Synthesis of least defect NaY membranes: Defining optimum heating and cooling rates of hydrothermal treatment (HT) and application of zeta potential measurement via different seeding methods

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INTRODUCTION

Zeolites is a type of microporous material which built of aluminium and silicon atoms that are tetrahedrally connected within each other to form a crystal framework. Due to the excess of aluminium atoms in the framework, it will has an excess of negative charges that are balanced by positive cations e.g. Na+, H+, Ca2+ etc. This crystal framework, which consists of tetrahedral aluminosilicates, forms extremely narrow pore sizes of molecular dimensions which able to show high molecular separations, chemical and thermal stabilities that have potential applications to be used as separators, reactors, sensors, catalysis and other fields (Mastropietro et al., 2015; Lang et al., 2011; Li et al., 2013; Sato et al., 2008a; Wang and Keller, 2009; Chew et al., 2011; Kita et al., 2001). Among the zeolite membranes that suitable for the separation of gases are FAU, MFI, A-type, DDR, T-type and SAPO-34 membranes (Chew et al., 2011; Wong et al., 2001; Hasegawa, Watanabe, et al., 2002; Hasegawa, Tanaka, et al., 2002; Gu et al., 2005; Sato et al., 2008b). Several methods are available in the preparation of zeolite membranes which are the direct crystallization method (in-situ), secondary growth method and vapour phase transformation method, in which secondary growth method has showed the most effective method in preparing least defects zeolite membranes as compared to the other methods (Cheng et al., 2004; Wei et al., 2008; Ma et al., 2014; Li et al., 2013; Feng et al., 2015; O’Brien-Abraham and Lin, 2010; Kosinov et al., 2016; Gu et al., 2005; Kuzniatsova et al., 2007; Science and Physics, 2004). In secondary growth method, it involves the process of attaching zeolite seeds crystals on the surface of the support or substrate which in this case, these seeds will facilitate the formation of zeolite membranes. This approach also serves to decouple the nucleation and the crystal growth steps as compared to in-situ process (Feng et al., 2015; O’Brien-Abraham and Lin, 2010; Kosinov et al., 2016; Cheng et al., 2004; Li et al., 2013).

MATERIALS AND METHODS

During this stage, heating and cooling rates (°C/hr) were varied in order to study their effects towards formation of zeolite membrane with least defects. Characterizations were performed by using X-Ray Diffraction (XRD) in order to identify degree of crystallization and amount of impurities while Scanning Electron Microscopy (SEM) was used in order to study surface morphology of the samples. From this study, it was found that densification effect from different seeding methods played important factor in forming zeolite membranes with least defects. Accordingly, suitable heating and cooling rates were required in order to optimize the growths of zeolite NaY seeds to form zeolite layer on top of the alumina support. In this case, due to thermal mismatch between the substrate and zeolite material, it could form some cracks on top of the alumina support. Thus, by implementing optimum heating/cooling rate, a zeolite NaY membrane with least amount of defects i.e. cracks and pinholes could be achieved with less degree of impurities i.e. zeolite NaP during HT process.

Keywords: NaY, zeolite membrane, zeta potential, dip-coating, spin coating, vacuum coating, seeding, cracks, pinholes

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There are 2 main issues in synthesizing zeolite membrane by secondary growth method which are on the methods applied in coating the seeds onto the support and the preparation of seeding solution (colloidal suspension of zeolite seeds) (Science and Physics, 2004). Accordingly, seeding quality is essential to affect the quality and reproducibilities of the synthesis process since it will affect the quality of the membranes that will be formed (Algiéri et al., 2005; Liu et al., 2011; Zhilin and Shuai, 2015; Kuzniatsova et al., 2007). Among seeding methods reported to be used in this secondary growth method of zeolite membranes are dip-coating, vacuum suction seeding, rub coating, spin coating, spray coating, cross-filtration coating, cationic polymer treatment and electrophoretic deposition (Liu et al., 2011; Peng et al., 2013; Gu et al., 2005; Wang et al., 2011). Nevertheless, dip coating method has found to be the simplest and widely used method for coating the supports with seeds as it is not time consuming and costly support pretreatments are not required. However, it requires more than one seeding layer in order to obtain uniform seeding layer due to negative effect of gravitation force (Algiéri et al., 2009). On the other hand, enhanced seeding method such as spin coating and vacuum coating may not suitable for various shapes of the support as well as they will be resulted with excessive crystal seeds accumulations.

Secondly, on the preparation of colloidal suspension of zeolite seeds, these zeolite particles need to be in stable state and properly dispersed in the solution before the seeding process can be performed. Instability in the dispersions of the zeolite particles will lead to agglomerations and hence, causing inhomogeneous coverage of seeds on the surface of the support e.g. formations of pinholes and dents (Kuzniatsova et al., 2007). This is crucial since uniform coverage of seeds onto the surface of the support will assist in the formation of continuous and least defects of zeolite membranes and hence, avoiding any formations of microcracks during subsequent hydrothermal (HT) process. Colloidal stability can be improved by several methods such as application of surface chemical modification of the zeolite crystals by charged polymers to achieve electro-steric colloidal stabilization and utilization of spontaneous charge-stabilization by adjusting the aqueous dispersion medium pH (Kuzniatsova et al., 2007). However, pH adjustments of the seeds solution are more widely used as the channels to modify the charges of the colloidal particles which in relation to the zeta potential of the particles (Alwani et al., 2013; Kuzniatsova et al., 2007). In general, zeta potential is another parameter which is crucial in controlling the dispersion stabilities of the particles, whereby according to DLVO theory, it relates to the energy barrier that resulted from the electrical double layer force of the Van Der Waals force (Xu et al., 2003; Wang and Keller, 2009). Thus, particles with high zeta potential value of similar charge, either positive or negative, will repel towards each other and hence, obtaining more stable suspension stability of the particles i.e. <-30mV and >+30mV will both be considered as a high zeta potentials (Alwani et al., 2013).

Likewise, heating and cooling rates that utilized during the synthesis process are also important factors in ensuring the synthesized zeolite membranes are free from cracks and defects. Zeolite films usually exhibit negative thermal expansion upon heating while the alumina substrate that used as the support will expand upon heating which later contributes to thermal mismatch between these two materials (Kosinov et al., 2016). This thermal mismatch between support and the zeolite film causes mechanical stress during heating and strain during cooling which responsible for the crack formations of the zeolite membranes (Gualtieri, 2006; Kosinov et al., 2016; Das et al., 2010; O’Brien-Abraham and Lin, 2010; Severance, 2014; Peng et al., 2013). These cracks are undesirable since they can offer several and selective transport pathways and hence, resulting in Knudsen diffusion to govern the separation mechanism of the zeolite membranes (O’Brien-Abraham and Lin, 2010). Several methods are available to reduce the effect of this thermal mismatch such as introduction of intermediate layer between the alumina substrate and the zeolite film (Fu et al., 2017; Das et al., 2010; Das et al., 2012; Xu et al., 2018; Dey et al., 2013; Huang et al., 2012b; Huang et al., 2012a). Likewise, another simple solution is by manipulating the heating and cooling rates which in this case, the rate of zeolite growth during heating process and shrinking while cooling would be properly controlled.

In this study, several seeding methods including dip-coating, spin coating and vacuum coating were investigated during the preparation process i.e. seeding process of the zeolite membranes whereby effect of pHs and seeds concentrations (wt%) were included in this study. By selecting proper pHs conditions inline with its zeta potential values together with optimized suspension concentrations, better dispersions of zeolite NaY seeds could be formed on the surface of alumina support. Additionally, heating and cooling rates during the hydrothermal (HT) synthesis process were also being investigated in order to form zeolite NaY membrane with less defects i.e. free from pinholes and cracks.

**EXPERIMENTAL**

**Materials**

All chemicals were directly used as received without any further purifications. The reactants used were Sodium Hydroxide (NaOH), Sodium Aluminate (Fischer, 53wt% Al2O3; 42.5wt% Na2O), Colloidal Silica (Ludox, AS-40), commercial zeolite NaY powder (HSZ-320NAA, SiO2/Al2O3 = 5.5; Tosoh) and deionized water (DI).

**Preparation of zeolite NaY seeds**

Precursor solution with molar composition of Al2O3: 12.8 SiO2: 17 Na2O: 975 H2O was used for hydrothermal synthesis of zeolite NaY powders. During this procedure, identified amounts of NaOH, Sodium Aluminate and DI water were mixed. The resultant solution was heated at 70°C for 1h until a clear solution was obtained. After cooling down to room temperature, Colloidal Silica was added drop-wise and stirred until completely dissolved. After aging for 24 hours, the mixture was transferred to a Polypropylene (PP) bottle and then kept inside a heated oven at 90°C for 24 hours. After cooling down, the solid product was vacuum filtered and washed with DI water repeatedly in order to remove any unreacted chemicals until it’s pH reached 7-8.

The seeding solution for coating process was prepared by dispersing NaY zeolite powders into DI water. Mixing was enhanced by ultrasonic treatment for 1 hour prior to the coating process. Aqueous HCl and NaOH were added into the seeding solution in order to obtain seeding solution at different pHs.

**Seeding supports**

The supports were macroporous α-Al2O3 supports with thickness of 3 mm and diameter of 20 mm that produced by Nishimura Advanced Ceramics Co. Ltd., Japan with average pore diameter, porosity percentage and bulk specific gravity of 0.1μm, 35% and 2.6, respectively. Three seeding methods of dip-coating, spin coating and vacuum coating were applied. The dip-coating procedure was performed on the supports mounted on a computer controlled with linear speed before and after dipping at 15mm/s and 1mm/s with time of supports immersed in the seed solution for 5 minutes. As for spin coating procedure, the support was placed in Holmarch spin coating apparatus and angular rotation of 3000 rpm was employed for 60s while it was vacuum locked in order to remove excess solution. Lastly, for vacuum coating, the support was placed on support holder and operated under pressure difference of 100 kPa for the duration of 60s. For both spin coating and vacuum coating, liquid volume (seeding solution) equal to the pore volume of the support was used during the seeding procedure. The seeded supports were then dried at 50°C overnight in a drying oven.

**Synthesis of zeolite NaY membrane**

Similar procedure was applied from previous synthesis of zeolite NaY powders in preparing the precursor solution for zeolite NaY membranes. The seeded support was placed horizontally and faced downward in the polypropylene (PP) bottle which earlier was filled with the precursor solution. The crystallization process was conducted via hydrothermal treatment (HT) process at 90°C for 24 hours. Once completed, the PP bottle was allowed to cool down at 40°C overnight. Then, the zeolite membrane was washed several times with deionized (DI) water and finally dried at ambient air for 24 hours. Table 1 shows different conditions applied in samples preparations for this study.
Characterizations

The synthesized NaY zeolite membranes and powders were characterized by using several techniques including X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM)/Scanning Electron Microscopy (SEM) and Energy dispersive X-Ray spectroscopy (EDX). X-ray Diffraction (XRD) was conducted by using Cu-Kα radiation with 40kV and 30mA in the measuring range of 2θ: 5-50° at a scanning rate of 4 min⁻¹. XRD was used to analyze the crystallinity of the samples with respect to sample reference (Commercial NaY from Tosoh). The zeta potential of zeolite NaY colloidal suspension was determined as a function of pH by using Horiba SZ-100 Nanopartica series after 30 min ultrasonication of the suspension. The measurements for each sample were repeated for at least 3 times for each samples. The morphology of NaY zeolite powder and NaY zeolite membrane samples were observed through SEM/FESEM at room temperature. The images of the samples were captured by ejecting electron over the surface of the sample at an acceleration voltage of 15kV. For Energy Dispersive X-Ray Spectrometer (EDX) attached to the FESEM, it was used to conduct elemental analysis of the zeolite NaY powder samples. The final Si/Al ratios for each samples were obtained by taking the average of at least 3 measurements at different spots.

RESULTS AND DISCUSSION

Zeolite NaY seeds synthesis

The XRD peaks for synthesized zeolite NaY seeds were compared with the XRD of commercial zeolite NaY (Tosoh). It was reported that the main diffraction peaks of should be appeared approximately at 2θ of 6.31°, 10.31°, 12.10°, 15.92°, 20.71°, 24.06°, and 31.95° (Motazedi et al., 2016). Fig. 1 shows the XRD patterns for the synthesized sample and commercial zeolite NaY (Tosoh) whereby it showed that the XRD pattern of synthesized sample was agreed well with the XRD pattern of the commercial zeolite NaY (Tosoh). Furthermore, as showed in Fig. 2, octahedral shape was observed from the synthesized zeolite NaY powders which was similar as those reported from previous studies (Chaves et al., 2016; Zhu et al., 1998; Sato, 2007; Li et al., 2002). Likewise from EDX analysis, the synthesized samples also displayed Si/Al molar ratio more than 1.5, which represented for zeolite NaY (Liu et al., 2016; Lang et al., 2011; Wang et al., 2013; Karami and Rohani, 2009).

Applications of zeta potential measurements in zeolite NaY seeding onto supports

DLVO (Derjaguin-Landau-Verwey-Overbeek) theory states that a potential barrier between surface charged particles in suspension may be resulted in colloidal meta-stability. This theory can be well explained by Van Der Walls forces and repulsion by the overlapping of electric double layer at the slipping plane in the dispersion medium which represents the location of zeta potential with respect to the bulk particles as showed in Fig. 3. Furthermore, if the repulsion between the adjacent particles is large enough, i.e. high value of zeta potential (> +/- 30mV), they will bounce within each other and maintain in dispersion state (Alwani et al., 2013). Thus, this parameter can be used as an indicator for dispersion stability whereby a high zeta potential value will promote stability as it will resist agglomerations (Xu et al., 2003; Alwani et al., 2013; Caro and Noack, 2008). In this case, the surface charge of zeolite particles was affected by the protonation or dissociation of the hydroxyl groups which was controlled by the pH, as shown in equations (1) & (2).

\[
\begin{align*}
\text{SiOH}_2^{\ominus} + \text{Na}^+ &\rightarrow \text{SiO}_2^{\ominus} + \text{Na}^+ \quad (1) \\
\text{AIOH}_2^{\ominus} + \text{Na}^+ &\rightarrow \text{AlO}^- + \text{Na}^+ \quad (2)
\end{align*}
\]

Fig. 4 shows the plots between zeta potential values (mV) vs. pHs of the seeding solution. As the pH was increased, the zeta potential was further reduced due to dissociation of hydroxyl groups of the aluminosilicates and hence, achieving lowest zeta potential near to pH 9.8. However, due to excessive addition of NaOH in the seeding solution, there was a reversal point of the zeta potential as the pH was further increased due to adsorption of Na⁺ ions on the surface of the zeolite particles that led to the reductions of negative charges of the zeolite particles which might eventually result in Isoelectric point (IEP) near to pH 13. At IEP point, there is zero zeta potential due to stabilization of charges between positive and negative charges at the slip plane of the particles. Thus, at this point, there are higher possibilities for the particles to agglomerate in the dispersion (Xu et al., 2003; Kuzniatsova et al., 2007; Alwani et al., 2013).
To investigate this, seeds depend on high seeds, the capability of the zeolite particles, (a) D1, (b) D2, (c) S1, (d) S2, (e) V1, (f) V2. Subsequent hydrothermal treatment (HT) process was performed onto the membrane samples in order to form second zeolite layer. Positive results were observed for samples D1 and D2, whereby the pinholes were already covered with no significant cracks being observed from SEM. However, for samples S1, S2, V1 and V2, the cracks were still observed as shown in Fig. 7. This could be the results of too thick seeds layer formed on top of the alumina support which promoted toward formations of cracks during the hydrothermal treatment (HT) process. In contrast, for samples prepared by dip coating method (D1 and D2), the zeolite seeds attached to the support were not dense enough and easily peeled off during the hydrothermal treatment, as highlighted from previous studies (Algieri et al., 2009; Science and Physics, 2004). Thus, samples D1 and D2 were less likely to form cracks during the hydrothermal treatment (HT) unlike samples S1, S2, V1 and V2. Nevertheless, by only manipulating zeta potentials at different pHs of the seeding solution, it was not sufficient to produce zeolite membranes with least defects. This could be observed from Fig. 6 and Fig. 7, whereby cracks were still observed on top of the zeolite layer which undergone hydrothermal treatment (HT) process, even though homogenous seeds were already achieved on the support previously.

Zeolite membrane synthesis

Each of the seeded supports that seeded by using different seeding methods i.e. dip-coating, spin coating and vacuum coating were taken into hydrothermal treatment (HT) process in order to form zeolite membranes. Fig. 6 shows the SEM images of the zeolite membranes that performed by dip coating, spin coating and vacuum coating, whereby it was clearly showed that cracks were observed for all zeolite membrane samples except those prepared by dip coating method. However, several pin holes were observed by sample D1 and D2, indicating insufficient coverage of the zeolite membranes onto the support. The density and quality of zeolite membranes that would be formed on the surface of the alumina support were already being covered by the seeding solution at pH 9.8 of the supports with seeding solutions prepared at different pHs of the seeding solution, it was not sufficient to produce zeolite membranes with least defects. This could be observed from Fig. 6 and Fig. 7, whereby cracks were still observed on top of the zeolite layer which undergone hydrothermal treatment (HT) process, even though homogenous seeds were already achieved on the support previously.

Following the correlations between zeta potentials and pHs of the seeding solution, it was important to maximize the colloidal stability by making the surface charges of zeolite NaY seeds as negative as possible which could be achieved by having the seeding solution to be at pH near to 9.8. To investigate this, seeds solutions were prepared at two different points which were at pH 7 (plain DI water) and at pH 9.8. Then, these seeds solutions were used to seed the α-Al2O3 supports by using different seeding methods of dip-coating, spin coating and vacuum coating. Fig. 5 shows the SEM micrographs of the seeded supports with seeding that performed at different conditions. The results showed that at pH 9.8 of the seeds solution, less agglomerations were formed on the surface of the alumina support and hence, forming a smoother surface of the seeds layer as observed from SEM images. This illustrated on how an enhanced charge stability of the zeolite particles through modifications of pHs of the seeds solution were able to form a smoother seeding layer on the surface of the alumina support.

Nonetheless, seeds concentrations were reduced to 0.5 wt% in order to study its effects towards the densification of seeds layer on the alumina support and the quality of zeolite membranes that would be formed. New membrane samples V3 and S3 were prepared by spin coating and vacuum coating methods with lower seeds concentration at 0.5 wt% and at pH 7. However, cracks were still observed for both membrane samples once they undergone the hydrothermal treatment (HT) as showed in Fig. 8. Accordingly, this could be explained by the densification effect which was not solely depend on high seeds concentration.
concentrations (wt%) but rather due to effect of vacuum locking which promoted towards excessive seeds accumulations on the supports and hence, forming cracks during the hydrothermal treatment (HT) process (Algieri et al., 2009).

Fig. 7 SEM images of second layer zeolite membrane as prepared at different conditions (a) D1, (b) D2, (c) S1, (d) S2, (e) V1, (f) V2.

Fig. 8 SEM images of first layer zeolite membrane as prepared at different conditions (a) S3, (b) V3.

Additionally, another study was performed by varying both the heating and cooling rates for sample S4, S5 and S6 as showed in Table 2. The SEM images from Fig. 9 showed that lower heating and cooling rates (20 oC/hr) were preferred as compared to higher heating and cooling rates in order to obtain zeolite membrane samples without cracks. In this case, densification effect from vacuum locking during spin coating method could be minimized by varying the heating and cooling rates during the hydrothermal treatment (HT). Lower heating and cooling rate (20oC/hr) could reduce the effect of thermal mismatch between support and the zeolite film and hence, reducing the mechanical stress upon the zeolite layer during heating process and strain during cooling process (Gualtieri, 2006; Kosinov et al., 2016; Das et al., 2010; O’Brien-Abraham and Lin, 2010; Severance, 2014; Peng et al., 2013). Thus, this would inhibit any formation of cracks during hydrothermal treatment (HT) of the zeolite membranes.

Fig. 9 SEM images of first layer zeolite membrane as prepared at different conditions (a) S4, (b) S5, (c) S6.

Fig. 10 XRD diffraction patterns for zeolite NaY membranes synthesized by different seeding methods (a) Dip coating, HT twice – D1, (b) spin coating, HT once – S1, (c) spin coating, HT once, 30ºC/hr – S5, (d) vacuum coating, HT once – V2. (* zeolite NaY; o zeolite NaP)

Table 2 Different heating and cooling rates applied in the preparation of the membrane samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Seeding Method</th>
<th>Seeds Concentration (wt%)</th>
<th>pH of Seeding Solution</th>
<th>Heating/ Cooling Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>S4</td>
<td>Spin Coating</td>
<td>1</td>
<td>7</td>
<td>Convection Heating/ Cooling</td>
</tr>
<tr>
<td>S5</td>
<td>Spin Coating</td>
<td>1</td>
<td>7</td>
<td>30ºC/hr</td>
</tr>
<tr>
<td>S6</td>
<td>Spin Coating</td>
<td>1</td>
<td>7</td>
<td>20ºC/hr</td>
</tr>
</tbody>
</table>
The dip coating process was proven to be the most effective and simplest process for preparing tubular NaY zeolite membranes. Microporous and Mesoporous Materials, 39(3), pp. 485–492.


