Dehydration of Natural Gas Using Synthesized Chabazite Zeolite Membranes

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Abstract

Chabazite zeolite membranes were synthesized for their potential application in dehydration of natural gas. The membranes were prepared using secondary growth method on porous $\alpha$-alumina substrates. Hydrothermal treatment was applied for the synthesis of chabazite seeds. The membranes were synthesized at four temperatures of 100, 120, 140, and 160°C; and duration of 20 h. Separation performance of as-synthesized membranes was evaluated through permeation of water vapor and methane as single gas. Moreover, the structure and morphology of as-synthesized chabazite zeolite membranes as well as seeds were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), and dynamic light scattering (DLS). The results revealed that the optimum temperature for the synthesis of chabazite membranes is 140°C while at lower and higher temperatures, lower separation performances were observed. At the optimum synthesis temperature, an ideal selectivity of 23 was obtained for water vapor/methane, while a thin and integrated chabazite zeolite layer of about 5 $\mu$m in thickness was synthesized over the surface of alumina substrate.

Keywords: Zeolite Membrane, Chabazite, Natural Gas, Dehydration, Secondary Growth

1. Introduction

Natural gas is one of the most important sources of fuel that is produced and purified in large amounts. Natural gas contains methane as the main component and other impurities. Common impurities of natural gas include carbon dioxide, hydrogen sulfide, and water. Water is the most common impurity of natural gas that can cause some unwanted problems in the processing and transport of natural gas [1]. Currently there are two common methods for separation of water vapor from natural gas, i.e. dehydration. The latter includes absorption using glycol solutions and adsorption using solid desiccants. These separation processes for dehydration of natural gas suffer from some disadvantages such as consumption of much energy, high capital costs, and difficult scale up [1,2].

Development of an alternative separation method with great potential and application in dehydration of natural gas is a subject of great interest. Membrane technology has shown great ability in removal of vapor from gas streams. Various membrane processes have

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been investigated in gas separation including zeolite membranes, and membrane contactors [2-6]. Polymeric membranes also have potential applications for removal of water vapor from natural gas in which hydrophilic polymers can be used for the synthesis of membranes. However, polymeric membranes suffer from some drawbacks such as low chemical and thermal stabilities, and short life time. Moreover, polymeric membranes are not strong enough to absorb operational shocks. These disadvantages of polymeric membranes make ceramic membranes the preferred choice for dehydration of natural gas.

Another efficient means that can be used for the removal of vapor from gas streams is zeolite membranes. Zeolites are porous materials made of aluminosilicates with regular pore dimensions in the order of molecular size. Zeolite membranes are formed on porous substrates such as alumina, titania, and zirconia via appropriate synthesis methods [7,8].

Different types of zeolites have been used as membrane for separation of gas and liquid mixtures such as X, Y, T, MFI, MOR, CHA, and A [9-14]. Among the common zeolites, CHA-type has shown great potential for the purification of gas streams. Chabazite, which belongs to the family of CHA-type zeolites, has been successfully used for the purification of liquid mixtures. The pore size of chabazite zeolite is estimated to be about 0.37 nm. Considering the kinetic diameter of H2O (0.26 nm), and also methane (0.38 nm), chabazite zeolite can selectively separate water vapor from methane by molecular sieving mechanism. Moreover, chabazite is a hydrophilic zeolite which makes it attractive for the absorption of water vapor from gas streams [4,5,15 and 16].

A few studies on the synthesis and application of chabazite zeolite membranes have been reported in literature. Chabazite membrane was first introduced by Hasegawa et al. [17,18] who synthesized and characterized the membranes via hydrothermal treatment. In their works, chabazite seeds were synthesized by transformation of H form of zeolite Y in the presence of K+ ions. The separation performance of chabazite membranes was evaluated in dehydration of alcohols using pervaporation, and high separation factors were achieved. Li et al. [6] prepared chabazite zeolite membranes without the aid of strontium ions in the synthesis gel. They claimed that their developed procedure was more economical than that reported previously by Hasegawa group for the synthesis of chabazite membranes. They also characterized the chabazite membranes for pervaporation dehydration of alcohols. The results showed poor separation performances compared to the membranes synthesized by Hasegawa et al. [19,20].

The main purpose of the present study is to synthesize chabazite zeolite membranes applicable to the dehydration of natural gas. The membranes are synthesized via secondary growth method with the aid of chabazite powder as seeds. The as-synthesized membranes are then characterized using solid characterization and permeation tests. To the best knowledge of the authors, there is no study on the synthesis and application of chabazite zeolite membranes on dehydration of methane as a model of natural gas.
2. Materials and methods

2-1. Materials

Sodium aluminate (BDH), aluminum nitrate (Fluka), strontium nitrate (Poch), colloidal silica (Ludox 40%, DuPont), sodium silicate (Merck), potassium hydroxide (KOH, 85 wt%, Merck), sodium hydroxide (pellet, 99 wt%, Merck), ammonium chloride (Merck), and deionized water were used for the synthesis of chabazite seeds and membranes.

2-2. Synthesis of chabazite zeolite seeds

Chabazite zeolite is prepared from NaY zeolite which belongs to FAU-type of zeolites. Indeed, NaY is considered as starting material for the synthesis of chabazite. Zeolite NaY was synthesized using a gel with chemical formula of 4.62Na2O:Al2O3:10SiO2:180H2O in a molar basis. The synthesis procedure was the same as reported by Robson [21].

Prior to synthesis of chabazite membranes, chabazite seeds are required for secondary growth of zeolite membranes. In this work, chabazite zeolite was synthesized from decomposition of zeolite Y and was ion-exchanged to prepare a fully-exchanged potassium chabazite zeolite. The HY zeolite (proton form of zeolite Y) was prepared by the use of NH4Cl as an ion exchange reagent. NH4Cl was completely dissolved in DI water, and afterward zeolite NaY was added to the solution. The resulting suspension was stirred at 90°C for 1 h, filtered and washed with DI water. The ion exchange process was repeated three times to ensure the formation of fully-exchanged zeolite Y. The resulting solid was dried at 100°C for 5 h. To complete the ion exchange operation, the dried powder was then calcined at temperature of 500°C to obtain the final H-form of zeolite NaY. The obtained HY zeolite is used as starting material for the preparation of chabazite in a hydrothermal treatment. Chabazite zeolites were prepared according to the solid-phase conversion route reported in literature [21].

2-3. Membrane synthesis

Chabazite zeolite membranes were synthesized using secondary growth method. The latter method has shown great reproducibility in the synthesis of high-quality zeolite membranes [7,12,17,18,22]. Porous discs of α-Al2O3 with diameter of=21 mm, and porosity of=45% were used as substrates. The alumina substrates were covered with the chabazite seeds. The seeding was carried out in a suspension of 1 wt% of chabazite zeolite during 30 s. The seeded substrates were then taken off from the zeolite suspension, and dried at 100°C.

Chabazite zeolite membranes were prepared using the gel formula of 12SiO2:1Al2O3:6K2O:1SrO:780H2O, on a molar basis [19]. The detailed procedure for the preparation of synthesis gel is reported elsewhere [17-20]. The chabazite membranes were synthesized at four temperatures, and a fixed synthesis duration of 20 h. The applied temperatures were 100, 120, 140, and 160°C. At the end of the membrane synthesis, the membranes were taken out, washed with DI water and air dried at ambient temperature.
2-4. Methods of characterization

The chabazite zeolite seeds were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (D5000, 35 kV, 20 mA, $\lambda=1.54056$ Å, Siemens) with Cu radiation. Morphology of the chabazite zeolite seeds and membranes were characterized by Scanning Electron Microscopy (SEM), Vega 3 Tescan. Particle size distribution of zeolite seeds was obtained via a Malvern apparatus model 3600 with Laser wavelength of 633 nm.

2-5. Gas permeation setup

Separation performance of the synthesized chabazite zeolite membranes was investigated via permeation of water vapor and methane through the membranes. The experimental setup used for the permeation experiments is illustrated in Fig. 1. Permeation of methane was measured at a transmembrane pressure of 1 bar across the membrane, and ambient temperature. The permeation measurements were conducted using a home-made membrane module sealed by means of polymeric o-rings to prevent any probable leakage of gas. The membrane module was made of PTFE with an active radius of 15 mm. The flow pattern for the measurement of water vapor was cross flow while dead-end pattern was used for the methane permeation experiments.

For measurement of water vapor permeation, an ultrasonic vapor generator was used to produce the water vapor at the ambient temperature and pressure. The downstream side was evacuated using a vacuum pump (JB, USA), and permeated vapor was condensed using a cold trap immersed inside liquid nitrogen. The picture of experimental setup as well as membrane module is shown in Fig. 2.

![Figure 1. Schematic representation of the gas permeation experimental setup.](image1)

![Figure 2. Experimental setup used in dehydration experiments, and membrane module.](image2)
3. Results and discussions

3-1. Characterization of zeolite seeds

Formation of zeolite chabazite phase was verified by XRD analyses. Since zeolite chabazite belongs to the CHA-type zeolite family, characteristic peaks associated with the CHA phase should be identified in the XRD pattern (assigned as CHA in Fig. 3). X-ray diffraction patterns for the chabazite seeds are shown in Fig. 3. As it is clearly seen, pure zeolite chabazite crystals were synthesized using the developed synthesis procedure.

Fig. 4 also illustrates SEM micrograph of as-synthesized chabazite zeolite seeds. As it is observed, the crystal structure of chabazite zeolite is dish-shape. As reported by Robson [21], the crystal habits of chabazite zeolite is either multifaceted or hexagonal platelets. The crystal size of zeolite chabazite is estimated by DLS observations. As shown in Fig. 5, chabazite crystal sizes are in the range of 300–1000 nm.

3-2. Influence of synthesis temperature on the performance of membranes

Separation performance of synthesized chabazite zeolite membranes were characterized in dehydration of natural gas. Methane was used as a model of natural gas in permeation experiments. The permeation of water vapor and methane as well as ideal selectivities of vapor/methane were determined and reported. The influence of synthesis temperature on the permeation of water vapor and methane are shown in Fig. 6. As it is observed, the chabazite membranes synthesized at temperatures of 100 and 120°C
show the highest gas and vapor permeation. It is also seen that permeations of water vapor are higher than those of methane for both synthesis temperatures. This behavior could be attributed to the hydrophilicity nature of chabazite zeolite which increases the adsorption of water vapor at the feed/zeolite interface. Moreover, the kinetic diameter of water vapor (0.26 nm) is lower than kinetic diameter of methane (0.38 nm) which causes faster diffusion of water vapor through the chabazite zeolite pores (0.37 nm).

Increasing synthesis temperature up to 140°C reduces the gas and vapor permeations considerably. Further increase in the synthesis temperature up to 160°C increases gas and vapor permeations slightly, so that the lowest gas and vapor permeations are observed for the chabazite membranes synthesized at temperature of 140°C.

![Figure 6](image1.png)

**Figure 6.** Effect of synthesis temperature on vapor and CH₄ permeances.

On the other hand, influence of synthesis temperature on the ideal selectivity of water vapor/methane is shown in Fig. 7. Ideal selectivity of vapor/methane slightly increases when the synthesis temperature increases from 100 to 120°C. Afterward, the ideal selectivity increases drastically as the synthesis temperature reaches 140°C. The ideal selectivity decreases thereafter for the synthesis temperatures up to 160°C.

![Figure 7](image2.png)

**Figure 7.** Effect of synthesis temperature on ideal selectivity of vapor/CH₄.

The behavior of chabazite membranes synthesized at various temperatures was analyzed using scanning electron microscopy (SEM). SEM images from the surface of chabazite zeolite membranes synthesized at temperatures of 120 and 140°C are shown in Figs. 8 and 9, respectively. For chabazite membranes synthesized at temperature of 120°C (Fig. 8), it is clearly seen that a complete zeolite layer is not formed on the surface of substrate. This observation could be attributed to the low synthesis temperature which is not good enough for the integration of zeolite layer (membrane).

SEM image of the synthesized chabazite zeolite membranes at temperature of 140°C is shown in Fig. 9. As it is seen, a dense and integrated zeolite layer has been deposited on the surface of the substrate at this temperature. This membrane also shows the best separation performance in permeation of water vapor and
methane (see Fig. 7). Moreover, a change in the morphology of chabazite membrane is observed when the synthesis temperature increases from 120 to 140°C. At low synthesis temperature (120°C), dish-shape crystals of chabazite can be observed, while for the membrane synthesized at 140°C, integrated crystals are thicker and different in shape (see Fig. 9).

It can thus be concluded that synthesis temperature has a dominant influence on the morphology and performance of the synthesized zeolite membranes. Indeed, temperature controls the rate of crystal growth during the membrane formation in the secondary growth method. The rate of crystal growth increases with enhancement of temperature. However, increasing synthesis temperature is not always a favorable factor for the synthesis of high-quality zeolite membranes because temperature needs to be controlled to avoid unwanted phenomena such as formation of cracks or pinholes. The latter could be the main reason for poor separation performance of chabazite membranes synthesized at temperature of 160°C.

SEM image of the cross section of the chabazite membranes synthesized at temperature of 140°C is shown in Fig. 10. As it is seen, a dense zeolite layer with a thickness of about 5 microns has been successfully formed on the surface of substrate. Moreover, Fig. 10 reveals that no significant intrusion of zeolite layer into the pores of substrate has occurred. The latter is an unwanted phenomenon in preparation of composite membranes which reduces the permeation drastically.

4. Conclusions

Effect of synthesis temperature on the gas and vapor permeations as well as on the ideal selectivity of vapor/methane for the synthesized chabazite zeolite membranes was studied. The membranes were synthesized via secondary growth method. The chabazite seeds for the membrane synthesis were
obtained through ion-exchange and recrystallization of zeolite Y. The membranes and seeds were characterized by SEM, XRD, and DLS analyses. The separation performance of chabazite membranes was investigated via single permeation of water vapor and methane through the membranes. The results revealed that the maximum ideal selectivity was obtained at the synthesis temperature of 140°C. This is due to the fact that the zeolite layer is densely deposited on the whole surface of the support. Increasing the synthesis temperature up to 160°C results in a reduction of the performance of membranes. At the optimum conditions, an active zeolite layer with a thickness of 5 µm was formed over the substrate, and an ideal selectivity of 23 for vapor/methane was obtained for the optimum membrane synthesized at temperature of 140°C.

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References


