compositions that Nano HS zeolite membranes have been synthesized. 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. These membranes showed very good membrane performance for separation of UDMH /water mixtures. Effect of operating condition at pervaporation process show that increasing pressure, feed rate and temperature increases the flux linearly.

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