A study on the pervaporation of aqueous mixtures through MFI Nano pore zeolite membranes

Mansoor Kazemimoghadam

Malek Ashtar University of Technology, Faculty of Chemical and Chemical Engineering, Tehran , Iran

Abstract

Nano pore MFI type membranes were prepared on the outer surface of a porous-mullite tube by in situ liquid phase hydrothermal synthesis. Inner and outer diameters and length of the support were 6, 14 and 100 mm, respectively. The hydrothermal crystallization was carried out under an autogenously pressure, at a static condition and at a temperature of 180 ºC with tetra propyl ammonium bromide (TPABr) as a template agent. The molar composition of the starting gel of MFI zeolite membranes were ZSM-5:SiO_2/Al_2O_3=100, Na_2O/Al_2O_3=0.292, H_2O/Al_2O_3=40–65, TPABr/ SiO_2=0.02-0.05 and silicalite-1: Na_2O/SiO_2=0.287-0.450, H_2O/SiO_2=8–15, $TPABr/SiO_2$=0.01-0.04. The zeolites were calcined in air at 530 ºC, to burn off the template (TPABr) within the zeolites. X-ray diffraction (XRD) patterns of membranes consist of peaks corresponding to the support and zeolite. The crystal species were characterized by XRD, and morphology of the supports subjected to crystallization was characterized by scanning electron microscopy (SEM). Performance of MFI nanoporous membranes was studied for separation of water–unsymmetrical dimethylhydrazine (UDMH) mixtures using pervaporation (PV). The best ZSM-5 zeolite membranes had a water flux of 2.22 kg/m^2.h at 27^{0}C. The best PV selectivity for ZSM-5 membranes was obtained to be 55. The best silicalite membranes had a water flux of 3.34 kg/m^2.h at 27^{0}C. The best PV selectivity for silicalite membranes was obtained to be 53.   © 2017 ijrei.com. All rights reserved
Keywords: Nano pore zeolite; MFI zeolite membrane; Pervaporation; Water–UDMH separation

1. Introduction

Removal of organic compounds from aqueous solutions is important for the recovery of valuable organic products, for the recycling of process water and for the treatment of waste water. Generally, distillation can be used to remove organic compounds from water. However, for low organic concentrations or thermally sensitive organic compounds, distillation is neither economical nor suitable. Furthermore, according to Fleming and alter, 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 the required driving force and (3) lower capital cost. Thus, relatively mild operational conditions and high effectiveness make PV an appropriate technique for such separations. Most PV studies have been recently focused on dehydration of organic mixtures. 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 [1-3].

UDMH is an important solvent; however it also finds many new applications as an oxygen scavenger for boiler-feed water, a starting material for drug and dye intermediates, a catalyst for polymerization reactions, etc. UDMH is very corrosive and its vapor is extremely toxic and carcinogenic [4-6].

Membrane-based PV technology has all the requirements for completely replacing extractive distillation for separation of the azeotropes. This can be combined with simple distillation as a hybrid process for enrichment of UDMH to high purity levels. Chitosan, a derivative of the naturally abundant biopolymer chitin, is fully stable in anhydrous UDMH and hence can be selected for its dehydration, keeping in minds its

Corresponding author: Mansoor Kazemimoghadam
Email Id: mzkazemi@gmail.com

highly hydrophilic nature and good mechanical strength. The promising potential of chitosan as a PV membrane has already been exploited for dehydration of alcohols such as ethanol and isopropanol. This polymer has recently been used to form selective and permeable blend membranes with poly (vinyl alcohol), sodium alginate, etc. However, unfortunately polymeric membranes behaved unsuitable in terms of selectivity and flux in general for water-UDMH mixtures (selectivity and flux of about 10 and 0.01 kg/m^2.h, respectively) [7-10].

There has been an increasing interest towards zeolite membranes due to their strong potential in separation of liquid mixtures by PV. Zeolite membranes can be prepared with different methods: in situ hydrothermal synthesis; chemical vapor phase method, spray seed coating, etc. Whatever the method, an inorganic porous support is required and its nature and structure may affect the quality of the composite zeolite membrane. A popular support is made of sintered alumina. Nevertheless, this support is expensive and makes the membranes uneconomical. It is thus important to study the possibility of obtaining membranes with cheap supports. Considering its abundant resource, its low cost and its easy processing into a support with a regular structure by sintering; kaolin is a good candidate for the zeolite membrane. Dehydration of organic solvents is presently the major market of PV. Zeolite NaA membrane were reported to be excellent materials for solvent dehydration by PV. However, under slightly harsh conditions and under hydrothermal stresses, zeolite NaA membranes turned out to be unstable due to hydrolysis. There are only a few attempts to develop hydrophilic highly siliceous zeolite membranes of different Si/Al ratios with improved hydrothermal stabilities. In this paper, preparation methods of the Nano pore ZSM-5 and silicalite-1 zeolite membranes on mullite support are reported. Performances of the membranes prepared by hydrothermal in situ crystallization were studied in separation of the water–UDMH by PV.

2. Experimental

2.1. 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.

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

Free silica (4SiO2) 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 1. 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^{0}C [11].

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.

2.2. Zeolite membrane synthesis

The zeolite membranes were synthesized on the outer surface of the porous mullite tubes. The molar gel compositions were ZSM-5: 0.292Na$_2$O:1.0Al$_2$O$_3$:100SiO$_2$:2.0-5.0TPABr: 40-65H$_2$O; silicalite-1: 0.287-0.450 Na$_2$O:1.0 SiO$_2$:0.01-0.04 TPABr: 8-15 H$_2$O, where TPABr was used as template [12-17]. Sodium silicate and sodium aluminate were used as the Si and Al sources, respectively. For ZSM-5 preparation, three solutions were used, solution A: sodium silicate; solution B: TPABr + H$_2$O (half of the total water); solution C: NaOH + Na$_2$Al$_2$O$_4$ + H$_2$O (other half of the water). Solution A was added to solution B and then solution C was added while stirring. For silicalite-1 preparation, two solutions were prepared; solution A: sodium silicate; solution B: TPABr + H$_2$O + NaOH. Solution A was added to solution B with stirring. To obtain a homogeneous gel, the mixtures were stirred for 2 h at room temperature.

For membrane preparation, two ends of the supports were closed with rubber caps to avoid any precipitation of the zeolite crystals on inner surface of the supports during membrane synthesis. The seeded supports were placed vertically in a Teflon autoclave. The solution was carefully poured in to the autoclave and then the autoclave was sealed. Crystallization was carried out in an oven at a temperature180 °C for 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 and then dried in the oven at 100 ºC for 15 h to remove water occluded in the zeolite crystals and then calcined in air at 530 ºC for 8 h at a heating rate of 1 ºC /min [18-25].

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).

3. Pervaporation Tests

While PV system was at steady state (after 20 min), weight of permeate was measured at 30 min period and then flux was calculated (surface area of the zeolite membrane was 44 cm^2). The zeolite membranes have been used for long-term dehydration of UDMH. 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.

The pervaporation setup is presented in Figure 5. 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 were measured using GC (TCD detector, Varian 3400, carrier gas: hydrogen, column: polyethylene glycol, sample size: 5 μm, column and detector temperatures: 120-150 °C, detector flow: 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/m^2.h) and separation factor (dimensionless). Separation factor of any organic aqueous solution can be calculated from the following equation:

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

Where X_{H2O} and $X_{organic}$ are weight fractions of water and organic compound, respectively [26-29].

4. Results and discussion

It is well known that PV performance of a dense polymeric membrane depends on ability of solvent species to be dissolved in the membrane at its interfaces, and their diffusion into the membrane. When a zeolite membrane is used as separation barrier, the solvent species can not be dissolved in the membrane phase but they are adsorbed on zeolite sites of the inorganic materials. Their adsorbed capacities depend on the affinity of membranes toward the solvents to be removed.

4.1. ZSM-5 performance

The membrane exhibited a high selectivity towards water in water/UDMH mixtures. The permeate water flux reaches a value as high as 0.67 kg/m^2.h for a UDMH concentration of 5 wt. %. The fact that the membrane has a high selectivity to water clearly indicates that the zeolite layer does not have any through-holes, and the transport is diffusive but not convective. The results also confirm that the ZSM-5 membrane behaves as a hydrophilic membrane, probably due to the presence of polar Al atoms in the zeolite crystal structure.

The ZSM-5 membrane showed a water/UDMH ideal selectivity of 55 at 27 ºC, indicating its reasonable quality. Even higher selectivities may be expected for higher quality membranes. The kinetic diameter of water is 0.26 nm. During PV, water permeates through both zeolite and non-zeolite pores because of its small diameter. The kinetic diameter of UDMH is larger than diameter that of the zeolite pores, thus, much of the UDMH flux is probably through the non-zeolite pores.

4.2. Silicalite-1 performance

The membrane exhibited a high selectivity towards water in water–UDMH mixtures. The permeate water flux reaches a value as high as 3.34 kg/m^2.h for a UDMH concentration of 5 wt. %. The fact that the membrane has a high selectivity to water clearly indicates that the zeolite layer does not have any through-holes, and the transport is diffusive but not convective. The silicalite-1 membrane showed a water-UDMH ideal selectivity of 10000 at 27 ºC, indicating its reasonable quality. During PV, water permeates through both zeolite and non-zeolite pores because of its small diameter. The kinetic diameter of UDMH is larger than the diameter of zeolite pores, thus, much of the UDMH flux passes probably through the non-zeolite pores. As the silicalite-1 is a week hydrophilic membrane, this causes water flux to decrease. The diffusing molecules in these mixtures pass via viscous flow and molecular sieve; whereas viscous flow requires a pressure gradient across the membrane. If the zeolite is defect-free, it means that in has no non-zeolite pore and thus, water can pass only through zeolite pores (Table 2). However, the non-zeolite pores usually exist and are larger than the zeolite pores. Non-zeolite pores have a size distribution and may also affect flux and selectivity. Transport through the non-zeolite pores has contributions from both surface diffusion and Knudsen diffusion, and possibly from viscous flow.

The MFI channel system is shown in Figure 6. The straight elliptical channels running in the b-direction have the dimensions of 0.53x0.56 nm and the sinusoidal channels running in the a-direction have the dimensions of 0.55x0.51 nm.

Figures 3 show XRD patterns of the mullite support and the zeolite membranes. Morphology of the support subjected to

crystallization was characterized by SEM (Figure 8). Figure 9 and 10 show morphology of the ZSM-5 and silicalite-1 membranes (surface and cross section). As seen, most of the crystals lie disorderly on the surface. The SEM photographs of the membranes (cross section) show that the mullite surface is completely covered by a zeolite crystal layer, whose thickness is larger than 40 µm. The crystal layer is composed of two layers; the top layer consists of pure MFI crystals and the intermediate one, of MFI crystals grown in to the mullite pores. As seen in Table 3, the best selectivity for ZSM-5 was 55 and the best water flux was 2.22 kg/m^2.h at 27 $^{\circ}$C. The best ZSM-5 membranes were prepared using the following gel molar composition: $0.292Na_2O$: $1.0Al_2O_3$: $100SiO_2$: $2.0TPABr$ $40H_2O$. As seen in Table 2, the best selectivity for silicalite-1 was 53 and the best water flux was 3.34 kg/m^2.h at 27 $^{\circ}$C. The best silicalite-1 membranes were prepared using the following gel molar composition: $0.287 Na_2O$:$1.0 SiO_2$:$0.04 TPABr$: $15 H_2O$.

5. Conclusion

MFI zeolite membranes were firstly used for dehydration of water-UDMH mixtures. The membranes were synthesized on the outer surface of porous mullite tubes by hydrothermal method. The mullite supports were made by extruding kaolin clay. The zeolite membranes showed much higher fluxes and separation factors than commercially available polymeric membranes. The membranes showed good membrane performance for separation of the UDMH-water mixtures. It is expected that even significantly higher fluxes, with similar separation factors, can be achieved at higher temperatures. Since the MFI zeolite membranes can withstand high temperatures and harsh environments (pH>12), dehydration of the water-UDMH mixtures can be performed. It was found that PV using the MFI zeolite membranes is an effective technique to separate water from the water-UDMH mixtures.

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Table 1: Analysis of kaolin clay

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: Flux and separation factor of the silicalite zeolite membranes

Sample	Na_2O/ SiO_2	$TPABr/ SiO_2$	H_2O/ SiO_2	$T (^0C)$	T (h)	UDMH (%)	Flux ($kg/m^2.h$)	Separation factor
1	0.450	0.01	8	180	24	5	1.02	4
2	0.287	0.01	8	180	24	5	1.67	8
3	0.350	0.01	8	180	24	5	1.7	23
4	0.350	0.01	15	180	24	5	3.34	53

Table 3: Flux and separation factor of the ZSM-5 zeolite membranes

Sample	Na_2O/ Al_2O_3	$TPABr/ SiO_2$	Al_2O_3/ SiO_2	H_2O/ Al_2O_3	T (°C)	t(h)	UDMH (%)	Flux $kg/m^2.h$	Separation factor
1	0.292	0.02	0.01	40	180	24	5	0.67	55
2	0.292	0.05	0.01	65	180	24	5	2.22	20
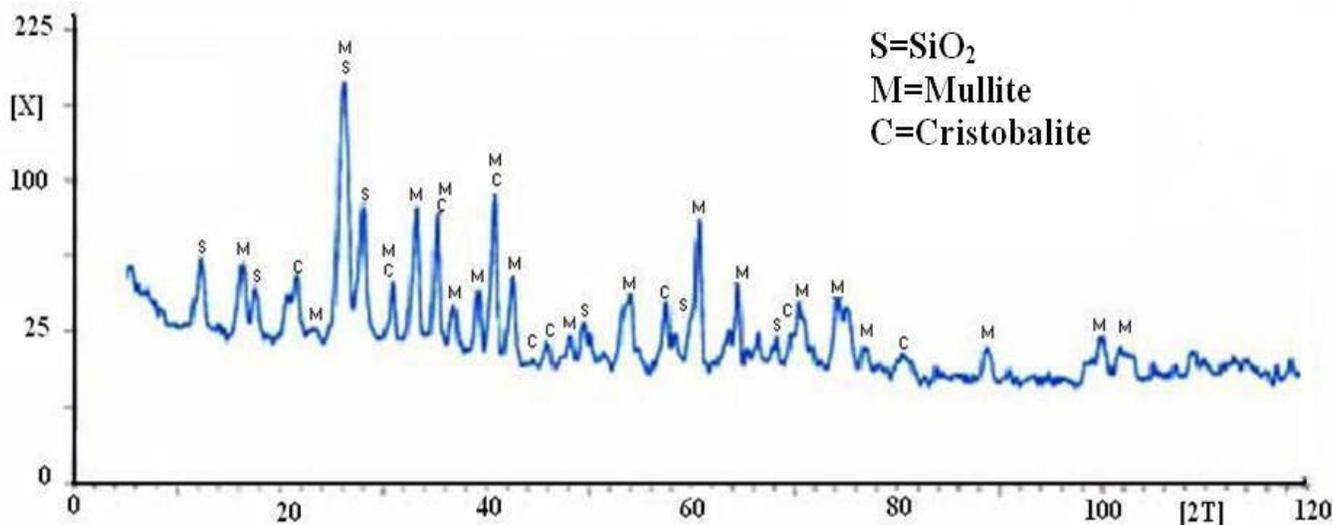
Figure 1: XRD patterns of the support
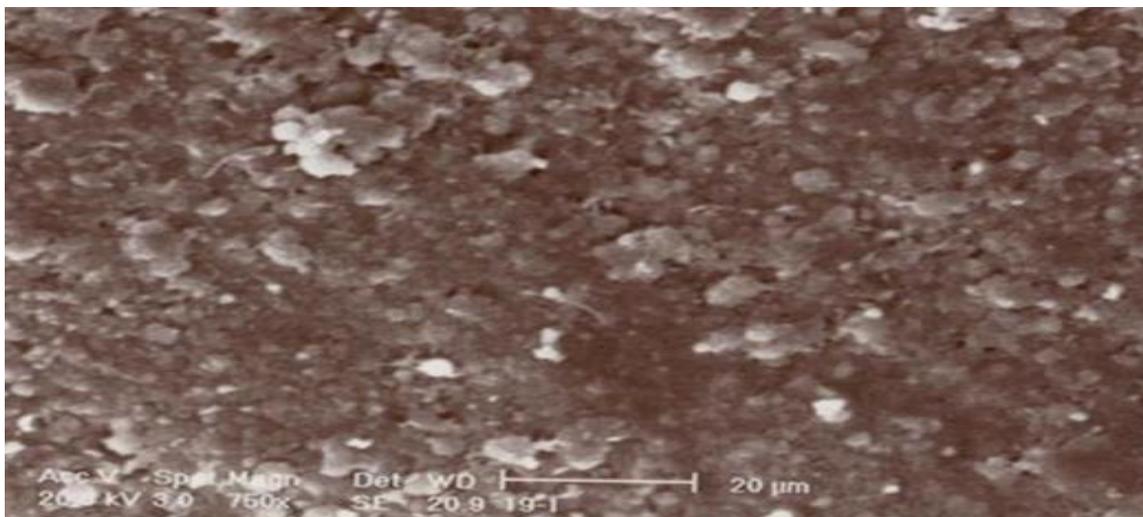
Figure 2: SEM micrograph of a) the support
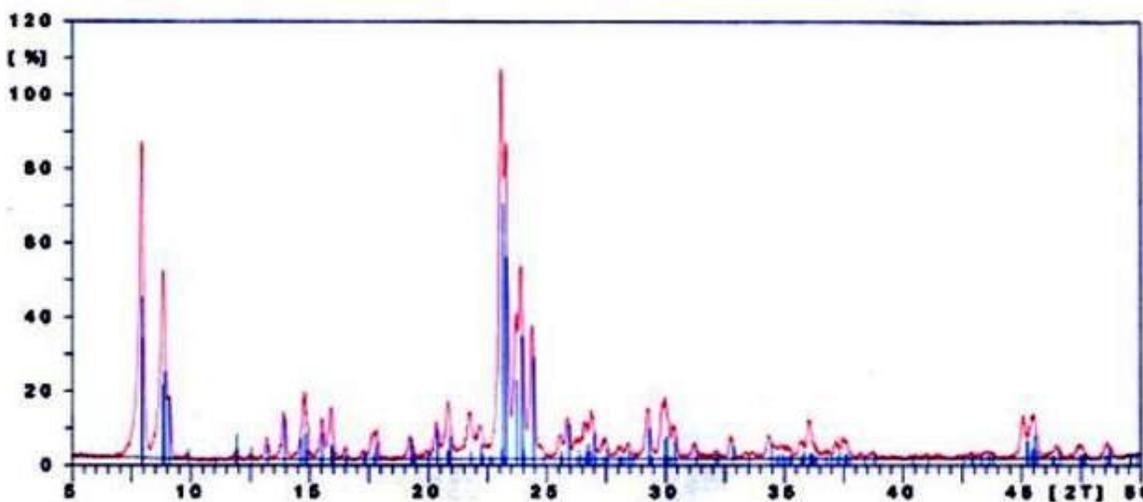
Figure 3: XRD patterns of the ZSM-5 zeolite membrane
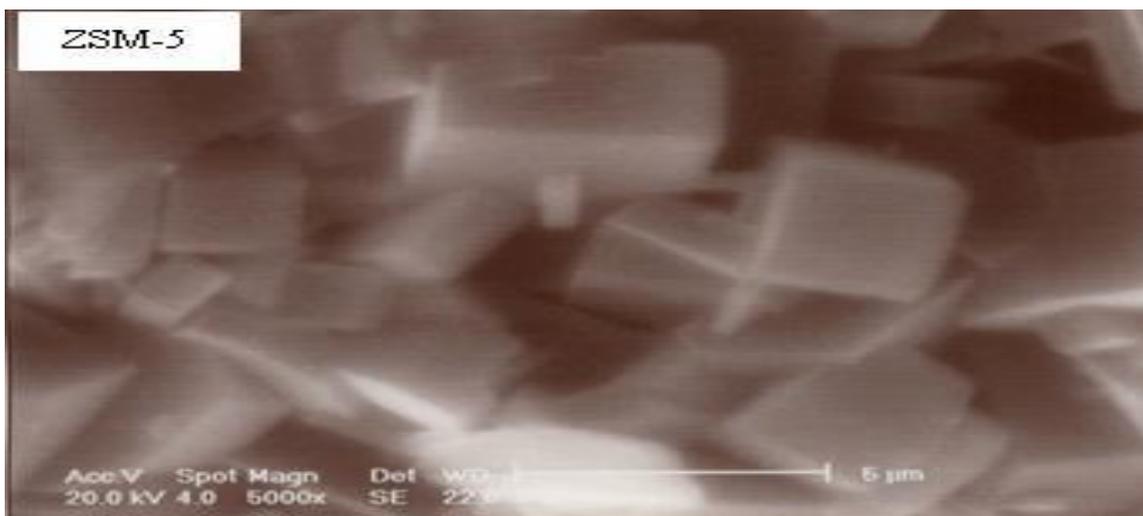
Figure 4: SEM micrograph of the ZSM-5 zeolite membrane
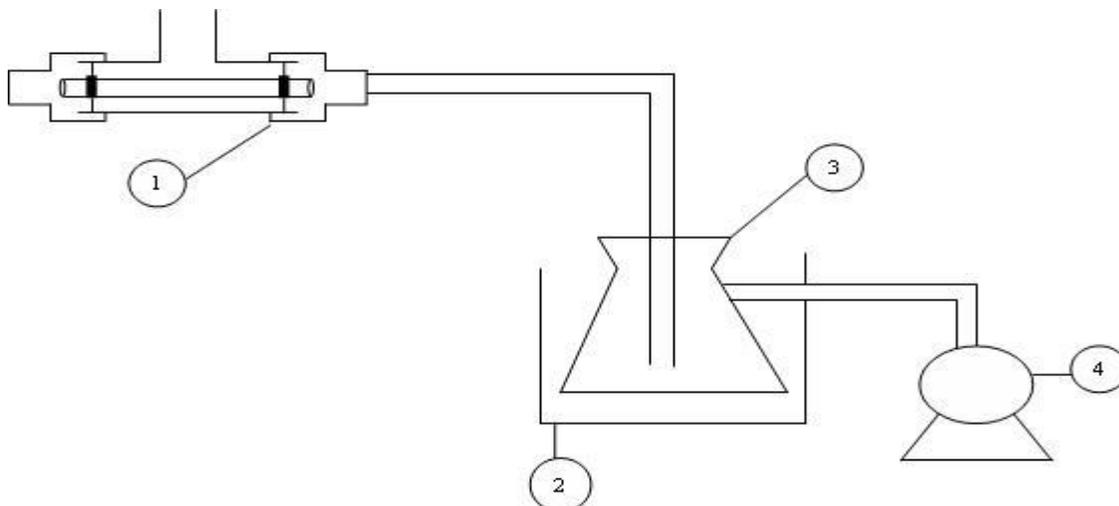
Figure 5: PV setup; 1- feed container and PV cell 2- liquid nitrogen trap 3- permeate container 4- three stage vacuum pump
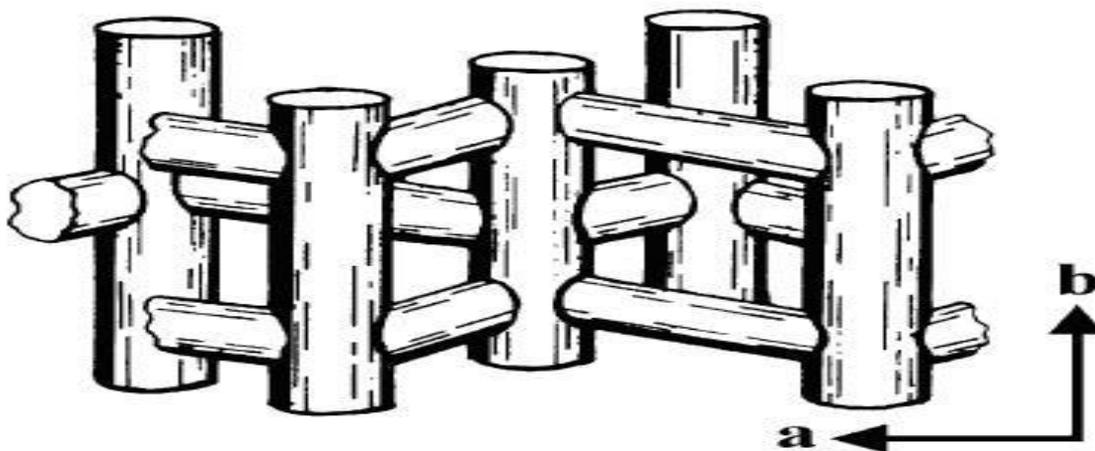
Figure 6: MFI channel system
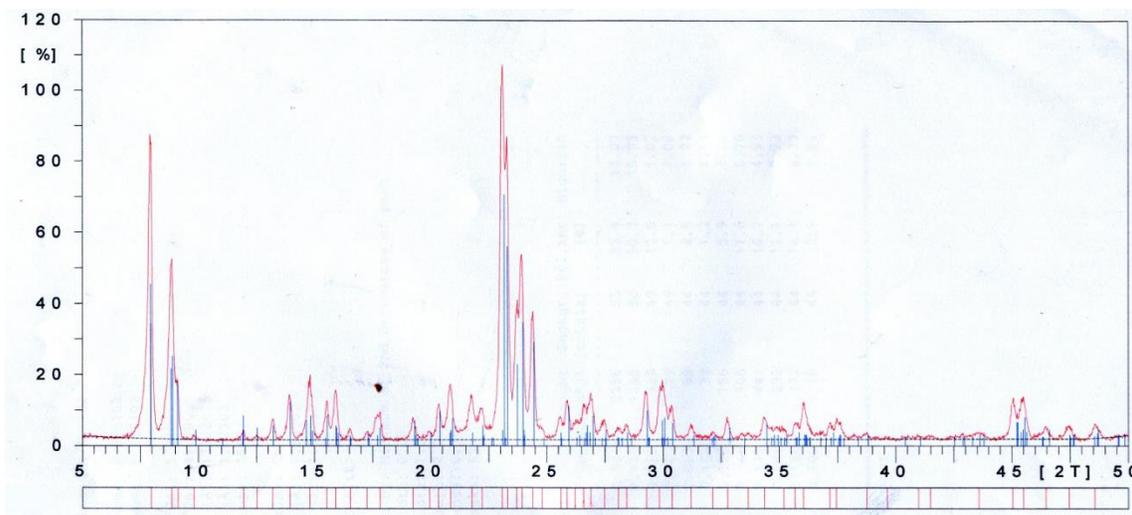
(a)
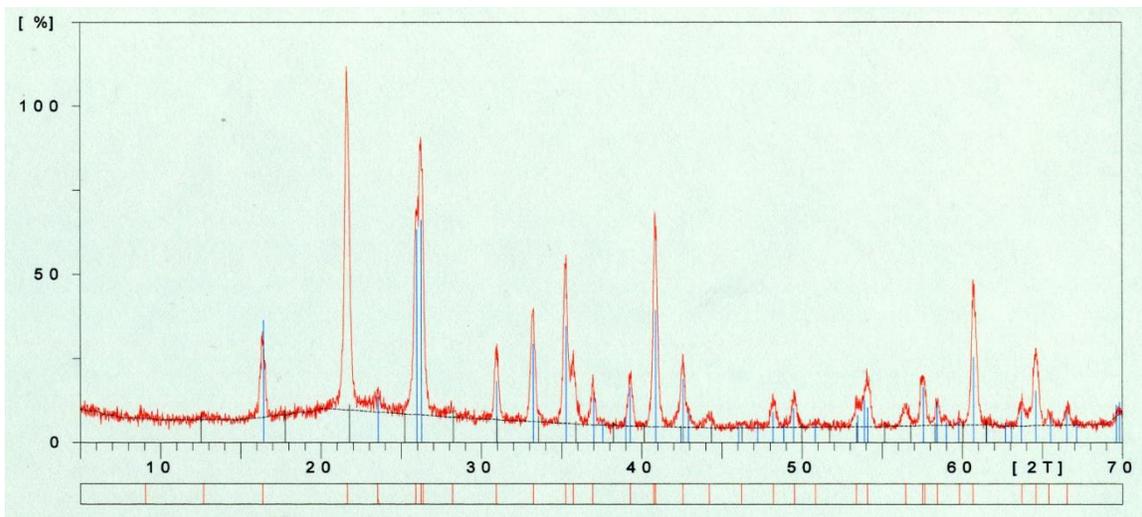
(b)

Figure 7: XRD pattern of the membrane support (a) ZSM, (b) silicalite
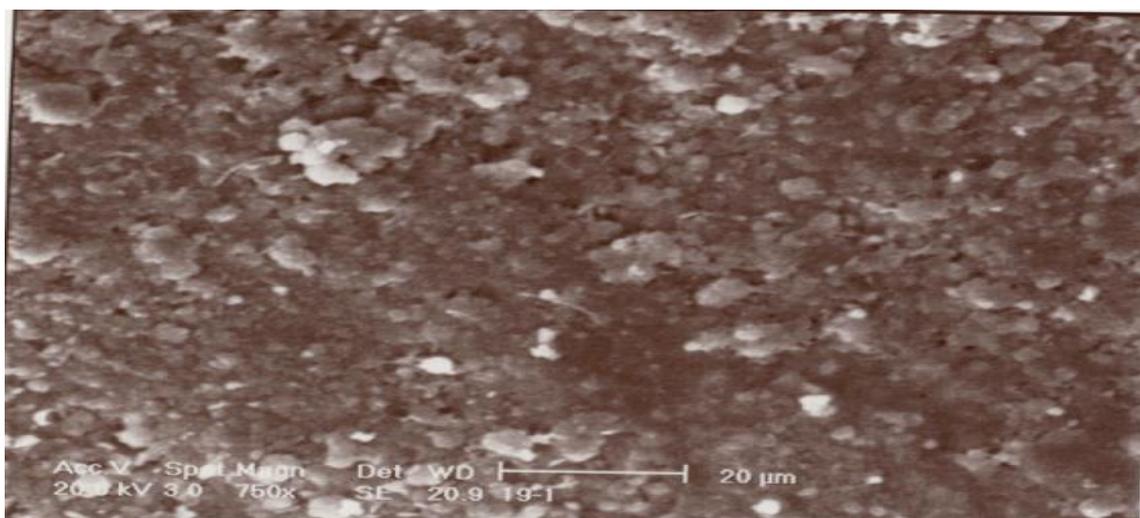
Figure 8: SEM of the mullite support
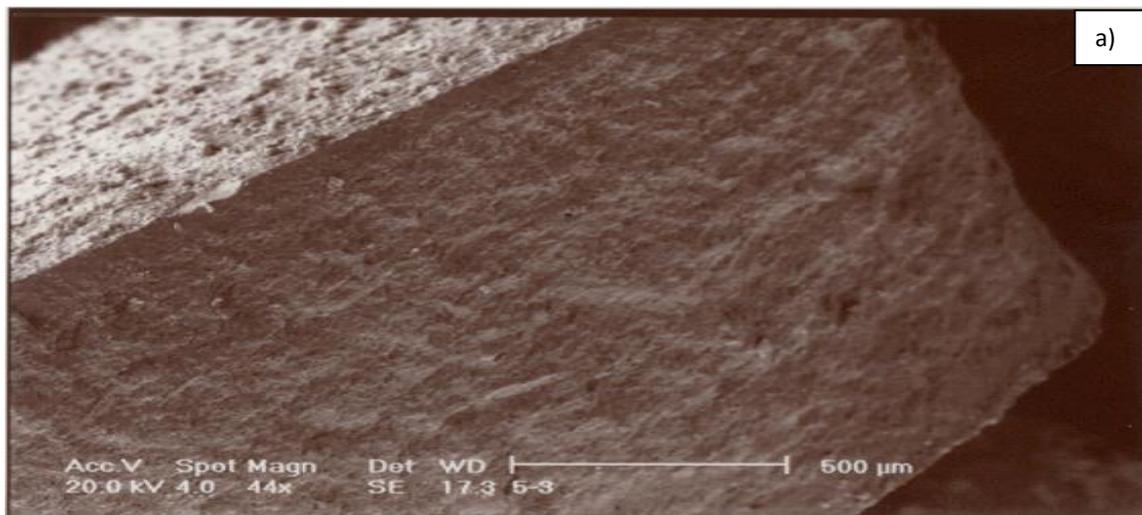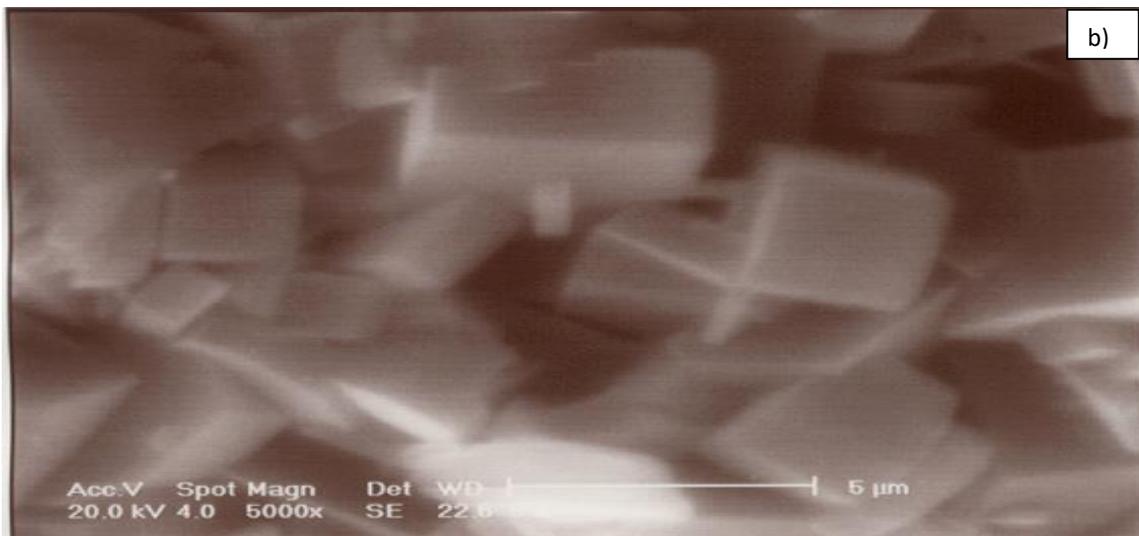
Figure 9: SEM of the ZSM-5 zeolite membrane (a) surface and (b) cross section
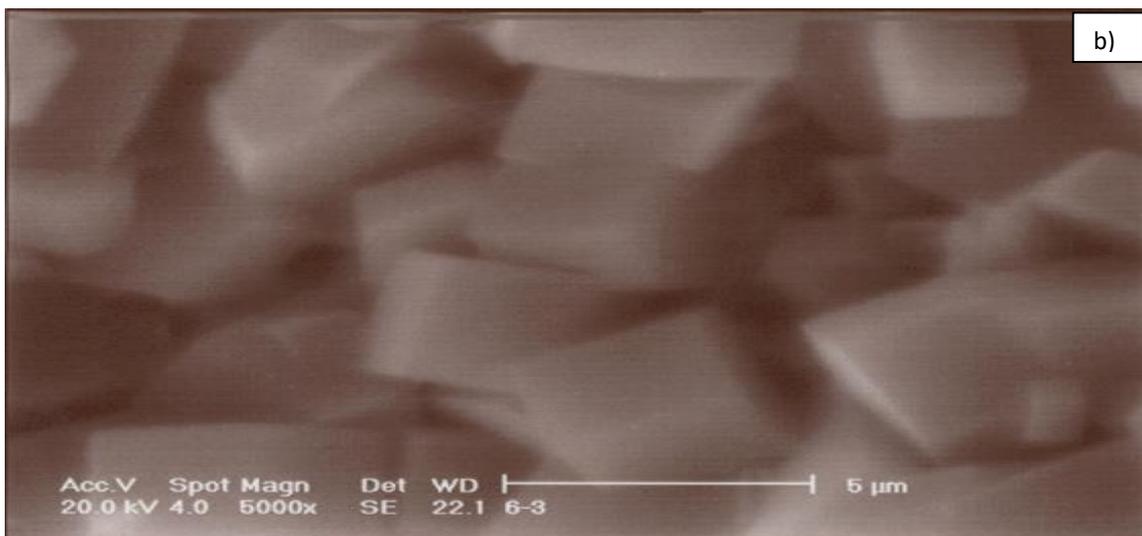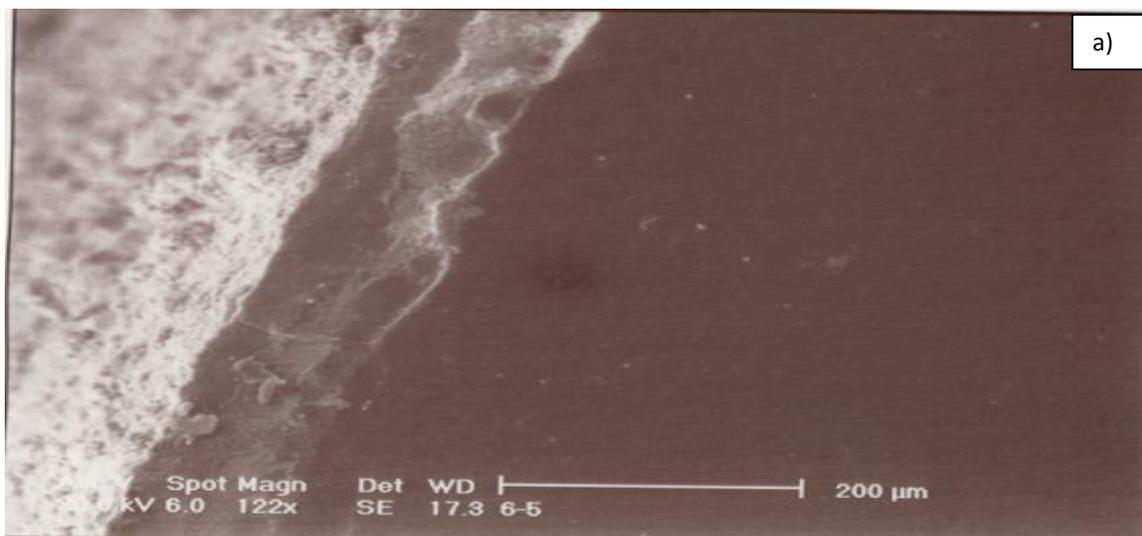
Figure 10: SEM of the silicalite zeolite membrane (a) surface and (b) cross section