Cation-exchanged NaY Zeolite: Effect of temperature and ion concentration to membrane performance

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Abstract. Zeolite membranes possess well defined pore structures which able to separate gasses with high selectivity. The separation between adsorptive and non-adsorptive gasses depends on the affinity of permeating gas molecules with the zeolites structures whereby different types of cations resides in the zeolitic framework will affect the permeselectivity of the membranes. Several efforts have been made to modify zeolite membranes in order to enhance their capability in gas separation by ion exchange process. Here, investigations were performed on the ion exchange process of zeolite NaY membrane with Ag$^+$ cation at different concentrations (0.1M, 0.025M) and temperatures (ambient temperature and 80°C). The results revealed that temperature plays significant role in maintaining the morphologies of zeolite NaY membranes. Dealumination process was also observed to occur simultaneously with the ion exchange process. Overall, CO$_2$/CH$_4$ selectivity of the cation-exchanged NaY zeolite membranes increased by 100% with less CO$_2$ flux reductions were recorded by samples which had been ion exchanged with less concentrated ion exchange solution i.e. 0.0125M at ambient temperature. Nevertheless, CO$_2$/CH$_4$ selectivity decreased for membrane samples which had been ion exchanged at higher temperature (80°C) due to dissolution of the zeolite membranes layer.

1. Introduction
Zeolite membranes with its polycrystalline structure and supported on a porous substrate have attracted so much research efforts recently. In general, zeolites are crystalline aluminosilicate which are built by tetrahedral units of AlO$_4^-$ and SiO$_4^-$ through shared electrons to form 3-dimensional frameworks. The presence of aluminium (Al$^{3+}$) ions in the framework resulted in net negative framework charge which later is balanced by cations that depends on the type of synthetic zeolite being synthesized [1,2]. These cations did not reside permanently in the zeolitic framework but rather could be exchanged by other cations through ion-exchange techniques [2-3]. There have been numerous studies that have been performed on the application of zeolite membranes for gas separation which includes zeolite FAU[5]. Various methods have been highlighted from previous studies in order to modify the permselectivity of these zeolite membranes hence to enhance their performance in gas separation such as through of ion exchange [6,7], chemical vapour deposition [8,9] and coking process [10–12]. Nevertheless, attention has been given to the ion exchange method in order to modify the adsorption and diffusion properties of these zeolites especially for zeolites with large pore size such as zeolite Faujasite (FAU) [3,13,14]. Unlike zeolite LTA and SAPO-34 which the main gas transport mechanism is by molecular sieving, FAU type zeolite membrane is governed by surface diffusion rather than activated diffusion whereby
Gas permeation of adsorbing gas molecules are commonly higher than those non-adsorbing gas molecules [7]. These gas molecules that are adsorbed through surface diffusion will preferentially enter the pore of the zeolite FAU membrane [15].

The method of ion exchange by introducing another metal cations into the zeolite framework has been applied since a decade ago [16]. Several studies have been performed on the ion-exchanged zeolite FAU with metal cations and on their performance on gas separations or adsorptions which also relates on the incorporations of these selected metal cations in the crystallographic sites of the zeolite FAU framework hence to facilitate the transport of the gas molecules towards the active sites [2-3,6-16]. In this study, zeolite NaY membrane which is a type of zeolite FAU, was ion exchanged with Ag⁺ cation. Current study aimed at investigating the property of Ag⁺ exchanged zeolite NaY membranes via different analytical methods including energy dispersive X-ray (EDX), Inductive Couple Plasma mass spectroscopy (ICP), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) and their CO₂ and CH₄ gas permeations towards CO₂/CH₄ gas selectivity.

2. Experimental
2.1. Materials
All chemicals were directly used as received without any further purifications. The reactants used were Silver Nitrate (AgNO₃) and deionized water (DI) while the zeolite membrane used were commercial zeolite membrane NaY-type.

2.2. Ion-exchange process
The ion exchange process was conducted through conventional reflux method following several previous research works [6,12,15,18,23,24]. During this process, zeolite NaY membranes were immersed in the ion exchange solution (AgNO₃) aqueous solution with different molar concentration of 0.1 mol L⁻¹ and 0.025 mol L⁻¹. The process was conducted and compared between two different conditions which are at temperature 80°C at ambient temperature for 4hrs as cited from previous works [5,7,15,25]. For both conditions, the zeolite NaY membranes were placed vertically on top of Teflon holder inside Teflon lined stainless steel autoclave. After the ion-exchange process, the zeolite membranes were thoroughly washed with deionized (DI) water for several times and then air dried at ambient temperature overnight. Table 1 showed the different conditions applied in the ion exchange process of the zeolite NaY membranes.

| Samples | Ion Ex. Temp (°C) | Ion Ex Conc. (M) |
|---------|------------------|-----------------|
| H1      | RT               | 0.1             |
| H2      | 80               | 0.1             |
| H3      | 80               | 0.025           |
| H4      | RT               | 0.025           |

2.3. Characterizations
The synthesized zeolite NaY membranes and ion-exchanged zeolite NaY membranes were characterized by using several analytical methods including X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy dispersive X-Ray spectroscopy (EDX) and Inductive Couple Plasma mass spectroscopy (ICP). 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 membrane samples. The morphologies of zeolite NaY 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 15kV. Energy Dispersive X-ray Spectrometer (EDX) was used...
to conduct elemental analysis and to calculate Si/Al and Ag/Al of the membrane samples. The final Si/Al ratios for each samples were obtained by taking the average of at least of 3 measurements at different spots. Inductively coupled plasma-atomic emission spectrometer (ICP-AES, Perkin–Elmer 4300 DV) was used to analyse elemental analysis of the ion exchange solution of the ion-exchanged zeolite NaY membranes. Lastly, single CO$_2$ and CH$_4$ gas permeations were performed at 1 barg feed pressure in order to quantify the quality of the ion-exchanged zeolite NaY membrane. Gas permeance is calculated from the following equation while the gas selectivity is defined by the ratio of gas permeances.

\[
\text{Permeance}(\text{mol. m}^{-2}.\text{s}^{-1}\text{Pa}^{-1}) = \frac{\text{mol of gas transferred per unit time, mol/s}}{\text{(membrane area, m}^2\text{)(Pressure difference, Pa)}} \tag{1}
\]

Converting to Gas Permeance Unit (GPU) = \(\frac{1}{3000} \times 10^{-6} \times (\text{mol. m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1})\) \tag{2}

\[
\text{Ideal selectivity, } \alpha_{a/b} = \frac{\text{permeance gas } a(\text{GPU})}{\text{permeance gas } b(\text{GPU})} \tag{3}
\]

3. Results and discussions

Figure 1 shows SEM images on the surface morphologies of zeolite NaY membranes at prior and post ion exchange treatment. It was observed that there were significant changes observed on the morphologies of all zeolite NaY membranes after the ion exchange treatment. This could be due to the result which the zeolite NaY membranes itself partly detached from the support during the ion exchange treatment. These observations are supported by ICP analysis for the ion exchange solution indicating presence of Silicon (Si$^{4+}$) ions in the solution after the ion exchange treatment as showed in table 2. Furthermore, higher amount of Silicon (Si$^{4+}$) ions were detected for samples H2 and H4 which had been ion exchanged at higher temperature indicating higher dissolution of zeolite NaY membranes at high temperature since the main source of Silicon (Si$^{4+}$) ion is from the zeolite membrane itself.

**Figure 1.** SEM images of zeolite membranes before ion exchange treatment: a) H1, c) H2, e) H3, g) H4 and after ion exchange treatment: b) H1, d) H2, f) H3, h) H4.
Table 2. Silicon and Sodium ions concentration in the ion exchange solution after the ion exchange treatment from ICP analysis

| Samples | Si (mg/L) |
|---------|-----------|
| H1      | 0.09      |
| H2      | 0.63      |
| H3      | 0.91      |
| H4      | 0         |

In terms of crystallinity of the samples, it was observed that no significant major changes were observed on the diffraction peaks for each of the zeolite NaY membranes from XRD analysis. However, for zeolite NaY membranes which were being ion exchanged at higher temperature i.e. H2 and H4, several peaks of Al₂O₃ were observed from the XRD diffractions as shown in figure 2. This is due to the results of zeolite NaY membranes which were detached from the support during ion exchange treatment hence exposing their Al₂O₃ support. These results are supported from XRD quantitative data analysis in table 3 indicating higher % of Al₂O₃ being recorded for samples H2 and H3. On the other hand, it was observed that the degree of crystallinity analysed from XRD for the support side of samples H2 and H3 were higher than samples H1 and H4. One of the possible reasons is due to higher solubility of AgNO₃ at high temperature in aqueous solutions resulted into higher degree of impregnation of the AgNO₃ precipitation at the support side of the zeolite NaY membranes at post ion exchange treatment. In this case, higher amount of AgNO₃ being impregnated at the support side of the samples will resulted into higher degree of crystallinity analyzed by the XRD as showed in table 4. Nonetheless, from previous studies [26], it was discussed that at higher temperature the exchanged capacity will be enhanced, however different findings were observed from this study whereby zeolite NaY membrane samples i.e. samples H2 and H3 were more easily detached from the support once taken into ion exchange treatment at high temperature.

![Figure 2](image_url)
Table 3. Quantitative analysis from XRD on phases available in ion exchanged samples

| Samples   | Phase          | %   |
|-----------|----------------|-----|
| Bare      | Zeolite Y (Na) | 100 |
|           | Al₂O₃          | -   |
| H1        | Zeolite Y (Ag) | 100 |
|           | Al₂O₃          | -   |
| H2        | Zeolite Y (Ag) | 85.87 |
|           | Al₂O₃          | 14.13 |
| H3        | Zeolite Y (Ag) | 48.47 |
|           | Al₂O₃          | 51.53 |
| H4        | Zeolite Y (Ag) | 93.48 |
|           | Al₂O₃          | 6.52 |

Table 4. Quantitative analysis from XRD on degree of crystallinity for the support side of the ion exchanged samples

| Samples | Degree of crystallinity (%) |
|---------|-----------------------------|
| H1      | 75.4                        |
| H2      | 81.4                        |
| H3      | 82.1                        |
| H4      | 77.2                        |

Table 5. Elemental composition analysis from EDX analysis on ion exchanged samples

| Sample | Ag/Al before | Si/Al before | % Si/Al before |
|--------|--------------|--------------|----------------|
| H1     | -            | 0.85         | 69.67          |
|        | 5.54         | 1.44         |                |
| H2     | -            | 1.08         | 27.94          |
|        | 5.27         | 1.39         |                |
| H3     | -            | 1.16         | 24.75          |
|        | 5.57         | 1.44         |                |
| H4     | -            | 1.48         | 64.88          |
|        | 5.59         | 1.48         |                |

Additionally, in order to study the degree of efficiencies of the ion exchange treatment at different temperatures and concentrations, each of the samples were analysed by using EDX in order to calculate their Ag/Al and Si/Al ratios. It was recorded from table 5 that Ag/Al ratio for all the samples were almost similar indicating similar values of ion exchanged density for the zeolite membranes after the ion exchange treatment [12]. Thus, effect of temperature and concentration were negligible in determining the ion exchange efficiency for the zeolite NaY membranes. Nevertheless, effect of temperature during the ion exchange treatment was more prominent towards affecting the integrity of zeolite NaY
membranes which could be seen from figure 2, table 2 and table 3 indicating zeolite NaY membranes were detached from the support as the ion exchange treatment was conducted at high temperature i.e at 80°C. Additionally, increased of Si/Al ratio was observed for the zeolite NaY membranes indicating dealumination process had occurred simultaneously with the ion exchange treatment as showed in table 5 [27]. It was observed that higher increase of Si/Al ratios (%) were observed for samples being ion exchanged at lower temperature as compared to zeolite NaY membranes being ion exchanged at higher temperature as showed in table 5. At high temperature i.e. 80°C zeolite NaY membranes were already detached from the support which hindering the effect of dealumination from being seen.

Lastly, zeolite NaY membranes were tested in terms of their CO₂/CH₄ gas separation and were compared once they had undergone the ion exchange treatment. In this case, the gas permeances for CO₂ and CH₄ changed zeolite NaY membranes were exchanged with Ag⁺ cations [13–15,18,28]. As showed in table 6, CO₂/CH₄ gas selectivity for samples H1 and H4 increased while samples H2 and H3 reduced after the ion exchange process. This is due to the reason that zeolite NaY membranes for samples H2 and H3 which were ion exchanged at high temperature detached from the support causing significant reductions in terms of their CO₂/CH₄ gas separation. On CO₂ permeation, higher concentration of AgNO₃ used for the ion exchange treatment causes higher reductions of the CO₂ gas permeation of the zeolite membranes. Moreover, for zeolite membranes which were ion exchanged at high temperature, higher reductions of CO₂ permeance were observed due to higher solubility of AgNO₃ at high temperature in aqueous solutions resulted into higher degree of impregnation of the AgNO₃ precipitation at the support side of the zeolite NaY membranes. This could be seen in table 4 whereby higher degree of crystallinity for samples H2 and H3 contributed by higher amount of AgNO₃ impregnated at the porous support side of the zeolite membranes during the ion exchange treatment.

Then again, these results could also be explained by dealumination process which occurred simultaneously with the ion exchange treatment. Accordingly, the increase of Si/Al ratio will resulted in lower electrostatic potential of the zeolite framework which reduce its ability to interact with polar molecules [29,30]. CO₂ gas has a linear structure which contains no dipole moment however it has high quadrupole moment due to the molecular arrangements which causes it to form adsorption complex with the supercages of zeolite framework thus reducing its diffusivities across the zeolite membranes [30–34]. Thus, since gas permeation through zeolite NaY membranes is a combination of adsorption and diffusion rather than molecular sieving alone, therefore lower electrostatic potential will resulted into lower adsorptivity of the zeolite framework hence higher CO₂ gas is allowed to permeate across the membranes. Henceforth, higher CO₂/CH₄ gas selectivity could be achieved as showed in table 6. Nonetheless, it was observed that CO₂ gas permeation was reduced for all zeolite NaY membrane samples due to impregnation of AgNO₃ during ion exchange treatment at the support side of the membranes.

| Samples | Ion exchange | CO₂ permeance (mol m⁻² s⁻¹ Pa⁻¹) | CO₂/CH₄ |
|---------|--------------|----------------------------------|---------|
| H1      | Before       | 9.45 x 10⁻⁷                      | 3.70    |
|         | After        | 1.88 x 10⁻⁷                      | 13.63   |
| H2      | Before       | 1.14 x 10⁻⁸                      | 6.20    |
|         | After        | 5.31 x 10⁻¹⁰                     | 1.64    |
| H3      | Before       | 1.88 x 10⁻⁷                      | 2.12    |
|         | After        | 6.87 x 10⁻⁹                      | 0.52    |
| H4      | Before       | 3.04 x 10⁻⁷                      | 8.89    |
|         | After        | 1.49 x 10⁻⁷                      | 13.63   |
4. Conclusion
Zeolite NaY membranes were successfully ion-exchanged with Ag⁺ cation through conventional reflux method at two different temperatures which are at 80°C and at room temperature. It was found that the zeolite NaY membranes were heat sensitive whereby at higher temperature (80°C) during the ion exchange treatment, the property of the zeolite membranes will be affected as the zeolite layer was observed to be detached from the support. Furthermore, it was observed that the dealumination process had occurred simultaneously with the ion exchange process. However, the results from dealumination process in terms of CO₂/CH₄ selectivity were insignificant for zeolite NaY membranes which ion exchanged at high temperature i.e. 80°C since the zeolite membranes layer were already detached from the support. These observations were supported by results from several characterizations from SEM, EDX and XRD. Overall, it is recommended that the ion exchange treatment to be conducted at lower temperature in order to preserve the property of the zeolite membrane hence its performance in gas separation.

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