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# Preparation and characterization of nanoporous ceramic membranes for separation of water from ethanol

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ABSTRACT

In this work, high performance nanoporous Linde Type A (LTA)-type zeolite membranes were synthesized via secondary growth method. The used substrate for growing membrane layer was porous mullite. To synthesize defect-free zeolite film on porous mullite discs, synthesis duration was optimized for hydrothermal treatment. The morphology and structure of synthesized zeolite membranes were characterized by scanning electron microscopy and X-ray diffraction. The defect-free LTA-type zeolite membranes were obtained at synthesis duration of 3 h and synthesis temperature of 100°C. The separation performance of synthesized LTA-type zeolite membranes were evaluated in dehydration of ethanol using pervaporation process. Influence of feed composition on separation performance of LTA membranes was also investigated. The best membranes showed a separation factor of 9,400 and total flux of 9.8 kg $m^{-2}$ $h^{-1}$ for dehydration of 10:90 (wt.%) water/ethanol mixture.

*Keywords:* Dehydration; Pervaporation; Nanoporous; Ceramic membrane; Ethanol; Mass transfer

## 1. Introduction

In the last two decades, membrane technology has attracted the attention of researchers in the separation of gases and liquids because of its great performance compared to the conventional separation processes, such as distillation, absorption, and adsorption. Among membrane separation processes, pervaporation (PV) is one of the rapidly developing membrane processes which is favorable in the separation of close-boiling point mixtures, azeotropes, and thermally sensitive compounds [1]. Recently, the PV process has gained interest in the chemical industry as an energy-efficient process for the separation of liquid mixtures [2]. This technology has better separation capacity and energy efficiency which could lead to 40–60% energy savings [3].

Inorganic membranes, such as zeolite membranes have been widely studied in PV of liquid mixtures due to their unique characteristics, such as uniform pore size, great adsorption properties, mechanical, chemical, and thermal stability over a wide range of applications [4,5].

Zeolites are crystalline aluminosilicate materials with microporous structures formed by tetrahedra groups of $TO_4$, where T refers to the Si or Al atoms. The tetrahedra groups are linked together to make the structure of zeolites. Zeolitic materials provide regular

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and defined pore sizes ranging from 0.3 to 1 nm. These pores sizes are close to kinetic diameters of most molecules, therefore, zeolites are appropriate for gas and liquid separation by molecular sieving and adsorption [6].

Among all kinds of zeolite membranes, Linde Type A (LTA)-type zeolite has attracted the most attention owing to its regular small pore size and strong hydrophilicity. The latter makes this zeolite superior for preparation of zeolite membranes to be used in separation and dehydration of organic solutions [4–11].

Recently, some works have been conducted to synthesize high-quality nanoporous LTA-type zeolite membranes for dehydration of alcohols and organic solvents. Researchers have developed various synthesis procedures to prepare high-quality LTA-type zeolite membranes. Some researchers tried to use nanoparticles of zeolite LTA as seed for the synthesis of high-quality membranes using secondary growth method. The latter approach showed to be efficient in preparation of high-quality zeolite membranes because of using nanoseeds. However, this synthesis procedure needs exact control of synthesis parameters which leads to a complicated and expensive synthesis procedure. Some other researchers used improvement of support surface by organic matters for membrane synthesis and prepared high-performance membranes [8–11].

Development of a simple and low-cost synthesis method for the preparation of defect-free and high-quality LTA-type zeolite membranes is of great importance. Synthesis of zeolite LTA on mullite support have shown to be a good strategy for the preparation of high-quality membranes because there are chemical similarities between mullite and zeolite LTA structure. Therefore, using mullite would be a good idea for the preparation of LTA zeolite membranes. Another idea for preparation of high-quality LTA-type zeolite membrane is optimization of synthesis parameters.

At the moment, synthesis of nanoporous ceramic membranes is carried out by complicated and expensive methods which are not appropriate for industrial applications. Synthesis of high-quality and defect-free ceramic membrane is carried out in this work by a low-cost method without adding any organic matter or template. This makes the preparation of these ceramic membranes suitable for industrial preparation and applications.

In the present study, nanoporous LTA-type zeolite membranes were synthesized on mullite support using hydrothermal synthesis method and characterized to evaluate the quality of synthesized zeolite NaA membranes. The effect of synthesis duration on the membrane performance was also investigated to obtain the optimum parameters. The separation performance of the synthesized nanoporous LTA zeolite membranes were studied using PV process for the dehydration of ethanol–water mixtures.

## 2. Experimental

### 2.1. Materials

The LTA-type zeolite membranes were synthesized via hydrothermal treatment. The mixtures for LTA (NaA) zeolite synthesis were prepared by mixing sodium aluminate (50–56% $Al_2O_3$, 40–45% $Na_2O$, Riedel), sodium silicate solution (25.5–28.5% $SiO_2$, 7.5–8.5% $Na_2O$, Merck), sodium hydroxide (98% NaOH, Merck), and deionized water (DI). The reagents were used without purification.

### 2.2. Seeding of supports

For synthesis of zeolite membranes by secondary growth method, the support must be seeded by zeolite particles. The latter pretreatment, would facilitate the formation of membrane layer over porous substrate. For synthesis of LTA-type zeolite membranes, homemade porous mullite supports with a diameter of 21 mm, thickness of 1.8 mm, water permeation of 190 $kg/m^2$ h bar, and porosity of 43% were used. At first, the surface of mullite supports were polished with 1,200 grit sand papers, and then the supports were cleaned with DI water in an ultrasonic bath [6].

Seeding of the mullite supports were carried out via dip-coating method. To do this, a fine suspension of 1 wt.% NaA zeolite particle was prepared by dispersing determined amount of zeolite particles in distilled water. The suspension was then sonicated for 20 min to prevent the agglomeration of zeolite particles and homogenize the suspension. The other side of the support was covered with Teflon tape to prevent growth of zeolite layer on both sides of the support. The supports were immersed horizontally in the suspension for 30 s and then were dried at 333 K overnight.

### 2.3. Hydrothermal synthesis of LTA-type zeolite membranes

The hydrothermal synthesis of LTA-type zeolite membranes were carried out in a Teflon autoclave. The solution for synthesizing zeolite membranes was prepared with a molar ratio of $Na_2O:Al_2O_3:SiO_2:H_2O$ = 45:1:5:950. Two reactant mixtures including the silicate solution and aluminates solution were prepared for membrane formation. The silicate solution was prepared by adding exact amount of sodium silicate with sodium hydroxide in DI water, and the

aluminate solution was prepared by adding sodium aluminate with sodium hydroxide in DI water. The aluminate solution was then added to the silicate solution and further aged for 2 h at room temperature under stirring. The synthesis solution was then transferred to the Teflon autoclave and placed in an oven. The synthesis duration and temperature were adjusted to find out the best conditions for membrane synthesis.

After the completion of hydrothermal synthesis, the membrane was taken off from solution and was washed thoroughly with DI water. The membrane was dried overnight with slow heating from room temperature to 110˚C [6–10].

### 2.4. Characterization of LTA-type zeolite membranes

After membrane preparation, the as-synthesized zeolite membranes were characterized via solid characterizations to ensure the formation of LTA zeolite layer on substrate. Surface morphology of membranes was characterized with scanning electron microscope (SEM, Hitachi, S-4700). The formation of LTA zeolite layer over support was identified by means of X-ray diffraction (XRD). XRD measurements were carried out on INEL diffractometer (EQuinox 3000) using Cu K$\alpha$ radiation operating at 40 kV and 30 mA. The step size for 2-theta in XRD measurements was 0.02˚.

### 2.5. PV tests

To further evaluate the quality of the synthesized zeolite membranes, separation performance of the LTA zeolite membranes was analyzed in PV experiments for separation of water from alcohols. Ethanol was considered as alcohol in the experiments. The membrane separation performance was calculated in terms of total permeation flux and selectivity of water to ethanol. The total permeation flux and selectivity are calculated as:

$$J = \frac{m}{S \times t} \quad (1)$$

$$\alpha_i = \frac{y_i/y_j}{x_i/x_j} \quad (2)$$

where $J$ is the total permeation flux (kg m$^{-2}$ h$^{-1}$), $m$ is the mass of the permeate (kg), $S$ is the active membrane surface area (m$^2$), $t$ is the duration of experiment (h), $y_i$ is the mass fraction of component $i$ in the permeate, and $x_i$ is the mass fraction of component $i$ in the feed, and $\alpha_i$ is the selectivity for component $i$ with respect to component $j$.

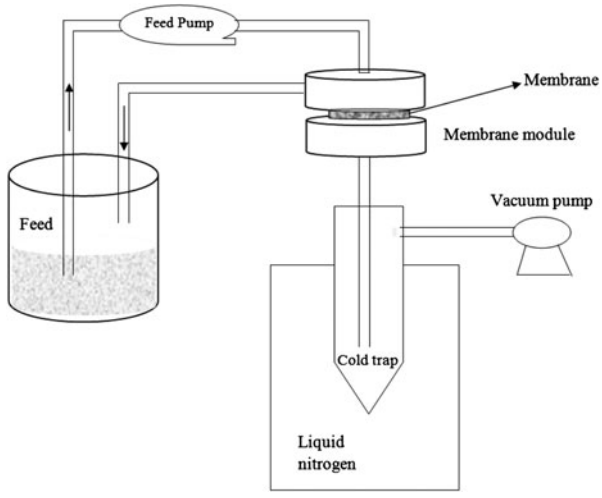


Fig. 1. Schematics of PV setup used in the experiments.

The experimental set-up used for PV is schematically illustrated in Fig. 1. As it is observed, the permeate side was evacuated and permeate vapor was condensed by a cold trap immersed in liquid nitrogen. The concentration of permeate flow was determined via a refractometer [6].

## 3. Results and discussion

### 3.1. Effect of synthesis duration on membrane formation

To examine the formation of zeolite layers on the surface of porous mullite supports during hydrothermal reactions, SEM images of membranes were collected and analyzed. Fig. 2 illustrates cross-SEM images of LTA-type zeolite membranes synthesized on mullite supports with various synthesis durations. As it is observed, in Fig. 2(a) which belongs to the synthesis duration of 1.5 h, a zeolite layer with thickness of about 2 μm was deposited at a synthesis temperature of 100˚C. It is clearly observed that zeolite LTA layer does not cover the entire surface of the support. The latter leads to formation of pinholes and cracks on membrane structure which reduces the membrane separation performance.

With increasing synthesis duration of up to 3 h, the membrane layer increases so that a zeolite film is formed over the support (Fig. 2(b)). A thicker zeolite layer was formed on the surface of support after 4 h of hydrothermal treatment at 100˚C (Fig. 2(c)). As shown in Fig. 2, with the increase of the synthesis duration from 1.5 to 4 h, the membrane thickness increases from 2 to 8 μm. Fig. 3 also shows the top image of the membrane that was synthesized after 3 h.

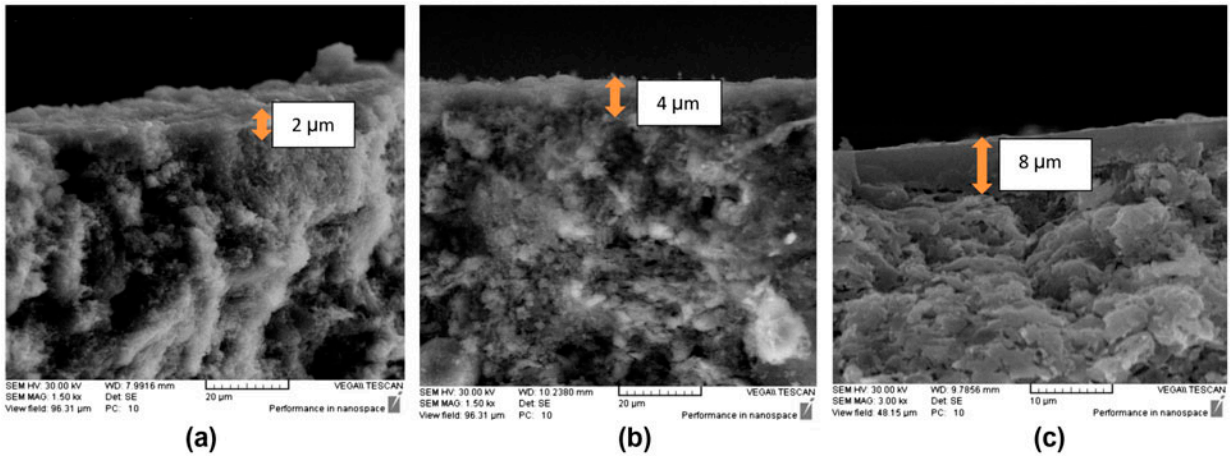


Fig. 2. Cross-SEM images of synthesized membranes.

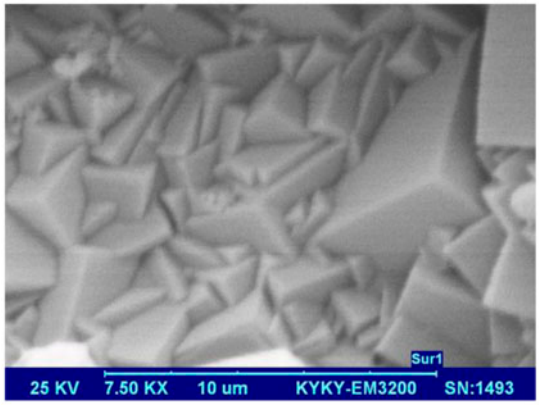


Fig. 3. Top SEM image of synthesized membrane after 3 h.

The XRD pattern of synthesized zeolite membranes is depicted in Fig. 4. As it is shown, pure LTA phase is formed during membrane synthesis after 3 h. The characteristic peaks associated with the mullite support are also detected and shown in Fig. 4. The peaks detected at 2-$\theta$ of 7, 10, 12, 16, 21, 24, 27, 30, and 34 belong to the LTA structure, and the peaks detected at 22, 26, 35, and 41 are for mullite support [6].

### 3.2. Effect of synthesis duration on membrane performance

Influence of synthesis duration on separation performance of zeolite membranes was also evaluated. The results for PV dehydration of ethanol are listed in Table 1. It can be seen that the synthesis duration of 1.5 h is not enough for the synthesis of high-quality membrane because it does not offer satisfactory separation factor. Existence of defects is confirmed from PV results. The results show that increasing the synthesis duration results in enhancement of separation factor, but decreases the permeation flux of water across the membranes. The results also reveal that the

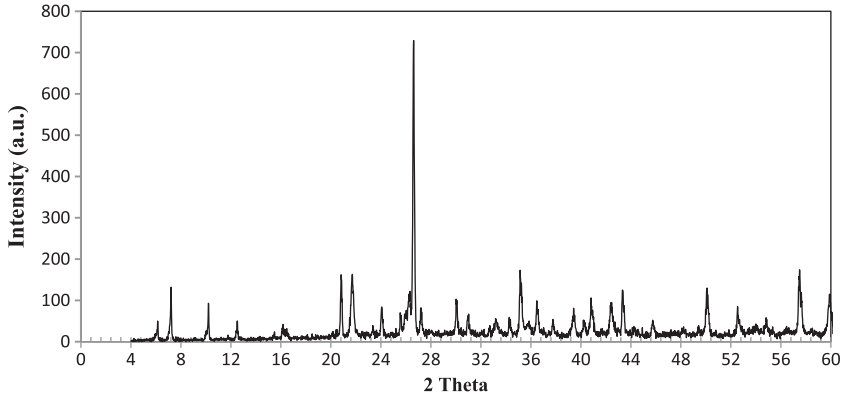


Fig. 4. XRD pattern of synthesized LTA membranes after 3 h.

Table 1
Effect of synthesis duration on membrane performance in dehydration of ethanol. Ethanol concentration in the feed = 97.5 wt.%

| Synthesis duration (h) | Permeation flux (kg $m^{-2}$ $h^{-1}$) | Separation factor |
|---|---|---|
| 1.5 | 12.2 | 25 |
| 3 | 2.6 | 12,600 |
| 4 | 1.1 | 13,200 |

best separation performance is obtained at the synthesis duration of 3 h. At higher synthesis temperatures, the thickness of membrane increases which caused the reduction of permeation flux. For choosing the best conditions for membranes synthesis, both flux and separation factor must be taken into account.

### 3.3. Effect of feed concentration on membrane separation performance

Fig. 5 indicates the effect of water content in the feed solution on the permeation flux and separation factor for dehydration of ethanol solutions by the LTA-type zeolite membranes synthesized at 100°C for 3 h. The results of PV reveal that the permeation flux increases with increase in water content in the feed. This could be attributed to the enhancement of concentration gradient across the membrane which in turn results in enhancement of mass transfer flux. Furthermore, with decreasing water concentration in the feed, few active sites on the membrane surface are occupied by water and this reduces water permeation through the membrane pores. On the other hand, separation factor decreases with increase in water content in the feed.

The PV results obtained in this work are compared with other PV results reported by other authors. The results are listed in Table 2. As it is observed, the comparisons confirm that the developed method of synthesis in this work is simple and inexpensive to prepare high-quality zeolite membranes for dehydration of alcohols.

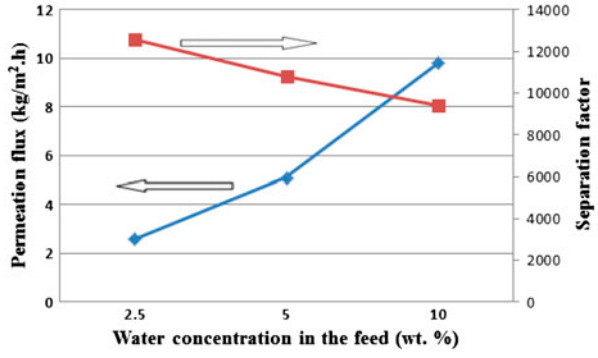


Fig. 5. Effect of water concentration in the feed on separation performance of membranes. Synthesis duration = 3 h, synthesis temperature = 100°C.

## 4. Conclusions

Synthesis and characterization of LTA-type zeolite membranes for dehydration of ethanol is carried out in this work. To find out the optimum conditions for synthesis of high-quality membranes, the synthesis duration of hydrothermal treatment was changed. The prepared membranes were characterized by scanning electron microscopy and XRD to ensure the synthesis of LTA phase and membrane formation on support. Porous mullite discs were used as support for secondary growth of membranes. Three synthesis durations of 1.5, 3, and 4 h were considered in the experiments. The results for PV dehydration of ethanol showed that the synthesis duration of 1.5 h is not enough for the synthesis of high-quality membrane because it does

Table 2
Comparisons of PV results between this work and previous publications for dehydration of ethanol using LTA zeolite membranes

| Support | Method of synthesis | Water content in feed (wt.%) | Flux (kg $m^{-2}$ $h^{-1}$) | Separation factor | Ref. |
|---|---|---|---|---|---|
| Titania | Continuous | 8 | 1.2 | 8,500 | [12] |
| Alumina | Semi continuous | 10 | 0.5 | 16,000 | [13] |
| Alumina | Centrifuge | 8 | 0.5 | 600 | [14] |
| Alumina | Microwave heating | 6 | 4.36 | 8 | [15] |
| Mullite | Secondary growth | 2.5 | 2.6 | 12,600 | This work |

not offer satisfactory separation performance. The results of PV experiments also revealed that the best zeolite membranes were prepared for the synthesis duration of 3 h and at synthesis temperature of 100˚C. At these conditions, an integrated and dense zeolite layer is deposited over the support surface.

## Acknowledgment

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## List of symbols

$J$ — total permeation flux (kg m$^{-2}$ h$^{-1}$)
$m$ — mass of permeate (kg)
$S$ — membrane surface area (m$^2$)
$t$ — permeation time (h)
$x_i$ — mass fraction component $i$ in the feed
$y_i$ — mass fraction of component $i$ in the permeate
$\alpha_i$ — selectivity for component $i$ with respect to component $j$

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