The effect of zeolite suspension concentration on the formation of seed layer via vacuum seeding prior to NaX zeolite membranes growth

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Abstract. In the present work, NaX zeolite membranes were synthesized via secondary growth using vacuum seeding method. NaX zeolite suspension solution for vacuum seeding was prepared at various concentration and the resultant seeded supports with homogeneous coverage were selected for hydrothermal synthesis. The resultant membranes were characterized using XRD, SEM and EDX analysis. The XRD results showed that NaX zeolite membranes were successfully formed and the SEM images revealed that continuous zeolite membrane layer was obtained.

1. Introduction

Natural gas often contains impurities such as carbon dioxide (CO2) and nitrogen (N2) which need to be removed in order to meet the gas pipeline specification of less than 2 to 4% [1]. CO2 can cause corrosion in the presence of water and reduces the heating value of natural gas. Conventional processes for the removal of CO2 usually use amine absorption and polymeric membrane separation. However, processing high pressure natural gas can be expensive for amine absorption [2] and polymeric membranes are known to be susceptible to plasticization by CO2 resulting in reduction of selectivity [3]. Porous inorganic membrane such as zeolite membrane which contain nano pores, are favourable for CO2 separation from CH4 because of their chemical resistance to CO2 induced plasticization and superior selectivity compared to polymeric membranes [2,4-5]. N2 presence in natural gas also reduces the heating value of the gas, and thus required removal. Cryogenic technology is another mature technology used for N2 removal from natural gas. However, this technology is expensive and energy intensive. Although polymeric membrane have been used for N2 removal from CH4 [6], its performance is low compared to the zeolite membrane.

Among all types of zeolites, the most interest for zeolite membrane studies has been focused on these 8 types of zeolite framework i.e., MFI, LTA, FAU, CHA, T, DDR, MEL, and AEI [7]. FAU-type zeolite which includes NaX (Si/Al ratio of 1-1.5) and NaY (Si/Al ratio >1.5) is within the large pore zeolite group with 12-membered rings and of approximately 0.74 nm in diameter. Because of its large pores, FAU membranes offer high CO2 flux at reasonable selectivity. It is able to separate CO2 and N2 from other gases due to its strong absorption affinity resulting in high selectivity for CO2/CH4 and moderate selectivity for N2/CH4 gases [5,8]. Another important advantage of FAU zeolites is that the preparation does not always require organic structure directing agent (SDAs), thus the cost of fabrication is cheaper compared to the other types of zeolite membrane. In addition, the removal of
SDA via calcination at high temperature is not required and thus, less energy are involved during the fabrication process [7]. Besides, heat induced cracks on the prepared membrane can be eliminated. Successful CO₂/CH₄, CO₂/N₂, CO₂/H₂ and N₂/CH₄ separation by FAU membrane have been reported [9-12].

One of the synthesis method that is widely applied for the preparation of zeolite membrane is secondary growth method where a layer of zeolite seeds is deposited on the membrane support prior to hydrothermal growth [13]. Similar techniques are also applied for the synthesis of FAU zeolite membrane. There are two challenging issues related to the synthesis of FAU zeolite membrane by secondary growth method, which are the preparation of colloidal suspension of zeolite particles, and homogeneous deposition of seeds onto the support surface [14]. Dip coating method is the most commonly used technique for seeding. However, it is reported that continuous seed layers are difficult to achieve as the zeolite seeds cannot closely attach to the support and the colloidal suspensions easily dribble when the supports are withdrawn [14]. Vacuum coating is another seeding method which has been applied by various researchers for the preparation of seed layer. This technique involved dead-end filtration and cross flow filtration method [15]. Vacuum seeding via dead end or cross flow mode can potentially allow a complete coverage and homogeneous distribution of seeds on the support surface [15]. However, proper technique and parameters are required in order to avoid excessive crystals accumulation and thus, uniform coverage of seed on the support surface can be obtained.

In this paper, synthesis of NaX zeolite membrane via secondary growth using vacuum seeding is reported. The effect of different zeolite suspension concentrations on the formation of seed layer via vacuum seeding method prior to the growth of NaX zeolite membranes is studied.

2. Experimental

2.1. Preparation of NaX zeolite seed

NaX zeolite powder was synthesized by in situ crystallization following procedure as described in literature [5]. The solution for the synthesis of zeolite powder was prepared by mixing sodium silicate, sodium aluminate, sodium hydroxide (NaOH) and deionized (DI) water with composition of Al₂O₃ : 4.8SiO₂ : 17Na₂O : 975H₂O. Then, the solution was stirred for 4 hours in order to age the mixture. The synthesis gel was filled into autoclave and hydrothermal synthesis was carried out at 90°C for 24 hours. After synthesis, the resultant crystals were filtered and washed with DI water as many times as required to reduce the filtrate pH to less than 10. The filtered crystal was collected and dried in oven at 90°C.

2.2. Preparation of zeolite seed layer and synthesis of NaX zeolite membrane

For the preparation of zeolite seed layer, a suspension of zeolite crystal was prepared by dispersing between 0.25 to 1.0 g NaX zeolite powder in 100 to 200 mL deionized water followed by an ultrasonic treatment for 60 minutes in order to avoid the aggregation of particles. Four different zeolite suspension solutions with concentration of 0.25 g/100 mL, 0.5 g/100 mL, 0.5 g/200 mL and 1.0 g/200 mL were prepared. The seed was attached onto the disc-type support via dead end vacuum filtration method. Table 1 shows the seeded supports prepared in the present work.

| Seeded Support | Concentration of Zeolite Suspension | Seeding Duration (minutes) |
|----------------|-----------------------------------|---------------------------|
| NaX-sA         | 0.25 g/100 mL                     | 3                         |
| NaX-sB         | 0.50 g/100 mL                     | 3                         |
| NaX-sC         | 0.50 g/200 mL                     | 6                         |
| NaX-sD         | 1.00 g/200 mL                     | 6                         |
The NaX zeolite membrane was synthesized using the same synthesis solution and hydrothermal synthesis parameters as those used for the preparation of NaX particles. Seeded disc support was placed in autoclave filled with synthesis solution prepared using the same molar composition that were used for the synthesis of NaX zeolite powder. Hydrothermal synthesis was carried out at 90°C for 24 hours. After synthesis, the membrane was washed with DI water and dried in air at ambient temperature.

The morphology of NaX zeolite membranes was determined by using scanning electron microscopy, SEM (Hitachi TM 3000). The powder samples collected were characterized using X-ray diffraction (XRD) and energy dispersive X-ray (EDX) analysis was used to confirm the Si/Al ratio of the sample.

### 3. Results and discussion

#### 3.1. Effect of vacuum seeding solution concentration on the formation of seeded layer

Figure 1 shows the SEM images of the distribution of zeolite seed layer on disc support surface using different suspension solution concentration. Referring to Figure 1(a) and 1(c), it can be observed that low to medium zeolite seed coverage are obtained. From the SEM images shown in Figure 1, zeolite suspension solution with concentration of 0.5 g/100 mL and 1.0 g/200 mL resulted in homogenous coverage of seeded layer (Figure 1 (b) and 1 (d)). Both of these support layer (NaX-sB and NaX-sD) are seeded with the same zeolite suspension solution concentration, but with different volume and amount of seed used, as well as the seeding duration.

![Figure 1. Distribution of zeolite seed layer on disc support surface using different zeolite suspension concentration of (a) 0.25 g/100ml (NaX-sA), (b) 0.5 g/100ml (NaX-sB), (c) 0.5 g/200ml (NaX-sC), and (d) 1.0 g/200ml (NaX-sD).](image)

#### 3.2. Formation of NaX zeolite membrane

Seeded supports with homogeneous seed layer, NaX-sB and NaX-sD were proceeded to NaX zeolite membrane growth via hydrothermal method. Figure 2 shows the SEM images of NaX zeolite membrane (NaX-B) growth on NaX-sB while Figure 3 shows the SEM images of NaX membrane (NaX-D) growth on NaX-sD. From Figure 2, it can be observed that the NaX zeolite membrane grown on NaX-sB exhibited full coverage and continuous zeolite membrane layer.

On the other hand, referring to Figure 3, non-homogeneous growth of NaX-D zeolite membrane is observed. This is mainly because of the zeolite seed layer coated during vacuum seeding was detached from the support surface. NaX-sD was coated with double the duration of NaX seed compared to NaX-sB and thus, resulted in thicker zeolite seed layer. According to Huang et al. [14] coating time and the zeolite seed suspensions concentration could affect the properties of the seeded layer and thus, the formation of the zeolite membrane. Longer coating duration causes the seeded layer to become too thick and crack can easily form which resulting in poor zeolite membrane formation.

On the contrary, shorter coating time produced non-continuous zeolite seed layer which could also affect the homogeneous growth of the zeolite membrane. In this case, a thicker zeolite seed layer was easily detached from membrane support during hydrothermal synthesis which resulted in membrane defects. Overall, from the result obtained in this work, zeolite suspension solution with concentration of 0.5 g/100 mL and coating duration of 3 minutes were found to be the most suitable seed solution concentration for vacuum seeding in order to obtain well intergrowth zeolite layer.
Figure 2. NaX-B zeolite membrane grown on seeded support formed using 0.5 g/100 mL of zeolite suspension solution at (a) 100x magnification, (b) 500x magnification and (c) 1000x magnification.

Figure 3. NaX-D zeolite membrane grown on seeded support formed using 1.0 g/200 mL of zeolite suspension solution at (a) 100x magnification, (b) 500x magnification and (c) 1000x magnification.

Figure 4 shows the XRD results for zeolite powder collected after hydrothermal synthesis of NaX-B and NaX-D zeolite membranes. The XRD pattern obtained was also compared with the XRD pattern obtained for the commercial zeolite NaX (Tosoh Corp., Si/Al ratio of 1.25). It can be seen from Figure 4 that the same zeolite phases were produced among these three samples. The resulting Si/Al ratio for NaX-B and NaX-D are 1.28 and 1.36, respectively, which confirmed the formation of NaX zeolite.

Figure 4. XRD results for NaX zeolite (a) NaX-B, (b) NaX-D and (c) Commercial NaX.

4. Conclusion
In this work, NaX zeolite membrane have been synthesized via secondary growth using vacuum seeding method and the structure of the zeolite membranes have been verified by XRD analysis. The
effect of zeolite suspension concentration on the formation of seed layer prior to membrane growth was studied. Zeolite suspension solution with concentration of 0.5 g/100 mL was found to be the most suitable seed solution concentration for vacuum seeding in order to obtain well intergrowth zeolite layer. However, it is noted that, this concentration is suitable for the surface area of membrane support used for this study. Membranes with different (higher or lower) surface area might need different concentration of zeolite suspension solution that is suitable to achieve thin and homogenous coverage zeolite seed layer. Further work will be focusing on the gas permeation testing of the membrane in CO₂/CH₄, CO₂/N₂ as well as N₂/CH₄ separation.

5. Acknowledgment
The financial support provided by PETRONAS and the technical supports provided by Institute of Contaminant Removal and PETRONAS are highly appreciated.

6. References
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