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Multi-stage synthesis of nanopore NaA zeolite membranes for separation of water/Ethanol mixtures

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Abstract

Multi-stage nanopore NaA zeolite membranes were successfully synthesized on a porous mullite support. NaA zeolite was coated on external surface of porous supports by hydrothermal synthesis. Effects of multi stage synthesis on the membrane performance were studied. Multi-stage synthesis of nanopore NaA zeolite membranes is a method for preparation of zeolite membranes without defects. The crystal species were characterized by X-ray diffraction (XRD) patterns and morphology of the supports subjected to crystallization was characterized by Scanning electron microscopy (SEM). Performance of the hydrophilic Nano zeolite membranes during separation of water/Ethanol mixtures was evaluated. These membranes showed very high selectivity of water for water/Ethanol mixtures. Separation factor as high as 10000 was obtained for ethanol feed concentration of 90%. Total mass flux was also obtained in a range of 0.243-0.973 kg/m^2.h.

Keywords: Nano, zeolite, pervaporation, multi-stage synthesis

1. Introduction

Polymeric membranes are not generally suitable for applications involving harsh chemicals due to membrane chemical instability. However, a recent development of chemical-and-temperature resistant hydrophilic ceramic membranes has made it possible to overcome the limitations of hydrophilic polymeric membranes [1]. 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 rate, PV results in energy cost saving and safe operation [2-3].

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 [4]. The investigation of nano zeolite membranes with nano pore size has attracted much attention. The pore size of NaA zeolite is 0.4 nm, i.e., smaller than that of the MFI zeolite (0.55 nm). The small pore size of NaA zeolite makes the separation of small molecules by difference in size possible. Thus small molecules, such as H_2O (0.27 nm), are expected to be separated from ethanol by molecular sieving or configuration diffusion using NaA zeolite membranes [5-7].

In this study, multi stage NaA zeolite membranes were fabricated for separation of water/ethanol mixtures was observed.

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, spinal, zirconium, 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 clay is thermally converted to mullite via high temperature calcinations. The mullitization reaction takes place when kaolin clay is utilized as the sole source of silica and alumina. The reaction can be represented by the following equation where the approximate chemical formula for kaolin (without the water of hydration) is given as $Al_2O_3.2SiO_2$ and the formula for mullite is $3Al_2O_3.2SiO_2$

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

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The term represented by $4SiO_2$ is the free silica generated as a result of the conversion. This free silica has been leached and then porous mullite bodies have been prepared. Mullite has several distinct advantages over other bodies such as alumina. Since these bodies are 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 the body prior to leaching,
(3) concentration of the leaching solution and
(4) Temperature

The kaolin material used in this study (SL-KAD grade) has been obtained from WBB cooperation. The 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 67-75% kaolin clay and 25-33% distilled water using an extruder.

Suitable calcinations temperatures and periods are those at which the clay converts to mullite and free silica. Good results have been achieved by calcining for about 3 h at temperatures of about 1250^0C [8].

Free silica has been removed from the calcined bodies by leaching with strong alkali solutions. Removal of this free silica causes mesoporous tubular supports to be made with very high porosity. Free silica removal has been carried out with aqueous solutions containing 20% by weight NaOH at a temperature of 80 °C for 5 h. Supports have been washed with 2 lit of water for 12 h at a temperature of 80 °C in order to remove NaOH. Porosity of the support before leaching is 24.3% while after treatment it increases to 49%. Flux of the support before and after free silica removal at 1 bar and 20 °C are 6 kg/m^2h and 10 kg/m^2h, respectively. The porosity of support has been measured by water absorption method [9].

2.2 Nano pore zeolite preparation

Thin zeolite NaA membrane layers were grown hydrothermally over the external surface of the porous supports. Synthesis solution was prepared by mixing aluminate and silicate solutions. NaOH was dissolved in distilled water. The solution was divided into two equal volumes and kept in polypropylene bottles. Aluminate solution was prepared by adding sodium aluminate (Aldrich, 50-56% Al_2O_3) to one part of the NaOH solution. It was mixed until cleared. Silicate solution was prepared by adding sodium silicate (Merck, 25-28% SiO_2) to another part of the NaOH solution. Silicate solution was then poured into aluminate solution and well mixed until a thick homogenized gel was formed. Composition of the homogeneous solution of zeolite NaA is represented by the following molar ratio: $SiO_2/Al_2O_3=1.926$, $Na_2O/Al_2O_3=3.165$ and $H_2O/Al_2O_3=128$ [10-14].

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 supports were placed vertically in a Teflon autoclave. The solution was carefully poured in the autoclave and then the autoclave was sealed. Crystallization was carried out in an oven at temperatures of 70, 100, and 130 °C for 1, 2, 3, 4 and 5 h. Synthesis procedure was repeated where fresh synthesis gel was added periodically to the cooled and cleaned samples. This causes more NaA zeolite crystals on the support to be formed after a two or three stage synthesis.

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. Samples were coated two and three times to study effect of number of coating. The zeolite membranes were used for dehydration of aqueous ethanol. Dilute ethanol mixtures (90 wt%) were used and experiments were carried out at room temperature (25°C) within a period of 30-60 min. Permeate concentrations were measured using GC (TCD detector, Varian 3400, carrier gas: hydrogen, column is polyethylene glycol, sample size: 5 micron, column and detector temperatures: 120°C- 150°C, detector rate of flow is 15 ml/min, carrier flow: 5 ml/min, column pressure : 1.6 kpa, GC input pressure: 20 kpa. Performance of PV was evaluated using (Figure 1) values of total flux ($kg/m^2.h$) and separation factor (dimensionless) [15]. While PV system was be steady state (after 20 min), we measured weight of permeate at 30 min period then flux is calculated (area of zeolite membrane is 44 cm2). The change in feed concentration due to permeation was negligible because the amount of permeate was small compared to total liquid volume in the system.

3. Results and discussion

As mentioned, the synthesis procedure was performed using different times and temperatures. The synthesis procedure was also performed using different temperatures. As seen in Table 2, increasing crystallization temperature at two stage synthesis of zeolite membranes cause to increases flux (sample 1). Also, it can be observed that there is no change in separation factor. This may be due to the fact that increasing crystallization temperature at second stage cause to make a better layer is formed. It is because, at higher temperatures, NaA zeolite crystals are smaller. This shows that these membranes behave very high selectivity. As a result, the crystallization temperature for two stage synthesis of nano pore NaA zeolite membranes in an increasing range of 70-130 $^\circ C$ was found to be very effective for making the NaA zeolite layer. The results show that decrease of crystallization time at three stage synthesis causes to make an effective zeolite layer on the support and high flux zeolite membrane (sample 4). Also, increase of crystallization time at three stage synthesis causes to make a low flux NaA zeolite membrane (sample 5).

As a result, the crystallization time for three stage synthesis of nano pore NaA zeolite membranes in a decreasing range of 3-2-1 h was found to be very effective for making the NaA zeolite layer. Therefore, quality of NaA zeolite membrane layer may be improved. The synthesized layers by a multi stage procedure are substantially better than the corresponding layers by a single stage. Figure 2 shows XRD patterns of the mullite support and the NaA zeolite membrane. The XRD pattern of NaA zeolite membrane confirms that zeolite NaA crystals were formed. Figure 3 shows SEM photographs of the mullite support (a) and the NaA zeolite membrane (b). Porous structure of the support and thin layer of the membrane can be easily observed.

4. Conclusion

Zeolite NaA membranes were synthesized on the porous mullite tubes by multi-stage hydrothermal method. This causes more NaA zeolite crystals on the support to be formed after a two or three stage synthesis. Therefore, quality of NaA zeolite membrane layer is improved. Multi-stage synthesis of nanopore NaA zeolite membranes is a method for preparation of zeolite membranes without defects. These membranes showed very good membrane performance for separation of ethanol/water 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	Total	100
Na_2O	0.1		
L.O.I	11.6		
Total	100		

Table 2: Flux and separation factor of NaA zeolite membranes

Sample	Number of coating	Crystallization time (h)	Crystallization temperature ($^\circ C$)	Concentration of Ethanol in feed (wt %)	Flux kg/m^2.h	Separation factor
1	2	3-3	70-130	90	0.451	>10000
2	2	3-3	100-100	90	0.347	>10000
3	2	3-3	130-70	90	0.243	>10000
4	3	3-2-1	100	90	0.973	>10000
5	3	3-4-5	100	90	0.306	>10000
6	3	3-3-3	100	90	0.292	>10000

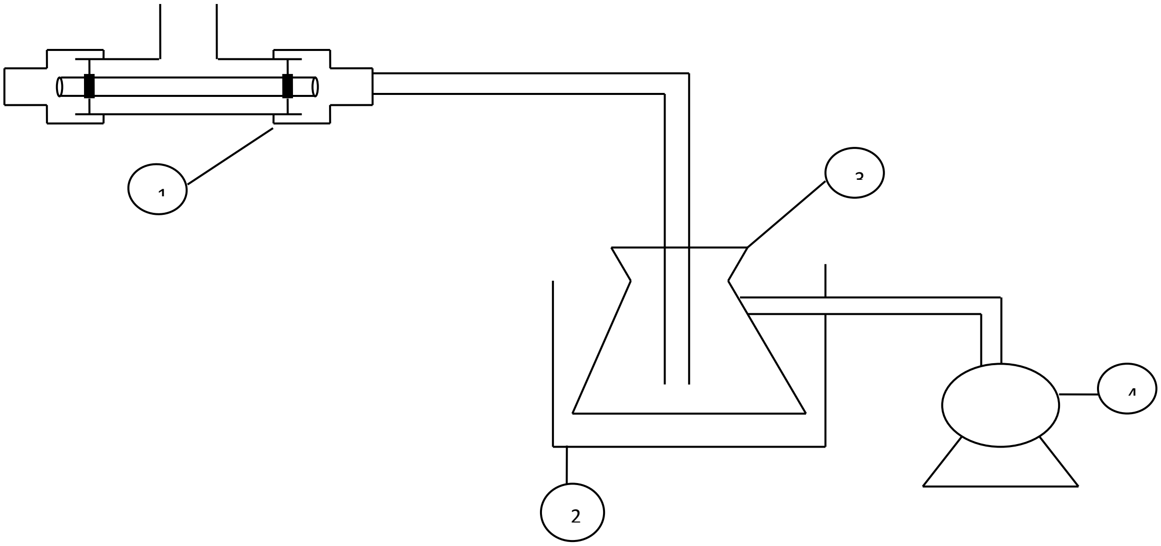


Figure 1: PV setup (dead end; 1- feed container and PV cell 2- liquid nitrogen trap 3- permeate container 4- three stage vacuum pump 5- centrifuge pump 6- tank feed

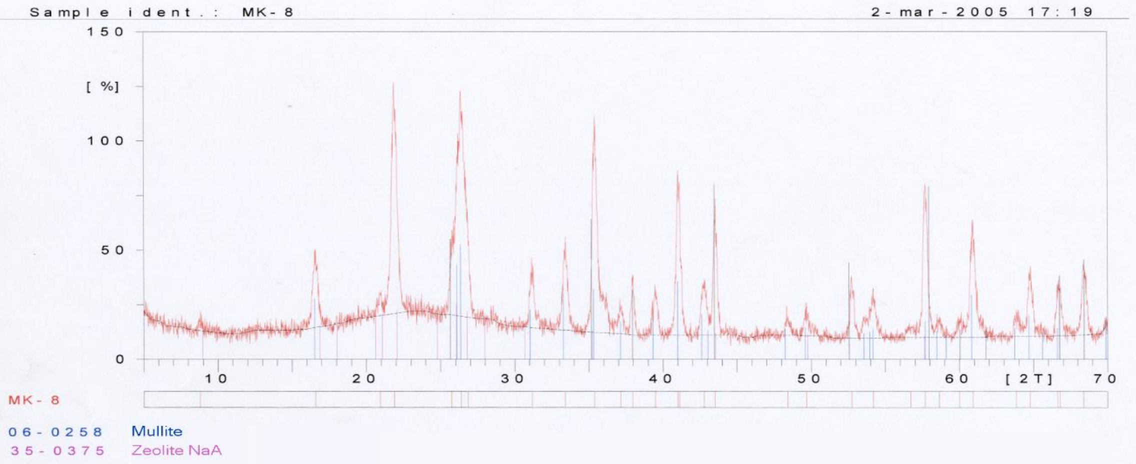
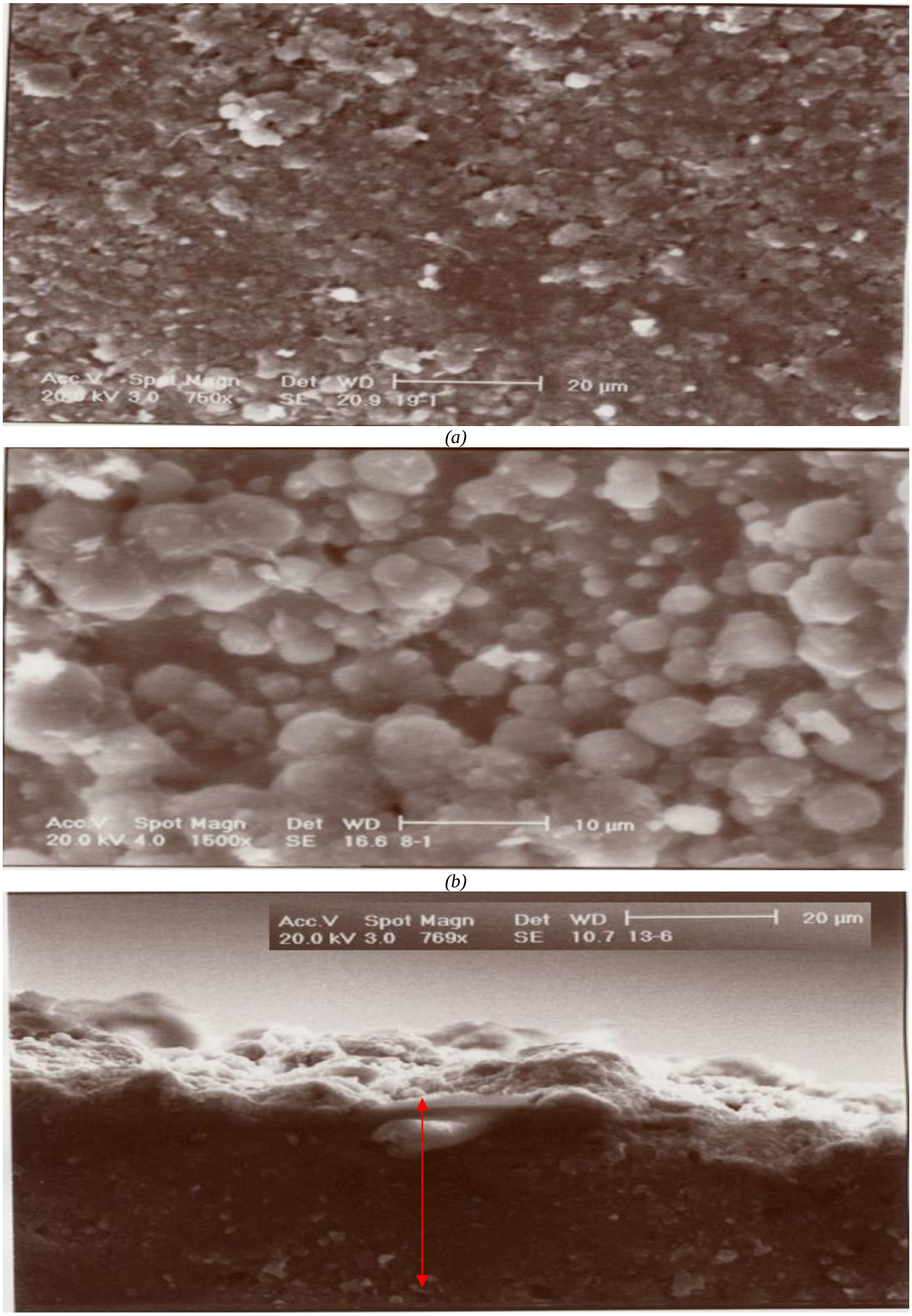


Figure 2: XRD of membrane with support



(a)

(b)

(c)

Figure 3: SEM micrograph of (a) the support, (b) the membrane, (c) thickness of membrane on support