

## Preparation of self-supported HS zeolite membranes by a new method

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Hydroxysodalite (HS) zeolite was synthesized successfully by hydrothermal method using the natural kaolin. Our approach to membrane synthesis was based on self-supported zeolite membranes. In this research, synthesis of HS 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 HS membranes was evaluated using pervaporation of water-UDMH mixtures. The membranes showed high water selectivity in the water-UDMH mixtures.

**Key words:** Kaolin, Nano, Zeolite, Hydroxysodalite, Self-supported membrane.

### Introduction

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 frame work 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. Zeolite membranes have uniform and nano-sized pores, and they separate molecules based on differences in the molecules size and diffusion properties. Different routes used to prepare zeolite composite membranes include growing zeolite layers from gels on porous supports. Zeolites are generally synthesized by the hydrothermal reaction of sodium aluminosilicate gels prepared from pure chemicals in alkaline medium using conventional heating systems [1-3].

Zeolite membranes are mostly composite materials, which are composed of a thin and compact zeolite layer on a thick, and macroporous support. Thin zeolite layer accomplishes separation while the macroporous support mainly provides mechanical strength to the membrane. Different types of support materials and geometries were used in the literature. The support is

chosen considering the resistance of the support to the flux, adhesion of the zeolite film to the support, leaching of support into the synthesis solution and the differences between the thermal expansion coefficients of the support and the zeolite film. Leaching of the support may locally change the chemical composition of the synthesis solution around the support so that undesired phases may form. The difference between the thermal expansion coefficients between the support and the zeolite layer may also cause formation of microcracks during the thermal treatment to remove water and organic template from the zeolite pores. The microcracks may drastically decrease the performance of the membranes in separation processes. These problems can be overcome by forming asymmetric membranes; both the separating layer and the support originate from the same material. Zeolites are conventionally synthesized from sodium alumina silicate gel prepared from pure chemicals in air ovens or autoclaves [4].

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. 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

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the binder less zeolite bodies. However, these techniques are rather difficult and the prepared bodies are usually smaller than a few centimeters [5]. The pore size of HS zeolite is 0.3 nm, i.e., smaller than that of the MFI zeolite (0.55 nm). The small pore size of HS zeolite makes the separation of small molecules by difference in size possible.

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

### 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 Ethanol mixtures. The structure of zeolite HS is shown in Fig. 1.

As shown in Fig. 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. Also, 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

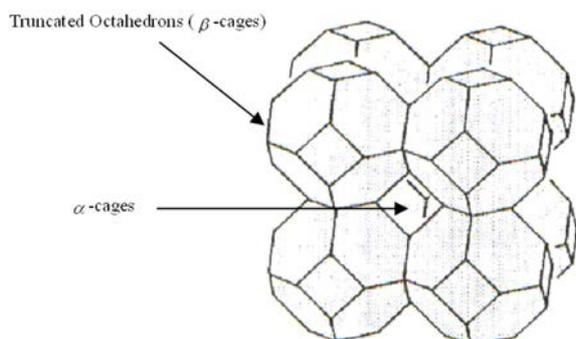


Fig. 1. Repeating unit of zeolite HS.

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  $\text{H}_2\text{O}$ . This effect is manifested in the fact that heat of adsorption of water into zeolitic adsorbents is unusually high (25-30 kcal/mole) [6].

### 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 [7-10].

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 Fig. 2, is composed of a sheet of vertex sharing  $\text{SiO}_4$  tetrahedral forming six-membered silicate rings that are linked by common oxygen atoms parallel to the c-axis to a sheet of edge-sharing  $\text{AlO}_6$  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

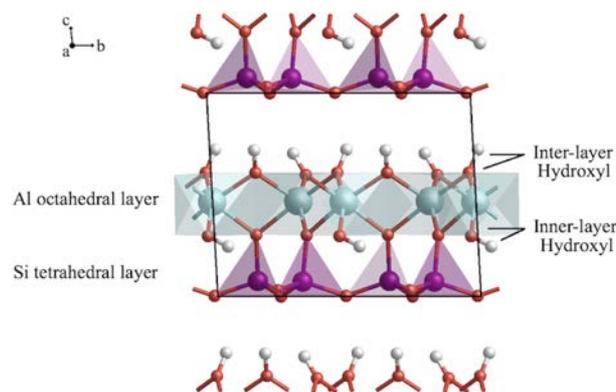


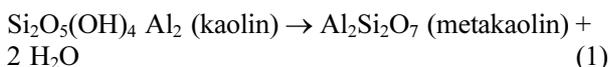
Fig. 2. Ideal layered structure of kaolinite, showing the constructed kaolinite unit cell. The location of the inter- and inner-layer hydroxyls is shown for clarity.

**Table 1.** Analysis of kaolin clay.

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

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 (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>), a calcined product of kaolin (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O) with Si/Al ratio 1 is a convenient starting material for the synthesis of zeolite HS. 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.

### Zeolite HS synthesis from kaolin

The low silica zeolite HS can be conveniently prepared by the hydrothermal reaction of the activated kaolinite with aqueous sodium hydroxide. Among naturally available raw materials, kaolin, which has Si/Al ratio of nearly 1 similar to zeolite HS, has been used as alternative cheap raw material for the synthesis of zeolite HS. The synthesis of zeolite HS from kaolin involves two basic steps: metakaolinization, which is the calcination of the raw kaolin at high temperature to change chemically stable kaolin into a very reactive but amorphous material, metakaolin, and hydrothermal treatment of the calcined kaolin with sodium hydroxide. Kaolin (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O) in its natural state is less reactive. Metakaolin (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>), a calcined product of kaolin with Si/Al ratio of 1 is a convenient starting material for the synthesis of zeolite HS. This process is usually performed between 450 and 900 °C. The transition of kaolin to metakaolin was obtained at about 500 °C. However, full conversion to metakaolin required a much higher temperature, with the loss of structural water with reorganization of the structure. Only a small part of AlO<sub>6</sub> octahedral is maintained,

while the rest are transformed into much more reactive tetra and penta coordinated units. The synthesis of HS 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 [11-14].

## Experimental

The first phase of the study was to synthesize the zeolite supports and second phase was to prepare zeolite membranes from support materials. The HS extrudates were prepared by crystallizing porous metakaolin extrudates in the presence of alkaline medium containing sodium hydroxide.

### 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.

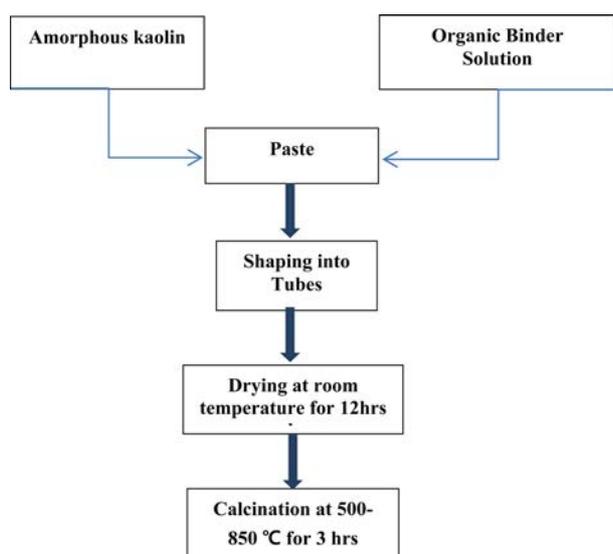
In this research, metakaolin supports have been prepared from kaolin clay. Kaolin is thermally converted to metakaolin via high temperature calcinations. The reaction can be represented by the following equation:



Metakaolin has several distinct advantages over other materials. Since kaolin is heated to high temperatures to achieve the metakaolin conversion reaction, strong inter-crystalline bonds between metakaolin crystals are formed and this results in excellent strength and attrition. 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. The heat treatment of kaolin extrudates transforms them into metakaolin extrudates. Suitable calcinations temperatures and periods are those at which kaolin converts to metakaolin. Good results have been achieved by calcining for about 3 hrs at temperatures of about 500-850 °C [15,-16].

As shown in Fig. 3, the steps involved for the preparation of porous metakaolin extrudates are as follows: (i) preparation of kaolin-starch extrudates; (ii)



**Fig. 3.** Flow diagram for the preparation of Methakaolin support from kaolin.

drying of the kaolin extrudates at 100 °C for 12 hrs; (iii) calcination of the kaolin extrudates for removal of the organic material (starch) and conversion to metakaolin at 500-700-850 °C. The kaolin extrudates were prepared by mulling kaolin, tri poly phosphate, and appropriate amount of water. The mulled mixture was extruded to form kaolin extrudates. The kaolin extrudates were dried at 100 °C for 12 hrs in an air oven. After drying, the kaolin extrudates were calcined at 500-700-850 °C (heating rate 1 °C/min) for 3 hrs.

Porosity of the supports is 49%. Flux of the supports at 1 bar and 20 °C is 10 kg/m<sup>2</sup>h. Porosity of the supports has been measured by water absorption method.

### 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.

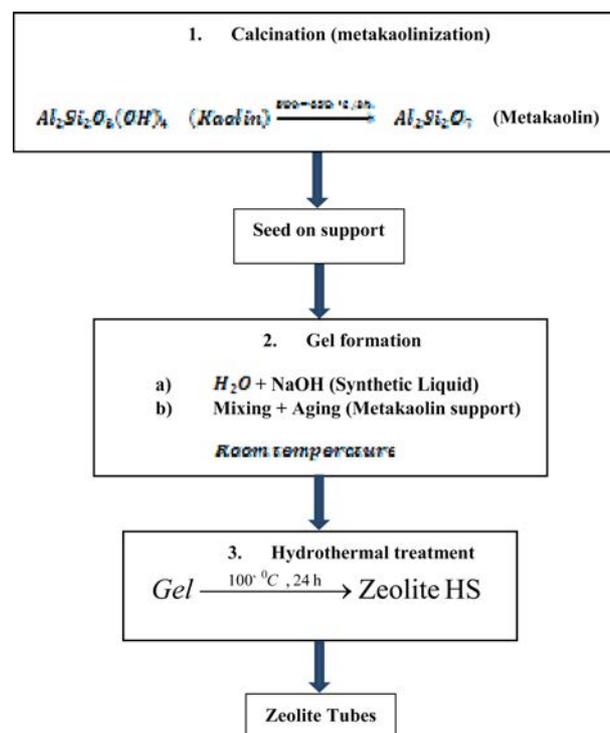
Porous methakaolin tubes as describe above have been used as supports. External surface of the supports have been polished with 600 grit-sand papers and then they have been washed and cleaned in boiling distilled

water for 5 min to remove loose particles created during polishing. Then, the supports have been dried at 100 °C for 3 hrs in air. In order to create a thin and uniform zeolite membrane layer over the methakaolin support, nucleation seeds should be small and uniform in size. 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 methakaolin supports in an 8% HS zeolite suspension once for 1 min. The 8% HS zeolite suspension has been prepared by mixing 8 g HS zeolite in 92 ml distilled water. After soaking, the supports have been dried at 100 °C for 3 hrs in air.

### Self-supported HS zeolite membrane

Prior to the hydrothermal synthesis, thermal activation of the very chemically inert kaolin is important. In the first step shown in Fig. 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 HS from both raw and purified kaolin have been conducted. Step 2 in Fig. 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 extrudates were converted into HS using



**Fig. 4.** Flow diagram for the studies parameters in the hydrothermal synthesis of Zeolite HS from kaolin.

a mixture containing NaOH and double-distilled water at 100 C for 24 hrs. The samples obtained at different intervals were thoroughly washed with distilled water and dried at 100 C for 12 hrs in an air oven. Zeolite membrane was synthesized from metakaolin support. Synthesis solution was prepared using by mixing metakaolin support surface and NaOH solutions.

Two ends of the supports were closed with rubber. HS membrane was grown hydrothermally on the surface of a porous tubular metakaolin support (14 mm outer diameter, 12 cm length) 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 24 hrs, 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 hrs in air. The molar composition of the resulting gel was  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2$ ,  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 65$  and  $\text{H}_2\text{O}/\text{Al}_2\text{O}_3 = 1000$ .

### Pervaporation tests

We used a PV experimental set up to be sure of successfully fabrication Nano pore HS 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 mbara at the permeate side, within a period of 30-60 min.

The pervaporation setup is presented in Fig. 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 have been

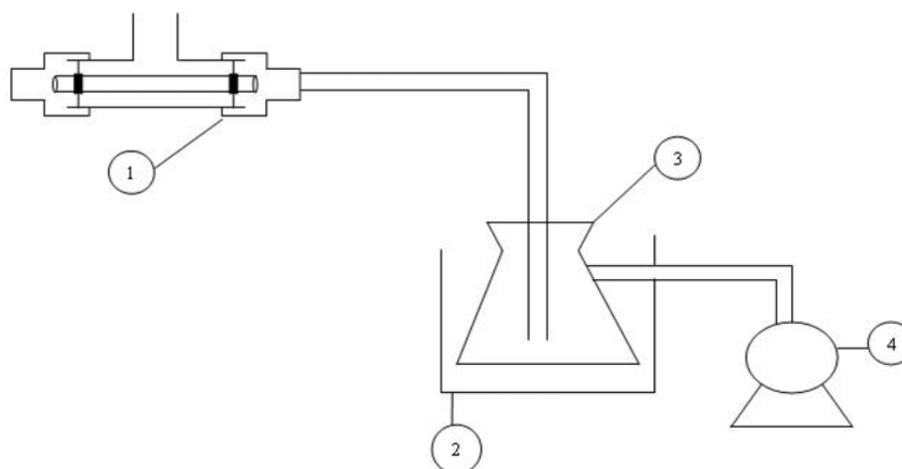
measured by a GC (TCD detector, Varian 3400). Performance of PV is usually evaluated by total flux ( $\text{kg}/\text{m}^2\text{h}$ ) and separation factor (dimensionless). Separation factor of any organic aqueous solution can be calculated from the following equation:

$$\text{Separation factor } (\alpha) = \frac{[X_{\text{H}_2\text{O}}/X_{\text{Organic}}]_{\text{permeate}}}{[X_{\text{H}_2\text{O}}/X_{\text{Organic}}]_{\text{feed}}} \quad (3)$$

Where and are weight fractions of water and organic compound, respectively.

## Results and Discussions

The HS zeolite membranes were synthesized by kaolin source. The methakaolin support was prepared from kaolin for zeolite membranes. The supports were prepared by extrusion of kaolin paste through an extruder into tubes. These extrudates were dried at Room temperature for 24 hrs, calcined at 500-850 C for 3 hrs. The seeded supports have been prepared by soaking the methakaolin supports in HS zeolite suspension. The hydrothermally synthesis was used for preparation of zeolite membranes from kaolin source. HS membrane was grown hydrothermally on the surface of support using by metakaolin support as a source for aluminates and silicate. The synthesis of HS 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 24 hrs in hydrothermal reaction of metakaolinite with aqueous NaOH medium. The HS membrane is highly selective for permeating water preferentially with the high permeation flux be-cause 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 HS 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.



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

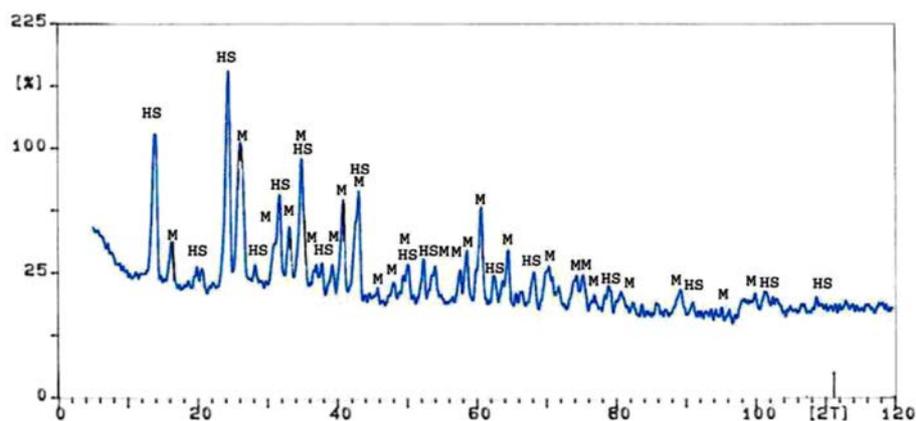


Fig. 6. XRD patterns the membrane from kaolin.

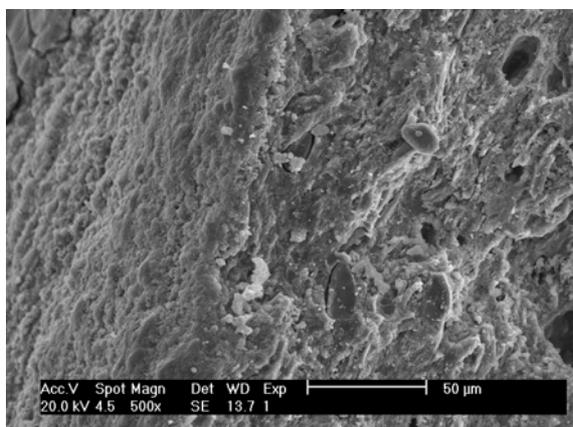


Fig. 7. SEM micrograph of the support.

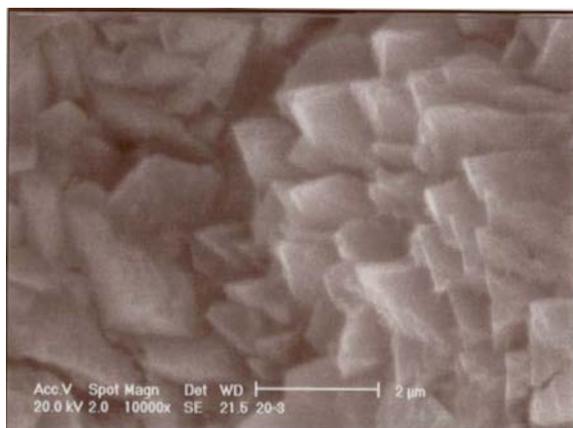


Fig. 8. SEM micrograph of the HS seed on support.

Phase identification has been performed by X-ray diffractometry (Philips PW1710, Philips Co., Netherlands) with  $\text{CuK}_\alpha$  radiation. Fig. 6 show XRD pattern of formation HS zeolite membrane from kaolin clay. The XRD pattern of HS zeolite membrane confirms that zeolite HS crystals were formed from kaolin clay. Morphology of the support and the membrane made by kaolin was examined by scanning electron microscopy. Figs., 8 and 9 show SEM micrographs of the methakaolin support and the HS zeolite membrane preparation by

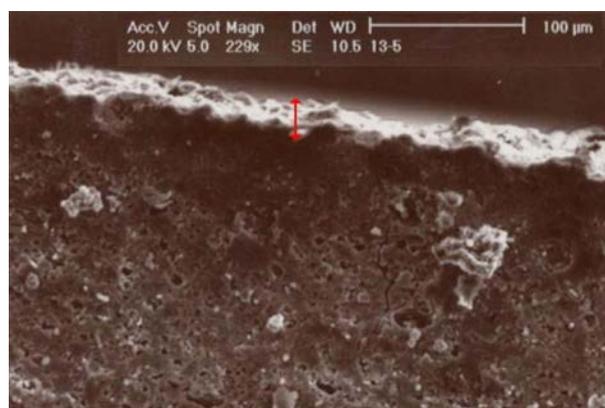


Fig. 9. SEM micrograph of zeolite HS membrane cross section preparation of kaolin source.

Table 2. Flux and separation factor of the membranes.

Sample	Calcination Temperature C	Concentration of UDMH (%)	Flux $\text{kg/m}^2\cdot\text{h}$	Separation factor
1	500	5	–	–
2	700	5	0.934	> 10000
3	850	5	0.67	> 10000

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

## Conclusions

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 HS membrane was successfully produced from kaolin.

This study aimed to synthesize thin zeolite HS layer over a zeolite HS support. The first phase of the study was to synthesize the zeolite supports and second phase was to prepare zeolite HS membranes. Self-standing, pure and porous zeolite HS bodies with tube shapes have been prepared. We have demonstrated that a HS zeolite membrane can be synthesized from kaolin on a porous metakaolin support by hydrothermal method. HS zeolite membrane was used for dehydration of aqueous organic mixtures. These membranes showed very good membrane performance for separation of UDMH/water mixtures.

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