



Using of cheap materials for making of zeolite membranes with an innovative method

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Abstract

In this research, two new innovations have been made. The first innovation involves the synthesis of zeolite membranes from the source of kaolin. In the first step, the kaolin was calcined at 700 °C to the metakaolinite phase. As a second step, the zeolitisation experiments have been carried out under hydrothermal conditions. The metakaolinite obtained has been reacted with NaOH solutions in autoclaves at 100°C. The second innovation to membrane synthesis was based on Self-supported zeolite membranes. Synthesis of nano NaA zeolite membrane from tubular extruded of kaolin was investigated. In the first step, kaolin has been calcined at 500-850 °C to the metakaolinite phase. As a second step, the zeolitisation experiments have been carried out under hydrothermal conditions. The metakaolinite obtained has been reacted with NaOH solutions in autoclaves at 100°C. X-ray diffraction (XRD) patterns of the membranes exhibited peak corresponding to the zeolite. The morphology of the support and membrane subjected to crystallization was characterized by Scanning electron microscopy (SEM). Separation performance of the NaA membranes was evaluated using pervaporation (PV) of water–organic mixtures. The membranes showed high water selectivity in the water–organic mixtures.

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Keywords: kaolin, Zeolite, pervaporation, Self-supported membrane, preparation

1. Introduction

Zeolites are a family of hydrated alumina silicate minerals that contain alkali and alkaline earth metals. Zeolite molecular sieves are crystalline porous alumina silicate minerals whose unique pore and channel systems in the molecular size range are the basis of their important contribution in catalysis, separation and ion exchange. Zeolites are porous three dimensional alumina silicates formed by the sharing of oxygen atoms in the framework aluminum and silicon tetrahedral. In recent years, attempts to develop zeolite membranes for separation and catalytic applications have been intensified considering their molecular sieving properties, uniform nano pore size, high thermal resistance, chemical inertness, and high mechanical strength. The investigation of nano zeolite membranes with nano pore size has attracted much attention. Zeolites are conventionally synthesized from sodium alumina silicate gel prepared from pure chemicals in air ovens or auto claves [1].

Using of the natural raw materials for the production of zeolites has economical advantageous comparing the synthetic chemicals. The kaolin mineral with a Si/Al ratio 1 has

conveniently been used as a raw material for the synthesis of low silica zeolites. Since the uses of zeolites in several branches of industry have been increasing, the production of zeolites by economical ways has gained great importance in material science [2-4].

Zeolite NaA membrane were reported to be excellent materials for solvent dehydration by Pervaporation (PV). In the preparation of zeolite macro bodies like beads or monoliths, clays are mostly used as binder. However, the inorganic binder decreases the purity of the zeolite bead and the accessibility to the zeolite pores by partially covering the surface of zeolite crystals. This problem can be overcome by preparing binder less zeolite macrobodies. Hydrothermal conversion of kaolinite type clays into zeolite beads, conversion of the amorphous alumina silicate gel particles formed in a shaping oil into zeolite spheres are the techniques used for the preparation of the binder less zeolite bodies. However, these techniques are rather difficult and the prepared bodies are usually smaller than a few centimeters [5].

In this paper, preparation method of the Nano pore NaA zeolite

membranes using by kaolin on mullite support is reported. In addition, kaolin was used to synthesize zeolite A by the two-step method. In this study, synthesis of asymmetric and self-supported zeolite A tubular membranes were aimed. This kind of a membrane consist of a thin and compact zeolite A layer on a thick and macroporous zeolite A support. Thus, the synthesis of the binderless zeolite A macrobodies as support is the first step to synthesize the thin zeolite A layer over it. Performances of the membranes prepared by hydrothermal in situ crystallization were studied in dehydration of solvents mixtures by PV.

2. Zeolite structure and transport mechanisms

The hydrophilic membranes used in this research were composite zeolite NaA membranes. The membranes were made of an active NaA layer, deposited on a ceramic porous mullite support. The active NaA layer is responsible for high separation factors achieved in PV of Ethanol mixtures. The structure of zeolite NaA is shown in Figure 1. As shown in Figure 1, the aluminosilicate framework of zeolite NaA 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 by a D4R linkage. Each b-cage encloses a cavity with a free diameter of 0.66 nm and each unit cell encloses a larger cavity (a-cage) enclosing a free diameter of 1.14 nm. There are two interconnecting, three-dimensional channels in zeolite NaA: (i) connected a-cages, 1.14 nm in diameter, separated by 0.42 nm apertures, (ii) b-cages, alternating with a-cages separated by 0.22 nm apertures. Thus, molecules smaller than 0.42 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 [6]. For a typical zeolite, a unit cell having the composition $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$, 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) [7].

3. Zeolite NaA synthesis from kaolin

The low silica zeolite NaA can be conveniently prepared by the hydrothermal reaction of the activated kaolinite with aqueous sodium hydroxide. The synthesis of low silica zeolites from the kaolinite essentially consists of two steps:

- (i) Thermal activation of the kaolinite in order to get metakaolinite.

- (ii) Hydrothermal reaction of metakaolinite with various aqueous alkalis medium.

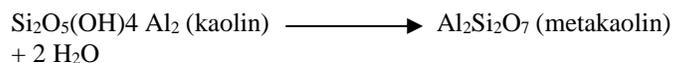
The activation process results in structural changes of the starting materials to promote their reactivity in the reactant solution for the direct transformation into zeolite from the constituent components.

3.1 Characterization of kaolin and metakaolin

Kaolin [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] is a dioctahedral 1:1 layer alumina silicate with two kinds of interlayer surfaces. One surface is made of a gibbsite-type structure where each aluminum atom occupies the center of an octahedron with oxygen atoms and hydroxyl groups in the vertices. The other surface is made of a silica-type structure, where each silicon atom occupies the center of a tetrahedron with oxygen atoms in the vertices. Therefore, one side of the layer (gibbsite side) has hydroxyl groups whereas the other side of the layer (silica side) has oxygen atoms [8-10].

Kaolinite, $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$, is classified as a 1:1 dioctahedral phyllosilicate and is the main component of the kaolin group of minerals. The framework structure of kaolinite, shown in Figure 2, is composed of a sheet of vertex sharing SiO_4 tetrahedral forming six-membered silicate rings that are linked by common oxygen atoms parallel to the c-axis to a sheet of edge-sharing AlO_6 octahedral forming four-membered aluminate rings. The silicate and aluminate layers are bound together by strong ion covalent bonds via apical oxygen's, and these layers are connected by much weaker hydrogen bonds. This is an idealized structure, as disorder is common in kaolin minerals. Since a pure kaolinite sample contains no interlayer water, no dehydration step will be present in the calcination process, and the thermally induced structural transformations of kaolinite will be completely governed by the dehydroxylation process.

Metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), a calcined product of kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) with Si/Al ratio 1 is a convenient starting material for the synthesis of zeolite A. The chemical analysis of the kaolin is listed in Table 1. The heat treatment of kaolin powders at 450-900 °C transforms them into metakaolin powders. Dehydration by thermal treatment converts kaolin to metakaolin, which is semi crystalline and much more reactive than the starting material:



The thermodynamically stable mullite phase forms in an exothermic reaction over 1100 °C with crystallization of cristobalite from the amorphous silica phase proceeding beyond that.

4. Experimental

4.1 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 and metakaolin supports have been prepared from kaolin clay. Kaolin is thermally converted to mullite (or metakaolin) via high temperature calcinations. The reaction takes place when kaolin is utilized as the sole source of silica and alumina. The reactions can be represented by the following equation:



Free silica (4SiO_2) is generated because of this conversion. The free silica has been leached out and then porous mullite bodies have been prepared.

Kaolin (SL-KAD grade) has been supplied by WBB cooperation, England. Analysis of the kaolin is listed in Table 1 [11].

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 (or metakaolin extrudes). Good results have been achieved by calcining for about 3 h at temperatures of about 1250°C for mullite supports and $500\text{-}850^\circ\text{C}$ for metakaolin supports [12-16].

As shown in Figure 3, the steps involved for the preparation of porous metakaolin extrudes are as follows: (i) preparation of kaolin-starch extrudes; (ii) drying of the kaolin extrudes at 100°C for 12 h; (iii) calcination of the kaolin extrudes for removal of the organic material (starch) and conversion to metakaolin at $500\text{-}700\text{-}850^\circ\text{C}$. The kaolin extrudes were prepared by mulling kaolin, tri poly phosphate, and appropriate amount of water. The mulled mixture was extruded to form kaolin extrudes. The kaolin extrudes were dried at 100°C for 12 h in an air oven. After drying, the kaolin extrudes were calcined at $500\text{-}700\text{-}850^\circ\text{C}$ (heating rate $1^\circ\text{C}/\text{min}$) for 3 h.

Phase identification has been performed by X-ray diffractometry (Philips PW1710, Philips Co., Netherlands) with $\text{CuK}\alpha$ radiation.

4.2 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 tubes as describe above have been used as supports. External surface of the supports have been polished with 600 grit-sand papers and then they have been washed and cleaned in boiling distilled water for 5 min to remove loose particles created during polishing. Then, the supports have been dried at 100°C for 3h in air. In order to coat a thin and uniform zeolite membrane layer over the mullite support, nucleation seeds should be small and uniform in size. To inhibit formation of the zeolites into the support pores, the seeds should not be too small to penetrate into the pores. High purity nucleation seeds ($2\ \mu\text{m}$ in size) have been synthesized by hydrothermal method. The seeds should be dispersed homogeneously over the support surface and the amount of seeds should not be too much. Otherwise, the synthesized zeolite membrane layer becomes heterogeneous or too thick. The seeded supports have been prepared by soaking the mullite supports in an 8% NaA zeolite suspension once for 1 min. The 8% NaA zeolite suspension has been prepared by mixing 8 g NaA zeolite in 92 ml distilled water. After soaking, the supports have been dried at 100°C for 3 h in air.

5. Zeolite membrane synthesis

5.1 NaA synthesis from kaolin source

NaA membrane was grown hydrothermally on the surface of a porous tubular mullite support (14 mm outer diameter, 12 cm length) using by kaolin powder as a source for aluminates and silicate. The hydrothermal synthesis of NaA zeolite membrane was performed as follows.

Synthesis solution was prepared by mixing metakaolin and NaOH solutions. NaOH was dissolved in distilled water. The solution gel was prepared by adding metakaolin powder to NaOH solution. The resulting mixture was stirred vigorously, producing a homogeneous gel. The molar composition of the resulting gel was $\text{SiO}_2/\text{Al}_2\text{O}_3=1.926$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=3.165$ and $\text{H}_2\text{O}/\text{Al}_2\text{O}_3=128$.

Two ends of the supports were closed with rubber caps to avoid any precipitation of the zeolite crystals on internal surface of the supports during membrane synthesis. The seeded support was placed vertically in a Teflon autoclave. The solution was carefully poured in the autoclave and then the autoclave was sealed [17]. After hydrothermal treatment at 100°C for 3 h, the sample was taken and the synthesized membrane was washed several times with distilled water. The sample was then dried at room temperature for 12 h in air.

5.2 Self-supported NaA zeolite membrane

The first phase of the study was to synthesize the zeolite supports and second phase was to prepare zeolite membranes from support materials. The NaA extrudes were prepared by crystallizing porous metakaolin extrudes in the presence of

alkaline medium containing sodium hydroxide. Prior to the hydrothermal synthesis, thermal activation of the very chemically inert kaolin is important. In the first step shown in figure 4, crystalline kaolin is converted to amorphous, but chemically reactive metakaolin by dehydroxylation process at high temperature under air. In the next two steps, hydrothermal synthesis of zeolite A from both raw and purified kaolin have been conducted. Step 2 in figure 4 consists of the gel formation parameters including NaOH concentration, temperature. In addition, time of aging. Finally, step 3 involves the hydrothermal synthesis. The final solids are washed and dried overnight before characterization.

Metakaolin extrudes were converted into NaA using a mixture containing NaOH and double-distilled water at 100 C for 5.5 h. The samples obtained at different intervals were thoroughly washed with distilled water and dried at 100 C for 12 h in an air oven. Zeolite membrane was synthesized from metakaolin support. Synthesis solution was prepared using by mixing metakaolin support surface and NaOH solutions.

NaA membrane was grown hydrothermally on the surface of a porous tubular metakaolin support using by metakaolin surface as a source for aluminates and silicate. The seeded support was placed vertically in a Teflon autoclave. The solution was carefully poured in the autoclave and then the autoclave was sealed [17-19]. After hydrothermal treatment at 100°C for 5.5 h, the sample was taken and the synthesized membrane was washed several times with distilled water. The sample was then dried at room temperature for 12 h in air. The molar composition of the resulting gel was $\text{SiO}_2/\text{Al}_2\text{O}_3=1.926$, $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=3.165$ and $\text{H}_2\text{O}/\text{Al}_2\text{O}_3=128$.

6. Pervaporation tests

We used a PV experimental set up to be sure of successfully fabrication Nano pore NaA zeolite membranes from kaolin source. PV tests were carried out using a standard PV apparatus. The experiments have been carried out at a temperature of 30 °C and a pressure of 1.5 mbar 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 mbar 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 ($\text{kg}/\text{m}^2\text{h}$) 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.

7. Results and discussions

The NaA zeolite membranes were synthesized by kaolin source. The mullite and methakaolin support was prepared from kaolin for zeolite membranes. The supports were prepared by extrusion of kaolin paste through an extruder into tubes. The seeded supports have been prepared by soaking the supports in a NaA zeolite suspension.

NaA membrane was grown hydrothermally on the surface of mullite supports using by kaolin powder as a source for aluminates and silicate. The synthesis of NaA zeolite from the kaolin source consists of two steps. At first, Thermal activation of the kaolinite in order to get metakaolinite. Then, hydrothermal reaction of metakaolinite with aqueous NaOH medium.

Self-supported NaA zeolite membrane was grown hydrothermally on the surface of metakaolin support using by metakaolin support as a source for aluminates and silicate. The synthesis of NaA zeolite from the metakaolin source consists of two steps. At first, Thermal activation of the kaolinite in order to get metakaolinite. Finally synthesized at 100 C for 5.5 hours in hydrothermal reaction of metakaolinite with aqueous NaOH medium.

Figures 6 and 7 shows XRD pattern of formation NaA zeolite membranes from kaolin clay. The XRD pattern of NaA zeolite membrane confirms that zeolite NaA crystals were formed from kaolin clay.

Morphology of the support and the membrane made by kaolin was examined by Scanning Electron Microscopy. Figures 8, 9, 10 and 11 show SEM photographs of the mullite (and metakaolin) supports and the NaA zeolite membrane preparation by kaolin source. Porous structure of the support and thin layer of the membranes can be easily observed.

As shown in table 2; the Pervaporation performance of NaA zeolite membrane formation of kaolin clay confirms that the kaolin is a cheap source for making NaA zeolite membranes. The prepared NaA zeolite membrane at 500 C, had not sufficient strength. Therefore, it is not good performance in pervaporation test.

The NaA membrane prepared by kaolin is highly selective for permeating water preferentially with the high permeation flux because of the micropore filling of water in the zeolite pores and/or the intercrystalline pores between zeolite crystals to afford water-selective permeation through the membrane. The performance of NaA zeolite membrane is the most favorable one among PV membranes that have been published so far and is very high enough to put these membranes into industrial applications.

8. Conclusion

Zeolites are usually synthesized from aqueous basic aluminosilicate precursor gels under hydrothermal conditions at elevated temperatures. They are preferably prepared from pure solutions of sodium silicate and sodium aluminates.

However, their production from cheap raw natural materials is of economic importance and hence it is necessary to production of zeolites by economical ways. Zeolite NaA membrane was successfully produced from kaolin. We have demonstrated that a NaA zeolite membrane can be synthesized from kaolin on a porous mullite (or metakaolin) support by hydrothermal method. NaA zeolite membrane was used for dehydration of aqueous solvent mixtures. The membranes were prepared by kaolin showed very good performance for separation of solvent /water mixtures.

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Table 1: Analysis of kaolin clay

Component	Percent (%)	Phases	Percent (%)
SiO ₂	60.1	Kaolinite	89
TiO ₂	0.1		
Al ₂ O ₃	29.2	others	11
Fe ₂ O ₃	0.6		
K ₂ O	0.5		
Na ₂ O	0	Total	100
L.O.I	9.5		
Total	100		

Table 2: Flux and separation factor of the membranes

Example	Feed	Type of zeolite	Calcination Temperature C	Concentration of water (%)	Flux kg/m ² .h	Separation factor
1	Solvent+ water	self-supported membrane	500	10	-	-
2			700	10	3.56	> 10000
3			850	10	2.67	> 10000
4		Kaolin source	1	10	0.375	> 10000

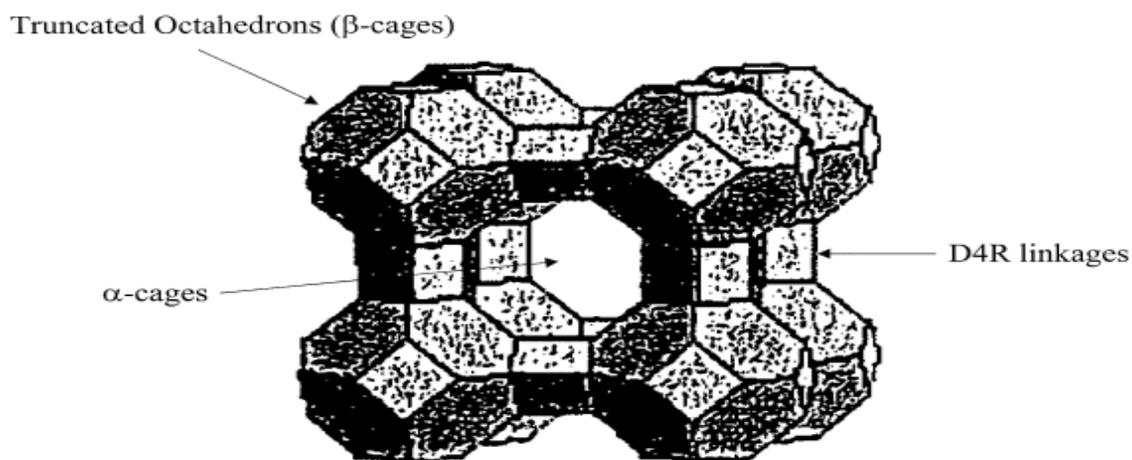


Figure 1: Repeating unit of zeolite NaA

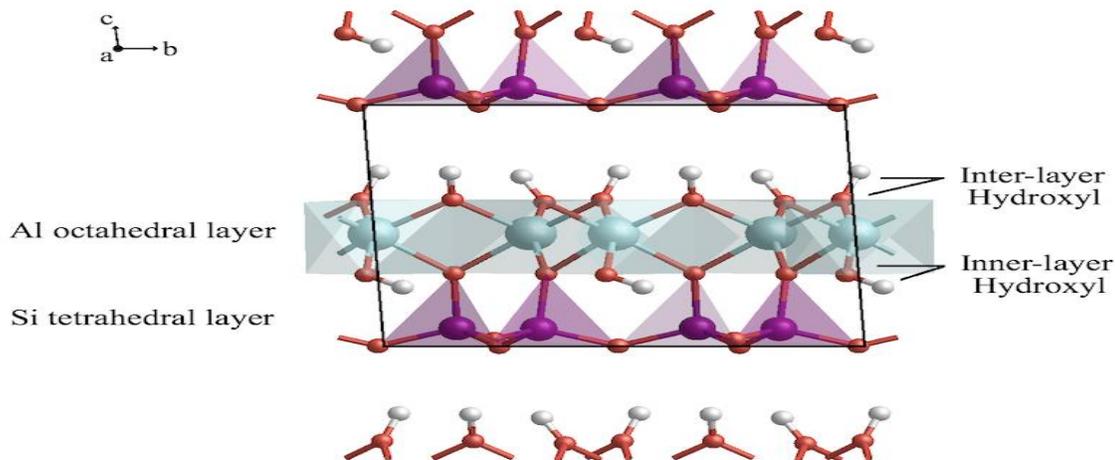


Figure 2: Ideal layered structure of kaolinite, showing the constructed kaolinite unit cell. The location of the inter- and inner-layer hydroxyls is shown for Clarity

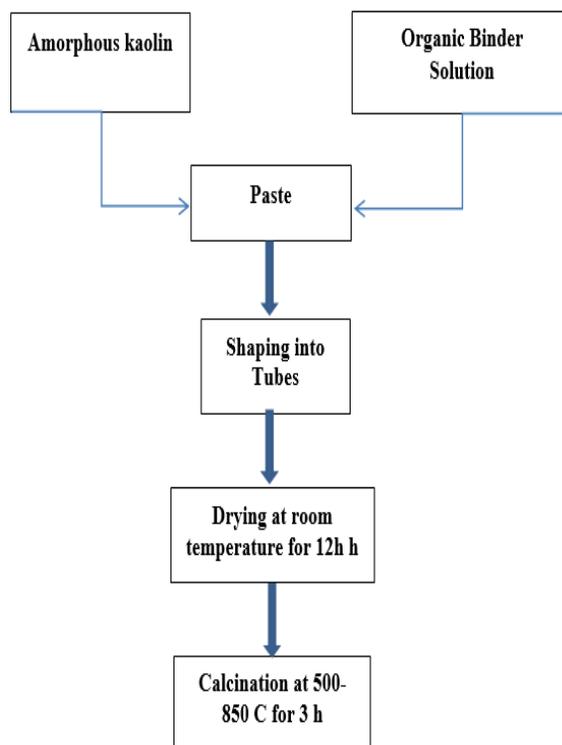


Figure 3: Flow diagram for the preparation of Methakaolin support from kaolin

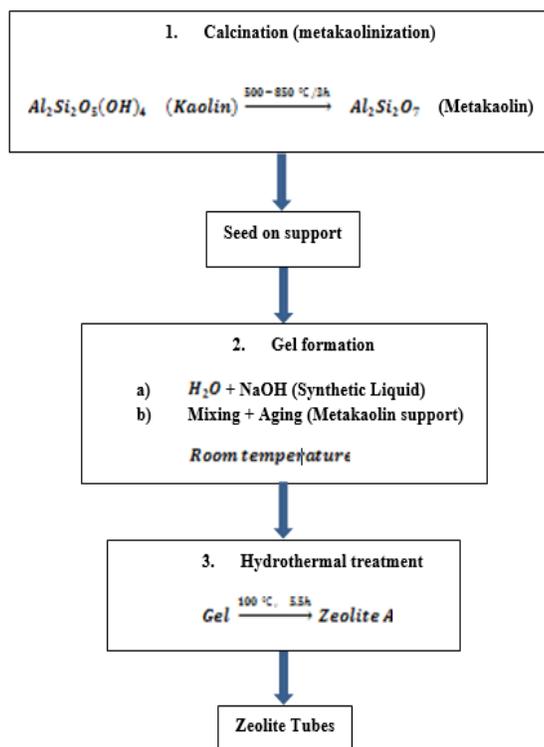


Figure 4: Flow diagram for the studies parameters in the hydrothermal synthesis of sZeolite A from kaolin

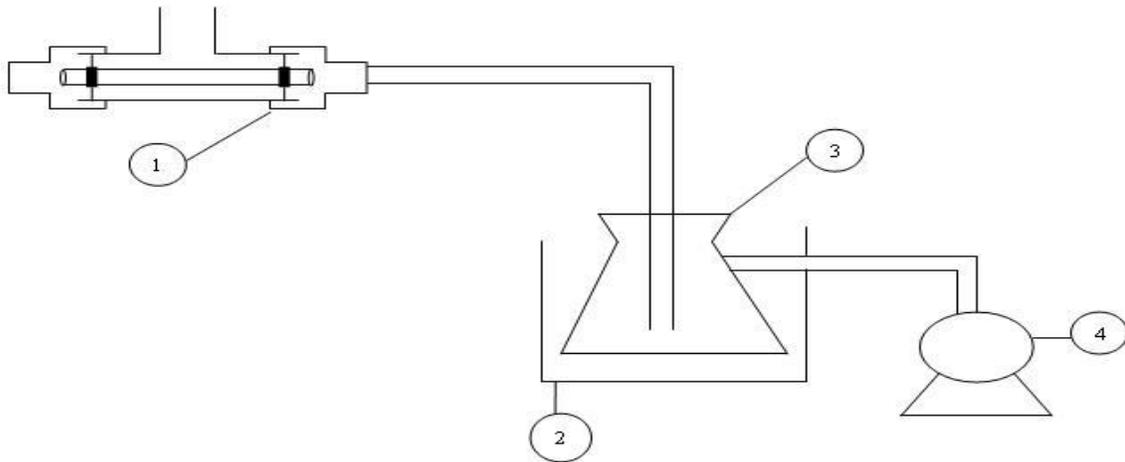


Figure 5: PV setup (dead end; 1- feed container and PV cell 2- liquid nitrogen trap 3- permeate container 4- three stage vacuum pump

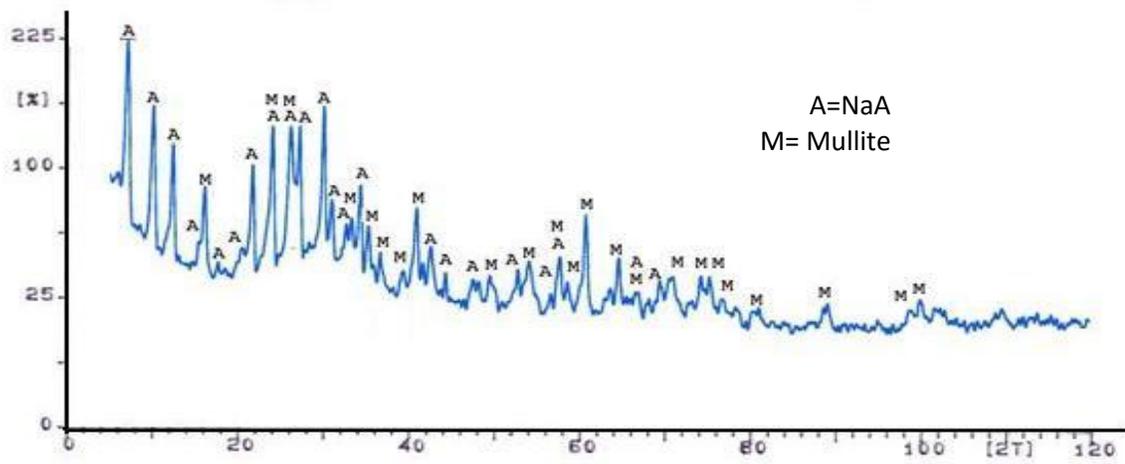
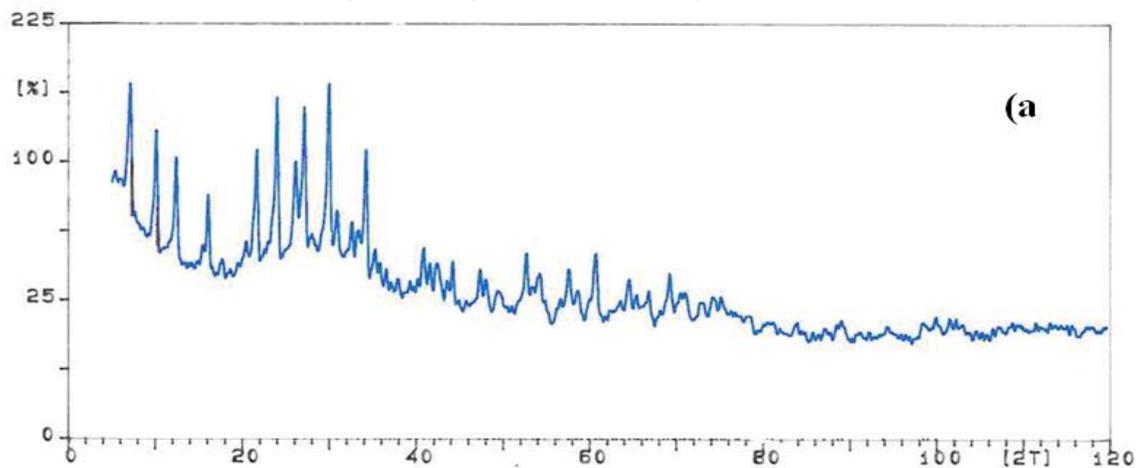


Figure 6: XRD patterns the membrane from kaolin



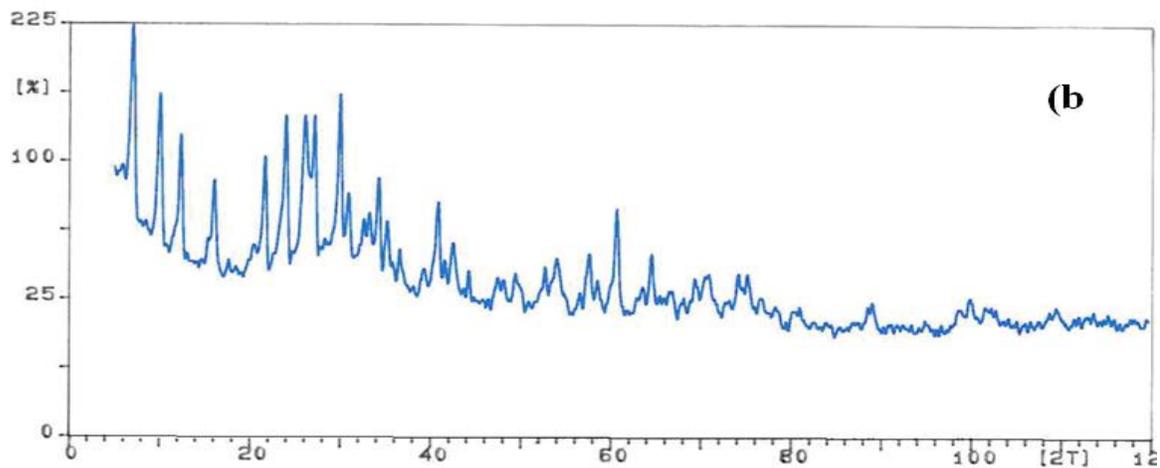


Figure 7: XRD patterns the self-supported membrane (a) 700°C, (b) 850°C

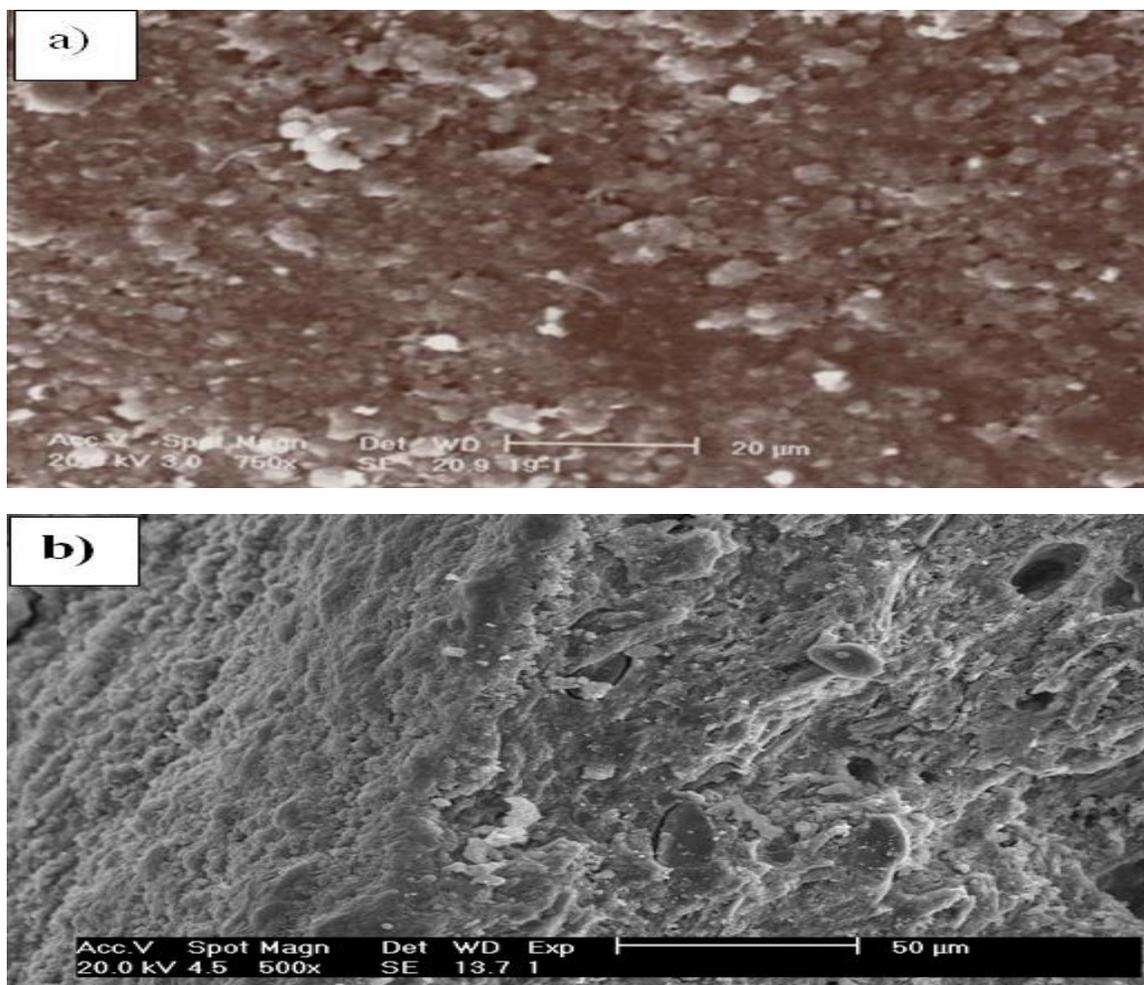


Figure 8: SEM micrograph of the support (a) mullite, (b) metakaolin

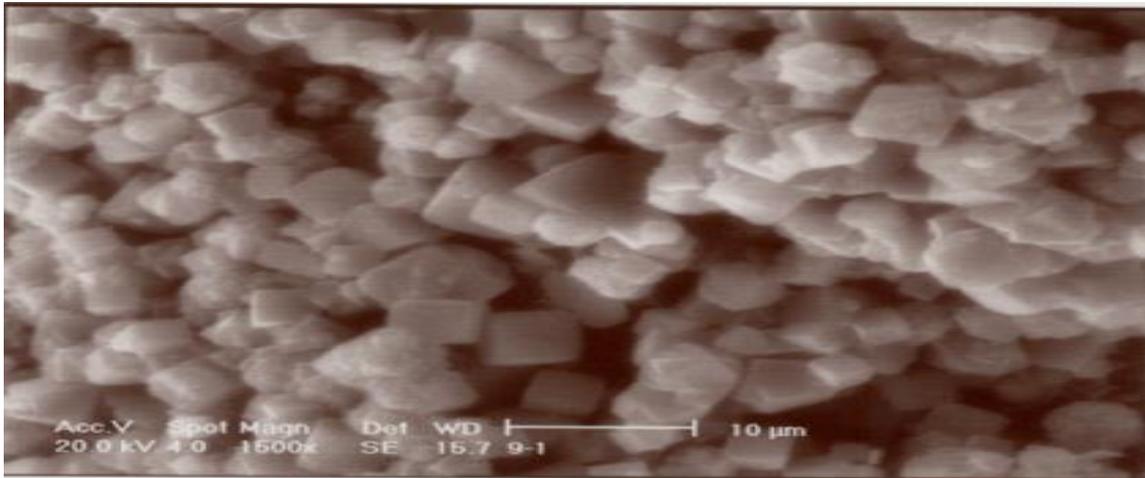


Figure 9: SEM micrograph of the membrane surface

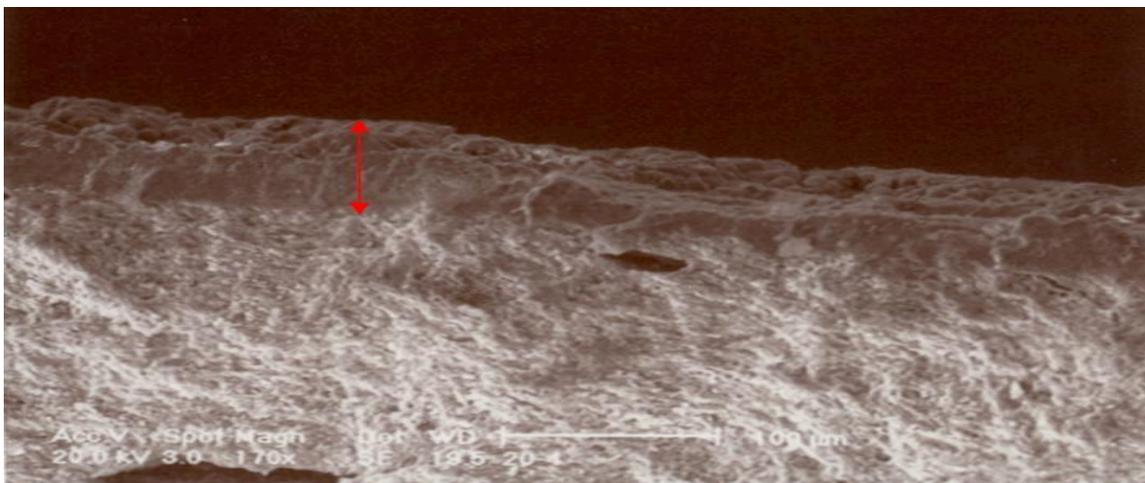


Figure 10: SEM micrograph of zeolite NaA membrane cross section preparation of kaolin source

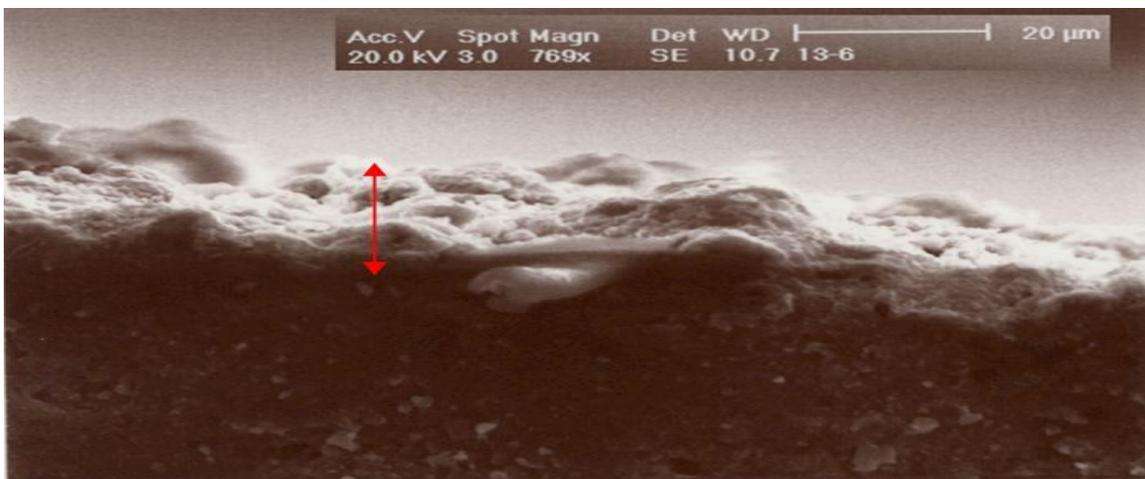


Figure 11: SEM micrograph of selfsupported membrane cross section preparation of kaolin source