Preparation of Zeolite X Membranes on Porous Ceramic Substrates with Zeolite Seeds

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Abstract: Zeolite X membranes were investigated by in-situ hydrothermal synthesis on porous ceramic tubes precoated with zeolite X seeds or precursor amorphous aluminosilicate, and porous α-Al2O3 ceramic tubes with a pore size of 50–200 nm were employed as supports. Zeolite X crystals were synthesized by the classic method and mixed into deionized water as a slurry with a concentration of 0.2–0.5 wt%, having a range of crystal sizes from 0.2 to 2 μm. Crystal seeds were pressed into the pores near the inner surface of the ceramic tubes, and crystallization took place at 95°C for 24–96 h. It was also investigated that Boehmite sol added with zeolite X seeds was precoated on ceramic supports to form a layer of γ-Al2O3 by heating, and hydrothermal crystallization could then take place to prepare the zeolite membranes on the composite ceramic tubes. The crystal species were characterized by XRD, and the morphology of the supports subjected to crystallization was characterized by SEM. The composite zeolite membranes have zeolitic top-layers with a thickness of 10–25 μm, and zeolite crystals can be intruded into pores of the supports as deeply as 100 μm. The experimental results indicate that the precoating of zeolitic seeds on supports is beneficial to crystallization by shortening the synthesis time and improving the membrane strength. The resulting zeolite X membrane shows permselectivity to tri-n-butylamine ((C4H9)3N) over perfluoro-tributyl-amine ((C4F9)3N), and a permeance ratio of 57 for ((C4H9)3N to (C4F9)3N could be reached at 350°C. Permeances of BZ, EB and TIPB through the zeolite membrane were also measured and were found to slightly increase with temperature.

Key words: inorganic ceramic membrane, zeolitic membrane, membrane preparation and characterization, membrane separation.

1. Introduction

In early studies, molecular sieves, as membrane materials, were implanted into organic membranes to enhance their permeability and permselectivity. Unfortunately, these membranes could not be used under higher temperatures due to their poor thermal stability. As a result, pervaporization processes using lower temperatures were usually employed to characterize their integrity and showed promise for practical use. In recent years, increasing attention has been paid to gas separation in high temperature and membrane reaction processes. Inorganic membranes, especially zeolite membranes, were especially considered as candidate because of their tolerance of high temperatures, resistance to chemical corrosion and good material strength. Therefore, the formation of the zeolite top-layer on the surface of inorganic porous substrates makes it possible to build a membrane that has properties of both molecular sieves and catalysts. This is not only favorable to improve the separation of the supports, but also to realize in-situ separation of the products during the reaction.

During the past decade a number of developments have been achieved in the synthesis of zeo-
lite membranes. Zeolite membranes can be formed on porous supports by in-situ hydrothermal crystallization, and most of the present research uses MFI zeolite membranes [1–3], eg. ZSM-5 or silicalite-1 membranes. Alkenes and alkanes of C_2-C_8 and their isomers are usually employed for the characterization of their permselectivity through the resulting membranes, eg. n-butane/i-butane/neopentane or benzene/cyclohexane, et al.

Other types of zeolite membranes, such as zeolite A, L membranes [4,5], have also been studied. In this research, we investigated the growth of zeolite X on porous α-Al_{2}O_{3} supports to form zeolite membranes. Zeolite X was difficult to grow on porous supports with a low n(Si)/n(Al) ratio. Therefore, traditional synthesis conditions needed to be improved and repeated synthesis was necessary in the preferable n(Si)/n(Al) ratio. In addition, the membrane strength in this experiment needed further enhancement for practical use.

Deckman et al. studied the growth of zeolite on supports precoated with silicalite sol. Tsapat-and repeated synthesis was necessary in the preferable strength in this experiment needed further enhancement for practical use.

This work investigates the growth of zeolite X on seeded supports precoated by amorphous aluminosilicate, ultrafine zeolite X powders. The aim of implanting seeds on the support is to speed up the growth of zeolite X. This is beneficial to form a continuous, crack-free zeolite top-layer on the support, because the seeds provide more crystallization nuclei and better interlocking between the support and zeolite top-layer.

2. Experimental

2.1. Preparation of membranes

2.1.1. Starting solution

Ludox LS silica sol (30wt%, Aldrich), Sodium aluminate (NaAlO_2, 99.9wt%, Strem Chemical Co.), Sodium hydroxide (NaOH, 97wt%, Aldrich), Sodium hydroxide, followed by sodium aluminate, was added to deionized water by stirring to form clear solution A. Next, Ludox LS silica sol was also added to deionized water by stirring to form transparent solution B. Finally, solution A was added into B slowly by stirring that continued overnight.

2.1.2. Supports

Porous α-Al_{2}O_{3} tubes from Veto (US-filter, 10 mm o.d., 7 mm i.d., 20 mm long and 50–200 nm pore size) were used as the tubes in membrane synthesis. One end of the ceramic tubes was hermetically sealed by glaze (Gare Incorporated, Haverhill), and the other end was glazed with a dense, 130 mm long, ceramic tube by calcining the glaze at 850°C for 1 h. The supports were washed successively with 1 mol/L HCl and (or) 1 mol/L NaOH solution under supersonication. The outer surface of the cylindrical support was tightly wrapped with Teflon tape to avoid crystallization. The autoclave for crystallization had an inner
2.1.3. Synthesis procedures

10 ml of starting solution was added into the ceramic tube. Compressed nitrogen was then applied inside the tube for a certain period of time at up to 345–360 kPa to eject the liquid from the tube and repeated as necessary. The sample was then dried overnight, calcined in a program-controlled manner at temperatures up to 180°C for 2 h, cooled naturally in the oven, rinsed with deionized water up to pH=7.0 and finally dried again. 10 ml of starting solution was again added to the autoclave, and the support wrapped with Teflon tape was vertically placed in the solution.

The autoclave was transferred into the oven pre-coated at 85–95°C, and hydrothermal crystallization was carried out under autogeneous pressure for 24–96 h without stirring. After synthesis, the sample was washed with deionized water up to pH=7.0, dried at 90°C overnight, calcined in the muffle oven with a in program-controlled manner up to 450°C for 4.0 h at a rate of 0.2°C/min, cooled to room temperature at a rate of 0.5°C/min in a program-controlled manner to remove water from the pores of the zeolite.

2.2. Charactization of membrenes

![Figure 1. Schematic of membrane cell for permeation measurement.](image)


The morphology of the synthesized supports was observed by SEM, and the species on the inner surface of the supports after synthesis were determined by XRD. The permeances of pure tri-n-butylamine and perfluoro-tributylamine through the synthesized supports were measured at 350°C to characterize the integrity of the zeolite top-layer growing on the supports. A schematic diagram of apparatus with the membrane cell for permeation tests is shown in Figure 1.

3. Results and discussion

Usually, the alumina support exhibits a positive charge on the surface, whereas the precursor zeolitic crystals in the solution are negatively charged. Therefore, the best solution for seeding should have a property of neutrality, or pH=7.0.

Lai and Gavalas deposited the zeolitic seeds on the support by dipping it into the seeding solution with neutral pH under supersonication. Crystallization took place on the seeded support. This resulted in a higher quality zeolite membrane than on the unseeded support. Their experimental results indicated that zeolite X could not be formed as film on the surface of supports by the above-mentioned method. In this work, the seeding solution was added inside the tube of the support, and then imposed by compressed nitrogen to make the seeds intrude into the support. The intrusion of seeds by compressed nitrogen could be operated repeatedly followed by thermal treatment to enhance the affinity between the support and the seeds on it before hydrothermal crystallization.

3.1. Composition of the starting solution

The starting solution contains (S3: $n(\text{Na}_2\text{O})/n(\text{SiO}_2)=1.30$, $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)=3.5$, $n(\text{H}_2\text{O})/n(\text{SiO}_2)=175$; S5 ($n(\text{Na}_2\text{O})/n(\text{SiO}_2)=5.32$, $n(\text{SiO}_2)/n(\text{Al}_2\text{O}_3)=4.5$ and $n(\text{H}_2\text{O})/n(\text{SiO}_2)=500$). First, starting solution S3 was added into the tube of the support, and compressed nitrogen was inserted up to 650 kPa to eject the liquid out of the tube under supersonication. After rinsing and drying, another 10 ml S3 was put in the tube, and it was placed into the autoclave. The autoclave was then vertically transferred into the preheated oven, where crystallization took place for a certain period of time. The crystallization could be repeated again but with S5 as the starting solution. The supports were subjected to calcination with an increasing rate of 0.5 °C/min in a programed-control manner up to 450°C for 4 h and then cooled down at the same rate. The coverage of zeolite X subjected to synthesis twice was scrutinized by scanning electron microscopy.
as shown in Figure 2(a) and 2(b). The unseeded supports are shown in Figure 2(c) and 2(d) for comparison. Because the supports were precoated with amorphous aluminosilicate gel deep in the pores of supports before crystallization, more crystals grew in the pores, resulting in the distinct intermediate layer on the supports offering more nuclei for crystallization. Therefore, it is apparent that better coverage was achieved on the seeded supports after twice synthesis than on unseeded supports, and crystallization times decreased as a result.

![Figure 2. SEM of the zeolite top-layer of the inner surface of the ceramic tube.](image)

(a), (b): tube precoated with amorphous aluminosilicate gel; (c), (d): fresh ceramic tube.

![Figure 3. XRD for zeolite toplayer on the seeded supports](image)

(a) powder of zeolite X; (b) crystal coverage on the support precoated with the starting gel; (c) crystal coverage on the support seeded with zeolite X.

After twice synthesis the species of the top-layer on the seeded supports were determined by XRD. Figure 3(b) shows an XRD of the crystal coverage on the supports precoated by the starting solution in comparison with that of zeolite X shown in Figure 3(a). XRD for the species crystallized on the seeded support three times is also shown in Figure 3(c).

3.2. Slurry containing zeolite X powders as the seed

The use zeolite powders as seeds has been widespread in the synthesis of zeolites. Our investigations also discovered the effect of zeolitic seeds precoated on the support on the growth of crystallization on the surface of the support. Further experimental results illustrated that the growth of zeolite on the support in the dilute solution was faster than that in the concentrated solution. Thus, it seems that the
stringent conditions for zeolite membrane synthesis can be relaxed by precoating a layer of zeolite seeds over the support.

The slurry of zeolite seeds was prepared as an aqueous gel by adding ultra fine zeolite X powders into neutral deionized water. The recipe for preparing zeolite X1 is as follows:

\[
\frac{n}{(SiO_2)}/\frac{n}{(Al_2O_3)}=4.0, \quad \frac{n}{(Na_2O)}/\frac{n}{(SiO_2)}=1.29, \quad \frac{n}{(H_2O)}/\frac{n}{(SiO_2)}=60.5, \quad 95\degree C, \quad 9 \text{ h}.
\]

Zeolite powder was first dried at up to 120\degree C for 3 h. 0.2562 g zeolite X powders were added to 49.7584 g deionized water while stirring overnight to form the slurry of zeolite X. Zeolite X powders with a diameter of about 10 \(\mu m\) in the slurry were characterized by a laser scattering granulometer (Brookhaven BI-90).

### 3.3. Effect of zeolite X seeds on the synthesis of zeolite membranes

Figure 4 shows the morphology of seeded ceramic supports subjected to the triple synthesis. Synthesis steps, conditions and results are shown in Table 1.

<table>
<thead>
<tr>
<th>Run</th>
<th>Seeding solution</th>
<th>Synthesis condition</th>
<th>(m\text{(seed)}/m\text{(supp)})</th>
<th>(m\text{(zeolite)}/m\text{(s-supp)})</th>
<th>(m\text{(zeolite)}/m\text{(supp)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>X1</td>
<td>S3, 95\degree C, 70 h</td>
<td>0.18</td>
<td>0.57</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>X1</td>
<td>S5, 90\degree C, 84 h</td>
<td>0.05</td>
<td>1.34</td>
<td>0.64</td>
</tr>
<tr>
<td>3</td>
<td>S6</td>
<td>S6, 90\degree C, 96 h</td>
<td>0</td>
<td>2.07</td>
<td>1.27</td>
</tr>
</tbody>
</table>

S6: \(n(SiO_2)/n(Al_2O_3)=4.0, n(Na_2O)/n(SiO_2)=7.72, n(H_2O)/n(SiO_2)=750; supp—support, s-supp—seeded support.

Continuous, crack-free zeolite coverage on supports with a thickness of 15 \(\mu m\) can be observed in Figure 4. Comparing that to the unseeded supports, we can see that more zeolitic crystals formed on the surface of the support during each synthesis. Zeolitic crystals stretched into the pores of the support as deeply as 100 \(\mu m\) to form an intermediate layer.

Figure 4. SEM of zeolite top-layer on the inner surface (a) and cross section (b) of a ceramic tube precoated with zeolite X seeds.

The permeances of nitrogen, helium, \(n\)-butane and isobutane and of pure steam of tri-\(n\)-butylamine and perfluoro-tributylamine through the zeolite membrane are shown in Table 2. The data were measured under stable flow by calculating the amount of permeated stream after condensation for a certain period of time. Gas permeances after triple synthesis decreased to less 1.0\% of those of the original support, and the decrease in permeance was especially sharp after the first two syntheses.

The pure steam of aromatic hydrocarbons such as benzene(BZ), ethylbenzene(EB) and triisopropylbenzene(TIPB) were also used to test the integrity of zeolite X membranes after three syntheses, and the results are shown in Figure 5.

A 2.7 permeance ratio of nitrogen to helium was achieved at room temperature, but pure \(n\)-butane and isobutane showed no difference in permeance through the zeolite membrane. Tri-\(n\)-butylamine permeated
up to 57 times faster than perfluoro-tributylamine at 350°C. This effect may be ascribed to molecular sieving by microporous pathways in the zeolite top-layer on the support. Nitrogen, helium, n-butane and isobutane have molecular diameters of 0.364 nm, 0.26 nm, 0.43 nm and 0.5 nm, respectively. These are all less than the kinetic diameter of the zeolite X micropores (0.78 nm). Therefore, nitrogen, helium, n-butane and isobutane could all be transported through the microporous pathways by the Kindsen diffusion mechanism, raising the permeance ratios in accordance with this mechanism. On the other hand, the permeation performance of tri-n-butylamine and perfluoro-tributylamine through the zeolite membrane agreed with their properties of adsorption in zeolite X. Tri-n-butylamine has a molecular diameter of 0.81 nm, approximately the same as the size of zeolite X micropores, and could therefore be adsorbed in zeolite X. However, perfluoro-tributylamine could not be adsorbed in zeolite X because its molecular size (1.02 nm) is larger than the pore size of zeolite X.

Table 2. Single gas permeability through zeolite X membrane on the seeded supports at 25°C, 206 kPa.

<table>
<thead>
<tr>
<th>run</th>
<th>Permeability/ ×10^{-7} mol/(m^2-s-Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
</tr>
<tr>
<td>0(support) \textsuperscript{b}</td>
<td>1140</td>
</tr>
<tr>
<td>1</td>
<td>310</td>
</tr>
<tr>
<td>2</td>
<td>79</td>
</tr>
<tr>
<td>3</td>
<td>8.89</td>
</tr>
</tbody>
</table>

(a) Temperature 350°C; (b) Pressure 27 kPa.

Figure 5. The effect of temperature on permeance of aromatic steam through zeolite X membrane.

(1) Benzene, (2) EB, (3) TIPB.

Therefore, a covering of zeolite X on the support as a dense zeolite membrane could be selective to preferably permeate tri-n-butylamine but not perfluoro-tributylamine. The experimental results indicated that the resulting zeolite X membrane could preferentially permeate tri-n-butylamine. The permeance ratio of tri-n-butylamine to perfluoro-tributylamine was as high as 57, showing the integrity of the resulting zeolite membrane and that the micropores of zeolite X were the main pathways for tri-n-butylamine through the zeolite membrane. Unfortu-nately, a small amount of perfluoro-tributylamine was still detected in the permeate, probably due to some defects in the zeolite top-layer.

Figure 5 also illustrates that the permeances of BZ, EB and TIPB through the zeolite membrane slightly increase with temperature. Chemical adsorption to aromatic hydrocarbons on the zeolite membrane becomes more important at higher temperatures. This makes it easier for BZ, EB and TIPB to pass through the zeolite membrane, resulting in the permeance enhancement. However, TIPB has a permeance of 2.40×10^{-8} mol/(m^2-s-Pa) even though its molecular size (0.85 nm) is greater than the pore size of zeolite X. This is further evidence proving that there were some defects in the zeolite top-layer.

3.4. Effect of synthesis time on the growth of zeolite membrane

In order to scrutinize the growth of zeolite X on the seeded supports, the crystallizations were subjected to take place at 90°C for 24 h, 48 h and 72 h, respectively. S5 was used as the starting solution, and the growth of zeolite X on the support is shown in Figure 6. A covering, not a continuous film of zeolite X, appeared on the seeded supports after 24 h. A continuous thin film seemed to form after 48 h, but there were still uncovered areas on the support. A
zeolitic top-layer with a thickness of several microns formed on the support after 72 h but was not well-distributed. Repeating the synthesis was necessary to obtain a well-distributed, continuous zeolite film. The weight of the support was increased by 2.0% for triple synthesis, while 5 to 6 synthesis times would be needed if the unseeded support was used.

The crystallinity (calculated by XRD) of the zeolitic top-layer on the support at 24 h, 48 h and 72 h is shown in Table 3. 64% crystallinity could be achieved after 24 h, after which no greater improvement followed by increasing the time. Crystallinity rose up to 84% after another 48 h of crystallization. The velocity of crystallization on the seeded support was faster than that on the unseeded support.

<table>
<thead>
<tr>
<th>Time/h</th>
<th>The unseeded support</th>
<th>The seeded support</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>20</td>
<td>64</td>
</tr>
<tr>
<td>48</td>
<td>50</td>
<td>77</td>
</tr>
<tr>
<td>72</td>
<td>76</td>
<td>84</td>
</tr>
</tbody>
</table>

Figure 6. Effect of synthesis time on the growth of zeolite X on the ceramic substrate.
(a) 24 h, (b) 48 h, (c) 72 h.

Figure 7. Well growth of zeolite X membrane on the seeded support.
(a) the surface, (b) cross section.

The experimental results indicated that the microstructure and strength of the resulting zeolite membrane could be improved by precoating zeolite seeds on the support. When hydrothermal crystallization took place, the seeds provided the crystallization nuclei around which zeolite crystals grew to gradually fill the interstices. Therefore, the inductive period could be ignored for the formation of heterogeneous nuclei in crystallization, resulting in a wider window of conditions for growth of the zeolite membrane and shortening the synthesis time. Consequently, the immersion time of supports in the synthesis solution could be shortened to relieve the corrosion of the supports (especially for ceramic supports) in the solution.

Starting solution S3 mixed with ultra fine zeolite X powders was also employed as a seed to be pre-
coated on the support. 0.5wt% zeolite X was added to the starting solution S3 and was expected to provide more amorphous aluminosilicate by using a mixture of the seeds when crystallization took place around the zeolite X seeds. Experimental results indicated that the membrane strength was not satisfactory even though a well-distributed layer of zeolite X grew on the seeded support.

3.5. Supports precoated by alumina sol mixed with zeolite X

In previous work, alumina sol was used to modify the porous ceramic tube by the sol-gel method, and a γ-Al2O3 top-layer with a pore size of 3.7 nm could be firmly formed on the ceramic tube [11]. The zeolite X powders were added to alumina sol in this experiment to prepare a mixture for precoating the supports. Alumina sol with a 0.2wt% Al³⁺ content was prepared by the method described in [12]. Next, zeolite X powders were added with 0.5wt% by the amount of alumina sol, stirring at 30°C overnight. Using the sol-gel method, alumina sol with zeolite X powders was coated on the supports to form an intermediate layer on which zeolite X could grow around the implanted zeolite X seeds to form a zeolitic film.

The supports precoated by alumina sol with zeolite X powders were subjected to calcination at up to 600°C, eventually forming a γ-Al2O3 layer. The growth of zeolite X on the γ-Al2O3 layer was investigated, and the SEM results are shown in Figure 8. It is apparent from Figure 8 that centers of crystallization existed because many clusters of zeolite islands emerged on the γ-alumina layer. This seems to imply that the implanted zeolite X seeds provided the centers of crystallization.

![Figure 8. SEM of zeolite top-layer on γ-Al2O3 tube implanted with zeolite X seeds.](image)

It is important for the γ-Al2O3 layer to be introduced between the zeolite top-layer and the support as an intermediate layer, especially for stainless steel supports. Namely, stainless steel can be used as the practical support instead of ceramic. This is meaningful for the preparation and use of composite zeolite membranes in future investigations.

4. Conclusion

The synthesis of the zeolite X membrane can be improved by precoating seeds on the supports. The precoating can be carried out by introducing the amorphous aluminosilicate gel of the starting solution or ultra fine zeolite X powders into the supports. The synthesis duration can be decreased on the seeded supports, and the corrosion of the supports in the synthesis solution can therefore be mitigated.

The formation of an intermediate layer with a thickness of 100 µm seems to be because of the existence of seeds near the inner surface of the supports, resulting in an improvement in the affinity between the support and the zeolite top-layer on it.

The good intergrowth of the zeolite top-layer on the support precoated by alumina sol mixed with zeolite X can be achieved, and the membrane strength can be improved greatly, especially for stainless steel supports.

The composite zeolite membranes have zeolitic top-layers with a thickness of 10–25 µm, and zeolite crystals can be intruduced into pores of the supports as deeply as 100 µm. The resulting zeolite X membrane shows permselectivity to tri-n-butylamine(((C₄H₉)₃N) over perfluoro-tributylamine ((C₄F₉)₃N). A permeance ratio of 57 for ((C₄H₉)₃N to (C₄F₉)₃N could be reached at 350°C, and permeances of BZ, EB and TIPB through the zeolite membrane slightly increase with temperature.

References

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