Formation of NaY zeolite membrane: influence of intermediate layer and its characterization

M Aimen Isaa, M Hanif Halim, Thiam Leng Chew, Yin Fong Yeongb,c
a PETRONAS Research Sdn. Bhd., Kawasan Institusi Bangi, Kajang, 43000 Selangor, Malaysia.
b Department of Chemical Engineering, Universiti Teknologi PETRONAS (UTP), Seri Iskandar, 32610 Perak, Malaysia.
c CO2 Research Centre (CO2RES), Institute of Contaminant Management, Universiti Teknologi PETRONAS (UTP), Seri Iskandar, 32610 Perak, Malaysia.

*aimen.isa@petronas.com.my

Abstract. In the synthesis process of zeolite membranes, the zeolites crystals are crystallized and grow during crystallization period to form polycrystalline film. Secondary growth method is an effective method to synthesis high quality zeolite membranes which involves two main steps which are coating and hydrothermal treatment (HT) synthesis. There are several problems associated with the coating process in secondary growth method such as lack of good adherence of the seeds, rough surface of the support, and thermal mismatch between the zeolite seeds and supports during hydrothermal process. In order to solve these issues, an intermediate layer (buffer layer) could be applied between the support and the seeds layer hence to reduce the defects forms during the hydrothermal treatment (HT) synthesis process. In current study, two different types of intermediate layer were studied and results were compared in terms of zeolite seeds coverage on the surface of the support and zeolite layer formed during subsequent hydrothermal treatment (HT) to form zeolite membranes. The formed zeolite membranes were characterized with X-Ray diffraction (XRD) and scanning electron microscopy (SEM) and energy dispersive X-Ray spectroscopy (EDX).

1. Introduction
Zeolite consists of aluminium and silicon atoms which are tetrahedrally connected to form a complete crystal structure. However, due to the excess of aluminium atoms in the crystal structure of zeolite, it will be balanced by positive cations e.g. Na+, H+, Ca2+ etc. This tetrahedral aluminosilicates in the zeolite crystal structure will form narrow pore size of molecular sized dimensions which able to show high molecular sieving properties [1–9]. Accordingly, due to this sieving properties zeolites are suitable for membrane application. This including zeolites FAU, MFI, A-type, DDR, T-type and SAPO-34 membranes which mostly utilized for gas separation [5,8,15,17–19]. Nevertheless, in order to ensure good gas separation, the zeolite membranes need to contain minimal amounts of defects and continuous [14–16]. 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 in preparing least defect zeolite membranes as compared to the other methods [12,19–27]. Among advantages of secondary growth method which are it involves the process of attaching zeolite seeds crystals on the surface of
the support or substrate which in this case, the seeds will facilitates the crystallization process apart from nucleation process will be decoupled from crystal growth process in order to form continuous layer of zeolite membranes. Hence, secondary growth method enables the formation of high-quality thin and oriented zeolite membranes with least defects [17,20–23].

In secondary growth method, the main process involves is on the seeding process whereby optimization of the seeding process is important as it will determine the quality of zeolite membranes formed [23,26]. It is particularly important to ensure a thin and continuous seeds layer deposition are obtained onto the support or substrate as this will determine the quality and reproducibility of the synthesized zeolite membranes [1,24,26,27]. Nonetheless, method to obtain a thin and continuous seeds layer rather complicated which among seeding methods reported including dip-coating, vacuum seeding, spin coating and etc. [1,13,28,29]. Still, dip coating method was found to be the simplest and widely used for seeding the supports as it is not time consuming and costly support pretreatments are not required. However the zeolite seeds seeded by dip coating method is not strongly attached to the support which causes it to be easily detached from the support during subsequent hydrothermal treatment (HT) for the formation of zeolite membranes and hence affect the quality of the formed zeolite membranes [25]. Thus, modifications of existing dip coating method is required which an intermediate or buffer layer could be introduced during the seeding process via various coupling agents such as polyvinyl alcohol (PVA), poly (methyl meth- acrylate) (PMMA), poly(ethyleneimine) (PEI) as Chitosan and 3-amin- opropyltriethoxysilane (APTES) [30,31]. This intermediate layers will acts as molecular linker through covalent bonding, ionic linkage and hydrogen bonding between the zeolite seeds and the substrate through hydroxyl groups hence to increase the zeolite seeds adherence to the supports prior the hydrothermal synthesis [14–16,30] as shown in Figure 1.

This study focus on the synthesis of zeolite NaY membranes by using two different methods which are in-situ method and secondary growth method. In secondary growth method, dip coating process was applied in order to coat the zeolite seeds onto the surface of the support. The seed solution for the coating process was prepared at 1wt% and the hydrothermal process was conducted at 90°C for 24 hour in order to form continuous polycrystalline zeolite film on the support. For some of the samples, the supports were modified by coating it first with polymer coating which is polyvinyl pyrrolidine (PVP) and (3-Aminopropyl)triethoxysilane (APTES) prepared at 1wt% and 0.2mM respectively in order to facilitate the adsorption of zeolite seeds. Comparisons were conducted in terms of the synthesis method (in-situ and secondary growth method) and application of intermediate layer on the characteristics of the synthesized zeolite NaY membranes. These synthesized membranes along with the seeded supports were characterized by Scanning Emission Electron Microscopy (SEM), Energy Dispersive X-Ray spectroscopy (EDX) and X-Ray Diffraction (XRD).

**Figure 1.** Partial negative of the intermediate layer connected to –OH group of NaY zeolite seeds, partial positive of the intermediate layer connected to –OH group of the support.
2. Experimental

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

2.2. 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 in this study. During this procedure, identified amount of NaOH, Sodium Aluminate and DI water were mixed until a clear solution was obtained. Then, Colloidal Silica was added drop-wise and stirred until completely dissolved. After aging for 24 h, the mixture was transferred to a Polypropylene (PP) bottle and then kept inside a heated oven at 90°C for 24 h. After cooled 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 were prepared by dissolving NaY zeolite powders into DI water. Mixing was enhanced by ultrasonic treatment for 1 h before the coating process.

2.3. Dip-coating of supports
The supports were macroporous α-Al₂O₃ supports with thickness of 3mm and diameter of 20mm produced by Nishimura Advanced Ceramics Co. Ltd., Japan with average pore diameter, porosity percentage and bulk specific gravity of 0.1 µm, 35 % and 2.6 respectively. Prior coating the supports with zeolite NaY seeds, some of the samples were coated with polyvinylpyrrolidone (PVP) and 3-aminopropyltriethoxysilane (APTES) respectively. An aqueous solution of PVP was prepared at 1 wt% while for APTES solution it was prepared at 0.2 mM in Toluene solution. For supports coated with PVP, they were let to be dried at 50°C overnight while supports coated with APTES were treated at 100°C for 30 min first before being dried at 50°C overnight.

All the supports were then coated with zeolite NaY seeds solution by using dip coating machine with computer controlled linear speed before and after dipping at 15 mm/s with time of supports immersed in the seed solution for 10 m each. The seeded supports were then dried at 50 °C overnight in a drying oven.

2.4. Synthesis of zeolite NaY membranes
Similar procedure was applied for the preparation of zeolite NaY seeds in preparing the precursor solution in order to synthesize zeolite NaY membranes. The seeded supports were placed horizontally in the polypropylene (PP) bottle together with the precursor solution. The crystallization process is proceed via hydrothermal treatment (HT) at 90 °C for the duration of 24 h. Once completed, the PP bottle was allowed to cool down to room temperature. Then, the zeolite membrane was washed carefully several times with deionized (DI) water and finally dried at ambient air for 24 h. Table 1 shows the different conditions applied in preparing the samples in the current study.

| Samples | Method          | Intermediate Layer |
|---------|----------------|--------------------|
| D1      | In-situ        | None               |
| D2      | Secondary Growth| None               |
| D3      | Secondary Growth| PVP                |
| D4      | Secondary Growth| APTES              |
2.5. Characterizations
The synthesized NaY zeolite membranes and powders were characterized by using several techniques including X-Ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-Ray spectroscopy (EDX). X-ray diffraction (XRD) was conducted by using Cu-Kα radiation with 40 kV and 30 mA 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 morphology of NaY zeolite powder and NaY zeolite membranes were observed through SEM at room temperature. The images of the samples were captured by ejecting electron over the surface of the sample at an acceleration voltage of 15 kV. 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 of 3 measurements at different spots.

3. Results and discussions

3.1. 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°[32]. Figure 2 shows the XRD pattern for the synthesized sample and commercial zeolite NaY (Tosoh) whereby it showed that the XRD patters agreed well with the XRD pattern of the commercial zeolite (Tosoh). The XRD results agreed well with the FESEM images as showed in Figure 3 whereby the structural of the synthesized zeolite NaY was in octahedral shape similar as reported by previous studies [36–39]. Furthermore, the synthesized samples displayed Si/Al molar ratio of more than 1.5 from EDX analysis which represents zeolite NaY [11,40–42].

![Figure 2. XRD patterns of (a) commercial NaY (Tosoh) and (b) synthesized zeolite NaY seeds.](image-url)
3.2. Zeolite NaY seeds synthesis

In secondary growth method, zeolite seeds were first introduced onto the support during seeding process prior the hydrothermal treatment (HT). Dip coating technique was applied as it is the most simple technique and applicable for wide variety of shapes and sizes of the supports. The seeded supports were characterized by using EDX in order to come out with an element mapping by EDX analysis for each of the seeded samples. Higher number of Aluminum element detected from EDX represents lower coverage of zeolite seeds attached onto the surface of the support which also translated into lower Si/Al ratio or Na/Al ratio. This could be explained that higher Aluminum element detected is due to poor coverage of zeolite seeds onto the support which its main source is from Al₂O₃.

Figure 2(a) –(c) shows element mapping by EDX analysis and table 2 shows Si/Al and Na/Al ratio for each of the seeded supports.

Both PVP and APTES which function as an intermediate layer enhance the zeolite seeds coverage on the surface of the support as shown in figure 4. The partial positive and negative of PVP and APTES molecules could behave as electron acceptor and donor respectively hence to be as linker between the zeolite seeds and the support surface [15]. Figure 1 illustrates partial positive and negative of an intermediate layer connected to the zeolite seeds and surface of the support through hydroxyl groups. In this case for PVP molecule, its carbonyl groups (\(>\text{C}=\text{O}\)) could interact with zeolite seeds and its polyvinyl chains could interact with the support trough hydrogen bonding[15,31]. As for APTES molecule, its \(-\text{(NH}_2\) groups could interact with the zeolite seeds and its \(-\text{(SiO}_3\) could interact with the surface of the support through covalent bonds [41,42].

Table 2. Si/Al & Na/Al ratio of the seeded supports from EDX analysis

| Samples | Si/Al | Na/Al |
|---------|-------|-------|
| D2      | 0.42  | 0.12  |
| D3      | 2.12  | 0.65  |
| D4      | 2.75  | 0.82  |
3.3. Zeolite NaY Seeds Synthesis

Seeded supports were brought into hydrothermal (HT) synthesis in order to form a zeolite membranes. The crystallization behaviors of the zeolite membranes were investigated by using XRD and SEM-EDX. Figure 5 shows the crystallization behaviors for each of the zeolite membranes synthesized. Comparing the diffraction patterns for each of the samples, Al₂O₃ peaks were observed for zeolite membranes synthesized by using in-situ method as well as secondary growth method which are using PVP as the intermediate layer. Al₂O₃ peaks were also observed for zeolite membranes which are synthesized through secondary growth without using intermediate layer. Introduction of intermediate layer during the seeding process of zeolite membranes were supposedly to enhance the bonding between zeolite seeds and the surface of the support however for samples D3 which was using PVP as the intermediate layer, higher peaks of Al₂O₃ were still observed from XRD. One of the reason is due to dissolution of PVP layer during the hydrothermal (HT) synthesis. PVP which is highly soluble in water could be easily dissolved in water especially at high temperature during hydrothermal (HT) synthesis. This will resulted majority of the seeds seeded on the surface of the support to be flushed off which leading to the formation of zeolite membranes which are not fully covered by the zeolite layer as showed in figure 6. This result is also supported by element mapping by EDX analysis as showed in figure 7.
Figure 5. XRD diffraction patterns for (a) Al₂O₃ support (b) D1, (c) D2, (d) D3, (e) D4. Al₂O₃ diffraction patterns were observed for samples which are not fully covered by the zeolite layer.

Figure 6. SEM images for (a) D1, (b) D2, (c) D3, (d) D4. Less coverage of zeolite layer were observed for samples D1 and D3.
Conclusions

In conclusion, zeolite NaY membranes were successfully synthesized with effects of the intermediate layer were successfully showed. Higher coverage of zeolite seeds during the seeding process was showed by samples being applied with intermediate layer before the hydrothermal treatment (HT). High coverage of zeolite layer was observed for zeolite membranes being applied with APTES as intermediate layer during the seeding process hence to form better quality of zeolite membranes. Nevertheless, selection of type of intermediate layer is crucial in determining the quality of zeolite membranes formed during subsequent hydrothermal (HT) synthesis. Water soluble intermediate layer like PVP is unsuitable for hydrothermal treatment (HT) as it could be easily washed off together with the seeded seeds on the surface of the support hence to form zeolite membranes with defects. Overall, it was proven that introduction of seeds prior hydrothermal treatment (HT) of zeolite membranes could form better quality of zeolite membranes. However, enhancement of the seeding process such as via application of intermediate layer is required in order to obtain more homogenous seeds layer during the seeding process which could assists in the formation of zeolite membranes with least amount of defects.

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5. References

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