MJFAS MALAYSIAN JOURNAL OF FUNDAMENTAL AND APPLIED SCIENCES
PRINT ISSN: 2289-5981 | ONLINE ISSN: 2289-599X

RESEARCH ARTICLE

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

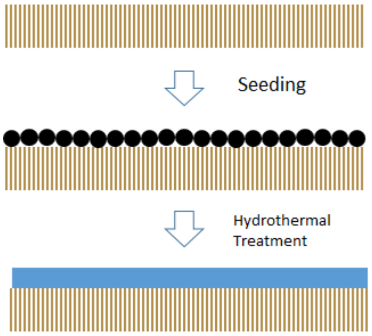
Muhammad Aimen Isa*, Muhammad Hanif Halim

Gas Sustainability Technology R&D Department, PETRONAS Research Sdn. Bhd, 43000 Kajang, Selangor, Malaysia

* *Corresponding author: aimen.isa@petronas.com.my*

Article history
Received 5 January 2019
Revised 14 February 2019
Accepted 11 March 2019
Published Online 1 October 2019

Graphical abstract



Abstract

Zeolite membrane is one type of microporous inorganic membrane which has gained so much interests among researchers as an alternative especially for gas separation. Among major challenges to produce high quality zeolite membranes with less defects are to have a good seeding and hydrothermal treatment (HT) method. On this matter, a study on the colloidal stability of the zeolite NaY seeds in the seeds solution in order to obtain homogenous seeds layer on top of the alumina support via several seeding methods and pHs of the seeds solutions were investigated. Then, the seeded samples were taken into HT process in order to form zeolite NaY membranes. 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

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 sieving properties (Liu *et al.*, 2011; Aoki *et al.*, 2000; Wang *et al.*, 2015; Hong *et al.*, 2007; Hasegawa, Watanabe, *et al.*, 2002; Sun *et al.*, 2011; Hasegawa *et al.*, 2001; Sato *et al.*, 2008b; Asghari *et al.*, 2008). As a result, supported zeolite films or membranes have attracted a lot of interest due to their properties of 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; Wee *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).

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 (Algieri *et al.*, 2009; 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 (Algieri *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 canbe performed. Instability in the dispersions of the zeolite particles will lead to agglomerations and hence, causing inhomogenous 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 converage of seeds onto the surface of the suppport 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 factor 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 to non-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% $N_{a2}O$), Colloidal Silica (Ludox, AS-40), commercial zeolite NaY powder (HSZ-320NAA, SiO_2/Al2O_3 = 5.5, Tosoh) and deionized water (DI).

Preparation of zeolite NaY seeds

Precursor solution with molar composition of Al_2O_3: 12.8 SiO_2: 17 Na_2O: 975 H_2O 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 its 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-Al_2O_3 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.

Table 1 Different conditions applied in the preparation of the samples.

Samples	Seeding Method	Seeds Concentration (wt%)	pH of Seeding Solution
D1	Dip-Coating	1	7
D2	Dip-Coating	1	9.8
S1	Spin Coating	1	7
S2	Spin Coating	1	9.8
S3	Spin Coating	0.5	7
V1	Vacuum Coating	1	7
V2	Vacuum Coating	1	9.8
V3	Vacuum Coating	0.5	7
S4	Spin Coating	1	7
S5	Spin Coating	1	7
S6	Spin Coating	1	7

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 (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).

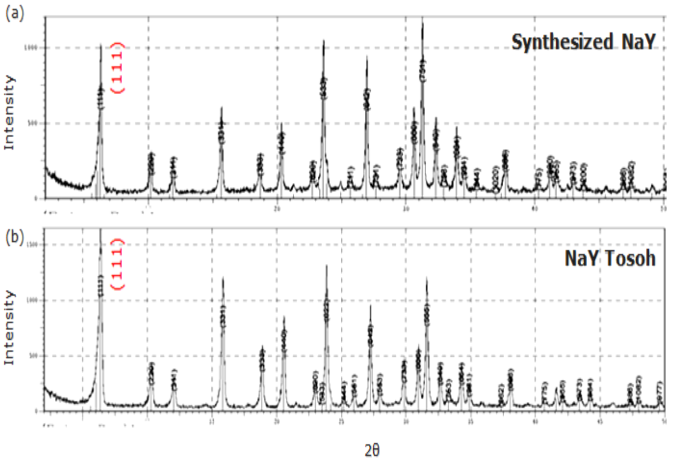


Fig. 1 XRD patterns of (a) synthesized zeolite NaY seeds and (b) commercial NaY (Tosoh).

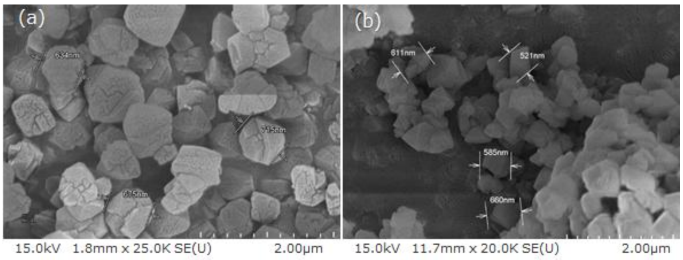


Fig. 2 FESEM images of (a) synthesized NaY zeolite seeds and (b) commercial NaY (Tosoh).

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).

$$SiOH_2^+ \xrightarrow{-H^+} SiOH \xrightarrow{-H^+} SiO^- \qquad (1)$$

$$AlOH_2^+ \xrightarrow{-H^+} AlOH \xrightarrow{-H^+} AlO^- \qquad (2)$$

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 pane 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).

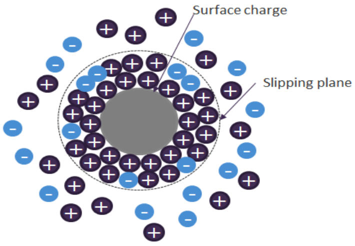


Fig. 3 Location of zeta potential at slipping plane with respect to bulk particle (surface charge).

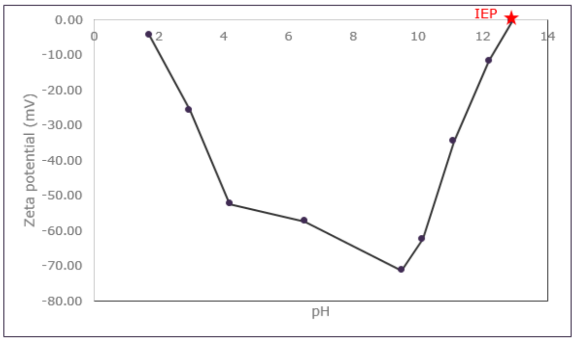


Fig. 4 Zeta potential of zeolite NaY seeds in aqueous solution at different pH conditions.

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-Al$_2$O$_3$ 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 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 smoother seeding layer on the surface of the alumina support.

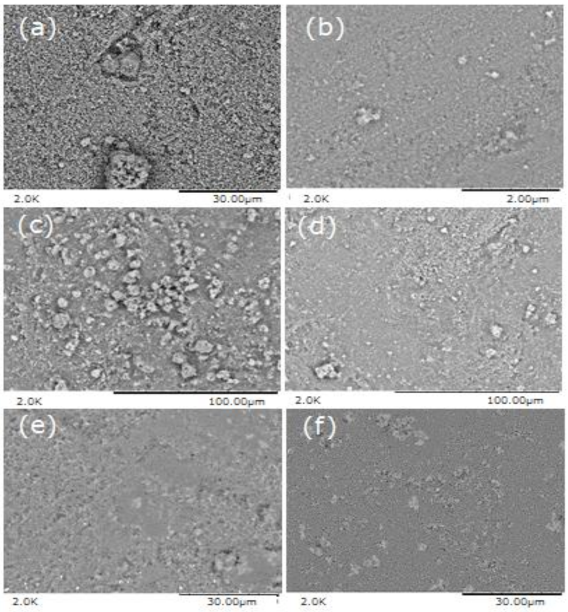


Fig. 5 SEM images of seeded support performed at different conditions; (a) D1, (b) D2, (c) S1, (d) S2, (e) V1, (f) V2.

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. 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 now 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 showed 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.

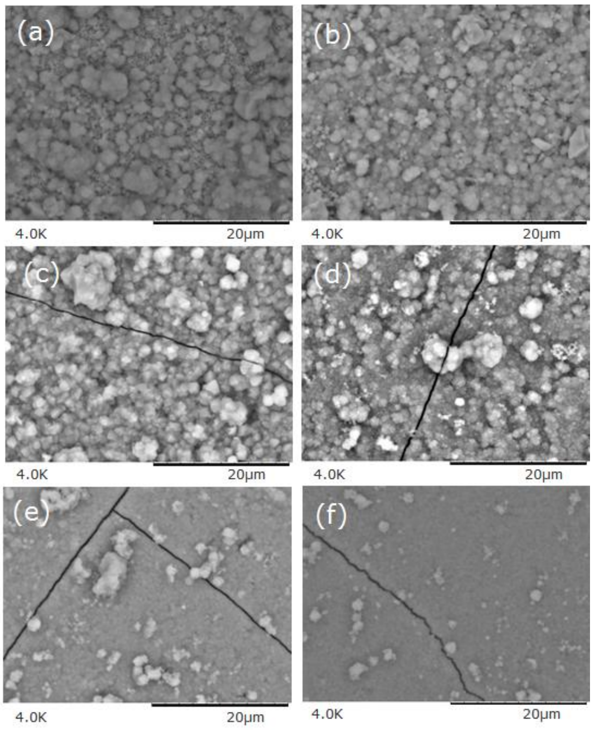


Fig. 6 SEM images of first layer zeolite membrane as prepared at different conditions (a) D1, (b) D2, (c) S1, (d) S2, (e) V1, (f) V2.

Nonetheless, seeds concentrations were reduced to 0.5wt% 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 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).

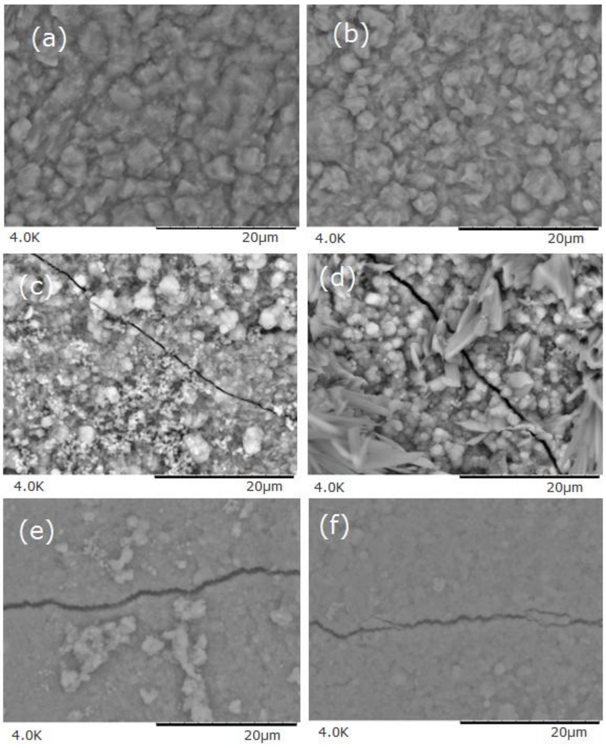


Fig. 7 SEM images of second layer zeolite membrane as prepared at different conditions (a) D1, (b) D2, (c) S1, (d) S2, (e) V1, (f) V2.

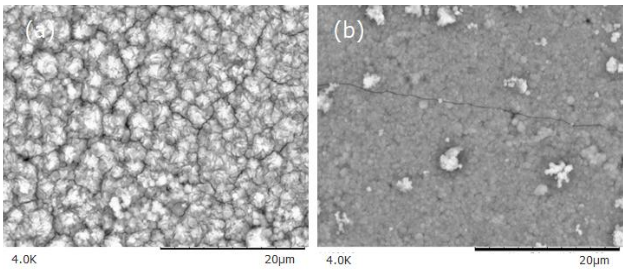


Fig. 8 SEM images of first layer zeolite membrane as prepared at different conditions (a) S3, (b) V3.

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^{o}C/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 (20^{o}C/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. 10 shows the XRD diffraction patterns for some of the membrane samples that synthesized by various seeding methods. It shows that these membrane samples synthesized were in agreement with the XRD patterns reported by previous literature which the diffraction peaks should be appeared approximately at 2θ of 6.31^{o}, 10.31^{o}, 12.10^{o}, 15.92^{o}, 20.71^{o}, 24.06^{o}, and 31.95^{o}. However peaks for zeolite NaP were started to appear together with zeolite NaY for membrane samples D1 and D2 which undergone the hydrothermal treatment (HT) process twice. Table 3 also shows the quantitative analysis by XRD in terms of amount of zeolite NaP formed together with zeolite NaY during the hydrothermal treatment (HT) process. In this case, membrane samples prepared by dip coating (D1and D2) were comprised of higher amount of impurities i.e. zeolite NaP as compared to membrane samples prepared by spin coating and vacuum coating methods. This was due to the reason of longer duration of the hydrothermal treatment (HT) process as the process was repeated twice for samples D1 and D2. This would promote towards phase transformation from zeolite NaY to zeolite NaP which was a denser and more stable type of zeolite structures (Gu *et al.*, 2005; Wang *et al.*, 2013).

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

Samples	Seeding Method	Seeds Concentration (wt%)	pH of Seeding Solution	Heating/ Cooling Rate
S4	Spin Coating	1	7	Convection Heating/ Cooling
S5	Spin Coating	1	7	30^{o}C/hr
S6	Spin Coating	1	7	20^{o}C/hr

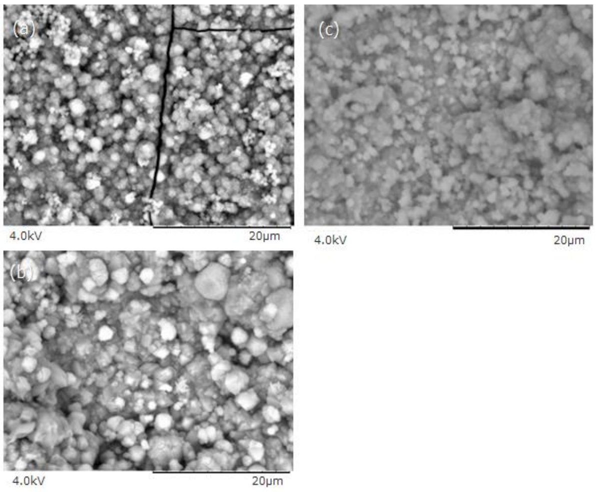


Fig. 9 SEM images of first layer zeolite membrane as prepared at different conditions (a) S4, (b) S5, (c) S6.

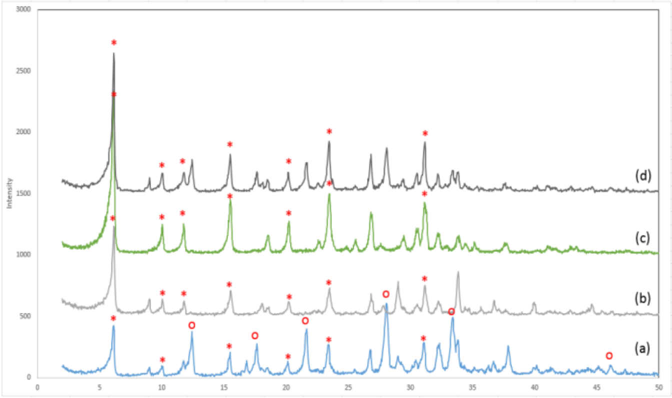


Fig. 10 XRD diffraction patterns for zeolite NaY membranes synthesized by different seeding methods (a) Dip coating, HT twice – D1, (b) spin coating, HT once – S1, (c) spin coating, HT once, 30^{o}C/hr – S5, (d) vacuum coating, HT once – V2. (***** zeolite NaY; **o** zeolite NaP)

Table 3 Quantitative analysis data by XRD for the membrane samples.

Samples	Seeding Method	Zeolite NaY (%)	Zeolite NaP (%)	Number of HT
D1	Dip-Coating	43.26	51.71	2
D2	Dip-Coating	66.47	23.29	2
S1	Spin Coating	96.81	1.45	1
S2	Spin Coating	96.11	2.78	1
V1	Vacuum Coating	97.35	2.65	1
V2	Vacuum Coating	98.27	1.22	1
S4	Spin Coating	94.71	3.47	1
S5	Spin Coating	93.83	6.17	1
S6	Spin Coating	97.65	2.35	1

CONCLUSION

Homogenous zeolite NaY layer by different seeding methods, dip coating, spin coating and vacuum coating on the surface of the α-Al_2O_3 supports could be achieved by performing the seeding process at stable aqueous colloidal dispersion. Measurements of zeta potential by varying the pHs values of the seeds solutions were found to be important parameters in order to obtain a stable colloidal dispersion. Nonetheless, another effect need to be considered which was on the densification effect of the seeds layer caused by the vacuum lock mechanism during spin coating and vacuum coating methods. This densification effect would contribute towards the formation of cracks onto the zeolite layer during hydrothermal treatment (HT) process. Yet, dip coating process was proven to be the most effective and simplest seeding method in order to form zeolite NaY membranes with less cracks, however, more than one zeolite layer were required in order to cover the pinholes. This apparently would contribute-towards formation of denser zeolite structure which was zeolite NaP. The main reason was due to the seeds attached to the support by dip coating method were loose enough as compared to spin coating and vacuum coating methods. Vacuum lock process during spin coating and vacuum coating might lead to denser and pack zeolite seeds on the supports which promoted towards formations of cracks during hydrothermal treatment (HT) process due to expansion and growth of seeds to form zeolite layer on top of the support. One of the options to solve this issue was by varying the heating/cooling rates (ºC/hr) during hydrothermal treatment (HT) in order to overcome the effect of thermal mismatch between support and the zeolite film and hence, reducing the mechanical stress upon the zeolite membrane during heating process and strain during cooling process. Thus, by having stable aqueous colloidal dispersion together with proper control of heating/cooling rate during hydrothermal treatment (HT), a zeolite NaY membrane with least amount of defects and impurities could be obtained.

ACKNOWLEDGEMENT

The financial support from GR&T PETRONAS Research Grant (cost centre: 0153C-025) was greatly appreciated. The authors would like to appreciate the technical support received from Institute of Contaminant Management, UTP and CO2 Research Centre (CO2RES), UTP.

REFERENCES

Aziz, S. A. A. Amirnordin, S. H., Rahman, H. A., and Abdullah, H. Z. 2013. Effect of zeta potential of stanum oxide (SnO2) on electrophoretic deposition (EPD) on porous alumina. Advanced Materials Research, 795, pp.334–337.

Algieri, C., Bernardo, P., Barbieri, G., and Drioli, E. 2009. A novel seeding procedure for preparing tubular NaY zeolite membranes. Microporous and Mesoporous Materials, 119(1–3), pp.129–136.

Aoki, K., Tuan, V. A., Falconer, J. L., and Noble, R. D. 2000. Gas permeation properties of ion-exchanged ZSM-5 zeolite membranes. Microporous and Mesoporous Materials, 39(3), pp.485–492.

Asghari, M., Mohammadia, T., Aziznia, A., Danayi, M. R. , Moosavi, S. H.,. Alamdari, R. F., and Agan, F. 2008. Preparation and characterization of a thin continuous faujasite membrane on tubular porous mullite support. Desalination, 220(1–3), pp.65–71.

Caro, J., and Noack, M. 2008. Zeolite membranes - Recent developments and progress. Microporous and Mesoporous Materials, 115(3), pp. 215–233.

Chaves, T.F., Pastore, H.O. and Cardoso, D. 2016. Synthesis and properties of zeolite FAU with nanocrystals. Microporous and Mesoporous Materials, 161(February), pp. 67–75.

Cheng, Z., Gao, E., Wan, H. and Processes, C. 2004. Novel synthesis of FAU-type zeolite membrane with high performance †. Chemical Communications, (c), pp.1718–1719.

Cheng, Z. and Han, S. 2015. Synthesis and separation performance of Y-type zeolite membranes by pre-seeding using electrophoresis deposition method. China Petroleum Processing & Petrochemical Technology, 17(4), pp.62–70.

Chew, T. L., Ahmad, A. L. and Bhatia, S. 2011. Ba-SAPO-34 membrane synthesized from microwave heating and its performance for CO2/CH4 gas separation. Chemical Engineering Journal, 171(3), pp.1053–1059.

Das, J. K., Das, N. and Bandyopadhyay, S. 2012. Effect of PVP intermediate layer on the properties of SAPO 34 membrane. Advances in Materials Science and Engineering, 2012, article ID 650127.

Das, N., Kundu, D. and Chatterjee, M. 2010. The effect of intermediate layer on synthesis and gas permeation properties of NaA zeolite membrane. Journal of Coatings Technology and Research, 7(3), pp.383–390.

Dey, K. P., Kundu, D., Chatterjee, M. and Naskar, M. K. 2013. Preparation of NaA zeolite membranes using poly(ethyleneimine) as buffer layer, and study of their permeation behavior. Journal of the American Ceramic Society, 96(1), pp.68–72.

Feng, C., Khulbe, K. C., Matsuur, T., Farnood, R. and Ismail, A. F. 2015. Recent progress in zeolite/zeotype membranes. Journal of Membrane Science and Research, 1(2), pp.49–72.

Fu, X.-L., Zeng, M., Zhou, J.-B. and Xu, C. 2017. A novel cellulose–silicalite-1 membrane with excellent gas separation property. RSC Advances, 7, pp.41070–41076.

Gu, X., Dong, J. and Nenoff, T. M. 2005. Synthesis of defect-free FAU-Type zeolite membranes and separation for dry and moist CO 2 / N 2 mixtures. Industrial & Engineering Chemistry Research, 44(4), pp.937–944.

Gualtieri, M. 2006. Synthesis and characterization of zeolite films and membranes (Unpublished PhD thesis). Luleå University of Technology, Luleå, Sweden.

Hasegawa, Y., Tanaka, T., Watanabe, K., Jeong, B.-H., Kusakabe, K. and Morooka, S. 2002. Separation of CO2-CH4 and CO2-N2 systems using ion-exchanged FAU-type zeolite membranes with different Si/Al ratios. Korean Journal of Chemical Engineering, 19(2), pp.309–313.

Hasegawa, Y., Watanabe, K., Kusakabe, K. and Morooka, S., 2002. Influence of alkali cations on permeation properties of Y-type zeolite membranes. Journal of Membrane Science, 208(1–2), pp.415–418.

Hong, M., Li, S., Funke, H. F., Falconer, J. L. and Noble, R. D. 2007. Ion-exchanged SAPO-34 membranes for light gas separations. Microporous and Mesoporous Materials, 106(1–3), pp.140–146.

Huang, A., Lin, Y. S. and Yang, W. 2004. Synthesis and properties of A-type zeolite membranes by secondary growth method with vacuum seeding. Journal of Membrane Science, 245(1–2), pp.41–51.

Huang, A., Wang, N. and Caro, J., 2012a. Seeding-free synthesis of dense zeolite FAU membranes on 3-aminopropyltriethoxysilane-functionalized alumina supports. Journal of Membrane Science, 389, pp.272–279.

Huang, A., Wang, N. and Caro, J., 2012b. Synthesis of multi-layer zeolite LTA membranes with enhanced gas separation performance by using 3-aminopropyltriethoxysilane as interlayer. Microporous and Mesoporous Materials, 164, pp.294–301.

Kita, H., Fuchida, K., Horita, T., Asamura, H., and Okamoto, K. 2001. Preparation of Faujasite membranes and their permeation properties. Separation and Purification Technology, 25(1–3), pp.261–268.

Kosinov, N., Gascon, J., Kapteijn, F. and Hensen, E. J. M., 2016. Recent developments in zeolite membranes for gas separation. Journal of Membrane Science, 499, pp.65–79.

Kuzniatsova, T., Kim, Y., Shqau, K., Dutta, P. K. and Verweij, H. 2007. Zeta potential measurements of zeolite Y: Application in homogeneous deposition of particle coatings. Microporous and Mesoporous Materials, 103(1–3), pp.102–107.

Lang, W. Z., Ouyang, J. X., Guo, Y. J. and Chu, L. F., 2011. Synthesis of tubular faujasite X-type membranes with mullite supports and their gas permeances for N_2/CO_2 mixtures. Separation Science and Technology, 46(11), pp.1716–1725.

Li, H., Wang, J., Xu, J., Meng, X., Xu, B., Yang, J., Li, S., Lu, J., Zhang, Y., He, X., and Yin, D. 2013. Synthesis of zeolite NaA membranes with high performance and high reproducibility on coarse macroporous supports. Journal of Membrane Science, 444, pp.513–522.

Li, Q., Creaser, D. and Sterte, J., 2002. An investigation of the nucleation/crystallization kinetics of nanosized colloidal faujasite zeolites. Chemistry of Materials, 14(3), pp.1319–1324.

Liu, Y., Yang, Z., Yu, C., Gu, X., and State, N. X. 2011. Effect of seeding methods on growth of NaA zeolite membranes. Microporous and Mesoporous Materials, 143(2–3), pp.348–356.

Liu, Z., Shi, C., Wu, D., He, S., and School, B. R. 2016. A simple method of preparation of high silica zeolite Y and its performance in the catalytic cracking of cumene. Journal of Nanotechnology, 2016, Article ID 1486107.

Ma, J., Shao, J., Wang, Z. and Yan, Y. 2014. Preparation of zeolite NaA membranes on macroporous alumina supports by secondary growth of gel layers. Industrial and Engineering Chemistry Research, 53(14), pp.6121–6130.

Mason, G., 2012. The development of online learning designs for patients with type 2 diabetes. Studies in Health Technology and Informatics, 2012, pp. 130–135.

Mastropietro, T. F., Brunetti, A., Zito, P., Poerio, T., Richter, H., Weyd, M., Wöhner, S., Driolia, E., and Barbieri, G. 2015. Study of the separation properties of FAU membranes constituted by hierarchically assembled nanozeolites. Separation and Purification Technology, 156(part 2), pp.321–327.

Motazedi, K., Mahinpey, N. and Karami, D., 2016. Preparation and application of faujasite-type Y zeolite-based catalysts for coal pyrolysis using sodium silicate solution and colloidal silica as silicon source. Chemical Engineering Communications, 203(3), pp.300–317.

O'Brien-Abraham, J. and Lin, J. Y. S., 2010. Zeolite membrane separations. In S. Kulpathripanja (ed.) *Zeolites in Industrial Separation and Catalysis* (pp.307–327). Retrieved from https://onlinelibrary.wiley.com.

Peng, Y., Zhan, Z., Shan, L., Li, X., Wang, Z., and Yan, Y. 2013. Preparation of zeolite MFI membranes on defective macroporous alumina supports by a novel wetting-rubbing seeding method: Role of wetting agent. Journal of Membrane Science, 444, pp.60–69.

Sato, K., Sugimoto, K., Sekine, Y., Takada, M., Matsukata, M., and Nakane, T. 2007. Application of FAU-type zeolite membranes to vapor/gas separation under high pressure and high temperature up to 5 MPa and 180°C. Microporous and Mesoporous Materials, 101(1-2 SPEC. ISS.), pp.312–318.

Sato, K., Sugimoto, K. and Nakane, T. 2008a. Mass-production of tubular NaY zeolite membranes for industrial purpose and their application to ethanol dehydration by vapor permeation. Journal of Membrane Science, 319(1–2), pp.244–255.

Sato, K., Sugimoto, K. and Nakane, T. 2008b. Synthesis of industrial scale NaY zeolite membranes and ethanol permeating performance in pervaporation and vapor permeation up to 130°C and 570 kPa. Journal of Membrane Science, 310(1–2), pp.161–173.

Severance, M. A., 2014. Nanocrystalline zeolites: Synthesis, mechanism, and applications (Unpublished PhD dissertation). The Ohio State University, Ohio, United States.

Shah, M. and Muzyyan, N. 2009. A novel approach for the synthesis of tungsten trioxide nanostructures. Journal of King Abdulaziz University-Science, 21(1), pp.109–115.

Sun, G., Liu, Y., Yang, J., and Wang, J. 2011. Seeded synthesis of small polycrystalline NaY zeolite membrane using zeolite structure-directing agent and its pervaporation performance. Journal of Porous Materials, 18(4), pp.465–473.

Wang, B., Ho, W. S. W., Figueroa, J. D. and Dutta, P. K., 2015. Bendable zeolite membranes: synthesis and improved gas separation performance. Langmuir, 31(24), pp.6894–6901.

Wang, P. and Keller, A. A., 2009. Natural and engineered nano and colloidal transport: Role of zeta potential in prediction of particle deposition. Langmuir, 25(12), pp.6856–6862.

Wang, Z., Ge, Q., Gao, J., Shao, J., Liu, C., and Yan, Y. 2011. High-performance zeolite membranes on inexpensive large-pore supports: Highly reproducible synthesis using a seed paste. ChemSusChem, 4(11), pp.1570–1573.

Wang, Z., Kumakiri, I., Tanaka, K., Chen, X., and Kita, H. 2013. NaY zeolite membranes with high performance prepared by a variable-temperature synthesis q. Microporous and Mesoporous Materials, 182, pp.250–258.

Wee, L. H., Tosheva, L., Itani, L., Valtchev, V., and Doyle, A. M. 2008. Steam-assisted synthesis of zeolite films from spin-coated zeolite precursor coatings. Journal of Materials Chemistry, 18(30), pp.3563–3567.

Wong, W. C., Au, L. T. Y., Ariso, C. T. and Yeung, K. L. 2001. Effects of synthesis parameters on the zeolite membrane growth. Journal of Membrane Science, 191(1–2), pp.143–163.

Xu, G., Zhang, J. and Song, G. 2003. Effect of complexation on the zeta potential of silica powder. Powder Technology, 134(3), pp.218–222.

Xu, K., Jin, H., Wang, L., Liu, Y., Zhou, C., Caro, J., and To, A. H. 2018. Seeding-free synthesis of oriented zeolite LTA membrane on PDI-modified support for dehydration of alcohols. Separation Science and Technology (Philadelphia), 53(11), pp.1741–1751.

Zhu, G., Qiu, S., Yu, J., Sakamoto, Y., Xiao, F., Xu, R., and Terasaki, O. 1998. Synthesis and characterization of high-quality zeolite LTA and FAU single nanocrystals. Chemical Materials, 4756(18), pp.1483–1486.