

Synthesis of NaA zeolite membrane on a ceramic hollow fiber

Xiaochun Xu^{a,b,*}, Weishen Yang^a, Jie Liu^a, Liwu Lin^a, Norbert Stroh^b, Herwig Brunner^b

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China

^b Fraunhofer Institute for Interfacial Engineering and Biotechnology, Nobelstrasse 12, Stuttgart D-70569, Germany

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Abstract

NaA zeolite membrane was successfully synthesized on a ceramic hollow fiber with an outer diameter of 400 μm , a thickness of 100 μm and an average pore radius of 0.1 μm . The as-synthesized membranes were characterized by XRD, SEM as well as gas permeation. A continuous NaA zeolite membrane formed after a three-stage synthesis. The membrane thickness was $\sim 5 \mu\text{m}$. Gas permeation data indicated that a relatively high quality NaA zeolite membrane formed on the ceramic hollow fiber support.

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1. Introduction

The last decade has witnessed a significant progress on zeolite membranes [1–3]. MFI zeolite membrane showed promising performance on organic separations, e.g., butane isomers and xylene isomers [4–10], while X-type and Y-type zeolite membrane showed good performance on carbon dioxide separation [11] and 1,3-propanediol separation [12]. The most significant progress was achieved by the A-type zeolite membrane in the pervaporation dehydration [13–17]. Okamoto and co-workers [14] firstly reported that a flux of 2.0 kg/m² and a water/organic selectivity of 10,000 were obtained. The separation performance was much better than that of the polymeric membranes. Since its high potential commercial value, A-type zeolite membrane became commercially available shortly after the publication [18–20]. Smart Company in UK makes different scales of separation modules for different applications [18]. Mitsui Engineering and Shipbuilding Co. Ltd. made the first large-scale plant using tubular-type module [19,20]. The plant was composed of 16 modules which comprised 125 pieces of zeolite membrane, respectively, and produced 600 l/h solvents at less than 0.2 wt.% of water from 90 wt.% solvents

at 120 °C. However, packing density (i.e., membrane separation area/module volume ratio) of the separation module was low as it was compared with that of the polymeric membranes. In order to compete with the polymeric membranes in the further scaling up of this process, high packing density is desired. For polymeric membranes, high packing density can be easily obtained in the hollow fiber architecture. For a given module size, packing density can be as large as a factor of 1000 than that of the ceramic membranes. Much effort has been paid in the preparation of ceramic membrane with high packing density [21–25]. Multi-channel monolithics and honeycomb multi-channel monolithics were developed [21]. Packing density can be increased from 30–250 m²/m³ for tubes, to 130–400 m²/m³ for multi-channel monolithics and to 800 m²/m³ for honeycomb multi-channel monolithics [21]. Nevertheless, compared to the polymeric membranes, their packing density is still low. A further increase in the packing density can be obtained by preparing the ceramic hollow fiber membranes. Packing density as high as 1000 m²/m³ can be easily obtained. Till now, porous glass hollow fibers and carbon hollow fibers have been prepared [21], and the ceramic hollow fiber is reported in the literature more recently [22–25]. However, packing density is only one of the factors that will result better space yield. To get better space yield, other factors, such as, membrane thickness, membrane perfection and support strength (to allow for higher pressure difference), should also be considered. The ceramic hollow fiber generally has relatively strong strength

* Corresponding author. Current address: 209 Academic Project Buildings, The Energy Institute, The Pennsylvania State University, University Park, PA 16802, USA. Tel.: +1-814-865-6617; fax: +1-814-863-7432.

E-mail address: xux1@psu.edu (X. Xu).

[23]. Therefore, for zeolite membranes on the ceramic hollow fiber, a thin and perfect membrane is preferred for better space yield and for module design. There is no report on the synthesis of zeolite membrane on the inorganic hollow fiber support. In this paper, the synthesis of NaA zeolite membrane on a ceramic hollow fiber with an outer diameter of 400 μm , a thickness of 100 μm and an average pore radius of 0.1 μm was reported for the first time. The quality of the as-synthesized NaA zeolite membrane was evaluated by gas permeation.

2. Experimental

A self-made porous ceramic hollow fiber was fabricated by a spinning-extrusion technique from a spinning mass containing organic binders [24,25] and was used as the support. Typically, the ceramic hollow fibers have an outer diameter of 400 μm , a thickness of 100 μm and an average pore radius of 0.1 μm . The length of the support can be spun to several meters and was cut into 10 cm in our experiment. Before synthesis, the support was cleaned in a deionized water bath by ultrasonic cleaner for ca. 3–5 min to remove the loose particles, after which the support was calcined in air at 400 °C for 3 h to burn off the organics on the support surface.

The synthesis mixture was prepared by mixing sodium hydroxide (Riedel-deHaen), sodium silicate solution (Fluka), sodium aluminate (Riedel-deHaen) and deionized water. The molar ratio of the synthesis gel is $2\text{SiO}_2:\text{Al}_2\text{O}_3:3\text{Na}_2\text{O}:200\text{H}_2\text{O}$. The support was placed vertically with a Teflon holder in a stainless steel autoclave to avoid any precipitation of zeolite crystals onto the support during the membrane synthesis. The crystallization was carried out at 90 °C under autogeneous pressure for 24 h. In order to improve the quality of the zeolite membrane, repeated synthesis (which is called multi-stage synthesis) was adopted. The membrane was turned upside down in the next stage of synthesis.

After synthesis, the as-synthesized zeolite membranes were washed several times with deionized water until the pH value of the washings became neutral, then dried in air at 423 K for 3 h. Low heating and cooling rate, ca. 1 K/min, was adopted. The phase of the as-synthesized membrane was determined by X-ray diffraction (XRD) patterns. The morphology and the thickness of the as-synthesized membrane were examined by scanning electron microscope (SEM). The integrity of the as-synthesized membrane was checked by a permeation test. Single gas permeance was measured at 25 °C and a feed pressure of 0.10 MPa by a GKSS automatic transient permeation set-up (shown in Fig. 1). The gas permeance measurement for each single gas was repeated until the permeance data for the successive 10 tests were close. The single gas permeance was the average of the 10 successive tests. The whole experiment process was automatically controlled by a computer.

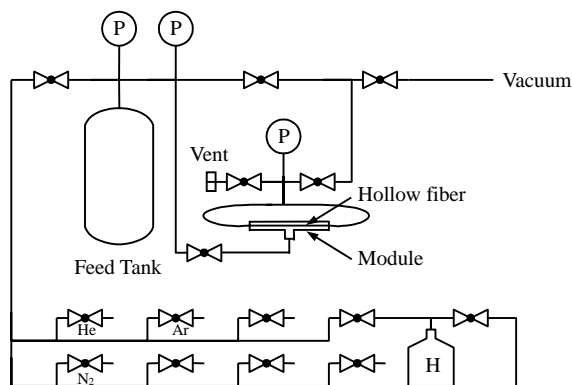


Fig. 1. Schematic diagram of the GKSS automatic transient single gas permeation set-up. P, pressure sensor; H, humidifier.

Between the measurements of two gases, the system was evacuated overnight followed by permeation with the next testing gas. The following equation was used for calculating the permeance:

$$Q = \frac{V_c}{S_m RT_0 (P' - P'')} \frac{dP'}{dt}$$

where V_c is the volume of the gas feed tank, S_m the permeating area of the membrane, P' and P'' are feed pressures and permeate pressure, T_0 is 298 K, and dP'/dt the rate of pressure decrease in the feed gas tank. The permselectivity of A/B is defined as the permeance ratio of gas A over gas B.

3. Results and discussions

Because the ceramic hollow fiber is too thin to be characterized in situ by XRD, the powders, which was synthesized simultaneously with the zeolite membrane in the same autoclave, was collected and characterized instead. From the XRD patterns of the powders (not shown), it can be learned that only the diffraction patterns of NaA zeolite appeared, which inferred that NaA zeolite was the only crystalline phase formed during the synthesis. The IR spectrum of the powders confirmed the XRD results. Our previous study also showed that only NaA zeolite membrane formed on a disk ceramic support by using the same synthesis condition [26]. From the SEM image (not shown), it can be seen that crystals formed on the ceramic hollow fiber support after one-stage synthesis. The crystals are typically in the morphology of NaA zeolite. However, the zeolite crystals were found to be not well intergrown and there was no continuous NaA zeolite membrane formed on the ceramic hollow fiber support. In order to synthesize a continuous NaA zeolite membrane on the support surface, multi-stage synthesis was carried out. Only after a three-stage synthesis did a continuous NaA zeolite membrane formed on the ceramic hollow fiber support. From the top-view SEM image (shown in Fig. 2), it can be seen that the crystals were all in the morphology of NaA zeolite type and did not transform

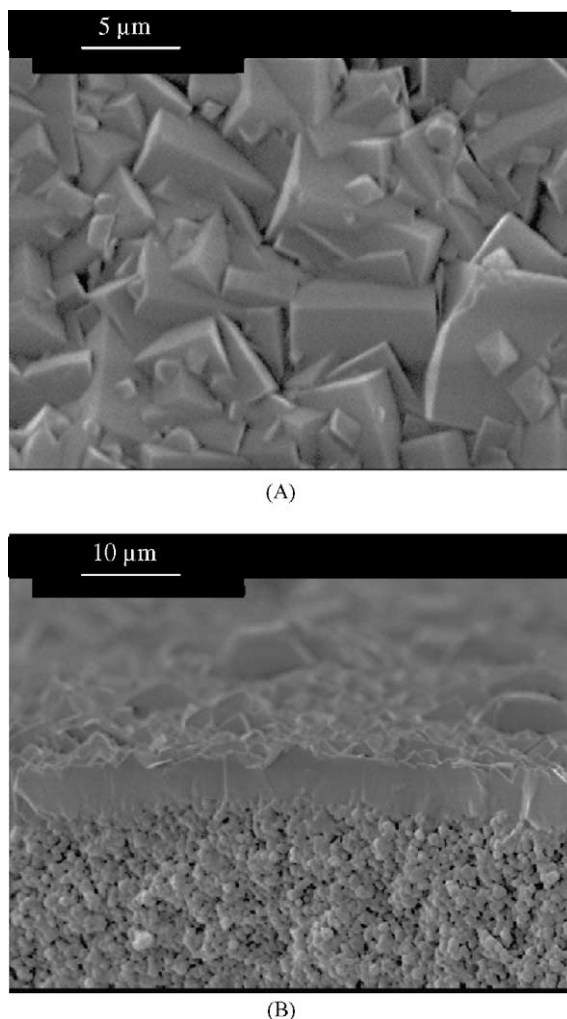


Fig. 2. SEM image of NaA zeolite after a three-stage synthesis. (A) Top view and (B) cross-section.

into other types of zeolites after a three-stage synthesis. The NaA zeolite crystals were found to be well intergrown. The thickness of the NaA zeolite membrane is about 5 μm . A similar phenomenon was observed in the synthesis of NaA zeolite membrane on a disk ceramic support under the same synthesis condition [26]. Meanwhile, only few NaA zeolite crystals formed on the inner wall of the ceramic hollow fiber and there was no continuous NaA zeolite membrane formed.

However, XRD and SEM can only indicate whether a continuous membrane formed on the support, they cannot confirm whether a high quality zeolite membrane formed [10,26]. The quality of zeolite membrane can only be evaluated by gas permeation performance [10,26]. Table 1 shows the gas permeation properties of the ceramic hollow fiber and the as-synthesized membrane after different stages of synthesis. After one-stage synthesis, the gas permeance of the membrane decreased three times and the permselectivity of He/N₂ and He/Ar increased when compared with those of the support, which indicated that NaA zeolite membrane began to form on the support surface. However, the perm-

Table 1
Permeance and permselectivity of the as-synthesized NaA zeolite membranes (permeance: 10^{-7} mol/m² Pa s)

Membrane	He	N ₂	Ar	He/N ₂	He/Ar
Knudsen diffusion ratio of H ₂ /gases	–	–	–	2.64	3.16
Support	53.54	26.67	22.10	2.01	2.42
One-stage synthesis	18.91	8.73	7.13	2.17	2.65
Two-stage synthesis	9.10	3.99	3.24	2.28	2.81
Three-stage synthesis	1.01	0.276	0.229	3.66	4.41
Four-stage synthesis	0.153	0.0527	0.0425	2.90	3.60

selectivity of He/N₂ and He/Ar were only 2.17 and 2.42, lower than those of the corresponding Knudsen diffusion ratio of 2.64 and 3.16, which meant that there are large defects in the NaA zeolite membrane. This was accordance with the SEM results that the NaA zeolite crystals were not well intergrown. After two-stage synthesis, the permeance of the membrane further decreased and the permselectivity of He/N₂ and He/Ar increased. But the permselectivity of He/N₂ and He/Ar were still lower than those of the Knudsen diffusion ratios. After three-stage synthesis, the permeance of the membrane decreased sharply and the permeance of argon was only 1% of the support, which indicated that a compact NaA zeolite membrane formed on the ceramic hollow fiber support. The permselectivity of He/N₂ and He/Ar were 3.66 and 4.41, larger than those of the corresponding Knudsen diffusion ratio of 2.64 and 3.16. When the synthesis stage increased to four times, the permeance of the membrane decreased. However, the permselectivity of He/N₂ and He/Ar also decreased. This was possibly caused by the formation of a thick zeolite membrane on the support surface and the thick membrane cracks during the dry process.

The gas permeation property of the NaA zeolite membrane in this paper was compared with those of the A-type zeolite membranes in the literatures in Table 2. The He/N₂ permselectivity of the NaA zeolite membrane in this study was close to those of the A-type zeolite membrane in the literatures. The A-type zeolite membrane in the literatures also showed a high H₂/n-C₄H₁₀ or He/n-C₄H₁₀ permselectivity. For example, Guan et al. reported that their NaA zeolite membrane showed a He/N₂ permselectivity of 3.78, which is nearly identical to the He/N₂ permselectivity of the NaA zeolite membrane of 3.66 in this study. Their NaA zeolite membrane showed a H₂/n-C₄H₁₀ and He/n-C₄H₁₀ permselectivity of 13.0 and 7.0, respectively, higher than those of the corresponding Knudsen diffusion ratio of 5.39 and 3.81, which indicated that a relatively perfect NaA zeolite membrane formed on the support. Therefore, it may be inferred that a relatively perfect NaA zeolite membrane also formed on the ceramic hollow fiber support. However, the permeation of n-C₄H₁₀ indicated that there were non-zeolite pores, larger than the pore size of NaA zeolite, in the NaA zeolite membrane, which was also reflected by the permeance of N₂ and Ar. The kinetic diameters of N₂

Table 2

Comparison of the gas permeation properties of the NaA zeolite membrane in literatures and in this paper (permeance: 10^{-7} mol/m² Pa s)

Membrane	H ₂	He	N ₂	<i>n</i> -C ₄ H ₁₀	SF ₆	He/N ₂	H ₂ / <i>n</i> -C ₄ H ₁₀	He/ <i>n</i> -C ₄ H ₁₀	H ₂ /SF ₆
Knudsen diffusion ratio of H ₂ /gases	–	–	–	–	–	2.64	5.39	3.81	8.54
This study	–	1.01	0.276	–	–	3.66	–	–	–
Guan et al. [27]	0.26	0.14	0.037	0.02	–	3.78	13.0	7.0	–
Aoki et al. [28]	0.064	0.064	0.014	0.012 (C ₃ H ₈)	–	4.57	–	5.33	–
Aoki et al. [29]	0.0065	0.0055	0.0040	0.00012	–	1.38	5.90	4.58	–
Okamoto et al. [30]	3.68	–	1.0	–	0.4	–	–	–	9.2

and Ar are 3.64 and 3.4 Å, respectively. If the NaA zeolite membrane was perfect, the permeation of N₂ and Ar should solely depend on the molecular size. The permeance of Ar should be higher than the permeance of N₂. However, the permeance of Ar is lower than the permeance of N₂ for the NaA zeolite membrane on the ceramic hollow fiber support, which indicated that a significant part of the gas permeance was from the gas permeation through the non-zeolite pores.

Besides the selectivity, the permeance is another important parameter to evaluate the quality of the membrane. While the thicknesses of the NaA zeolite membrane are similar, the gas permeance of the NaA zeolite membrane on the ceramic hollow fiber support was significantly higher than those of the NaA zeolite membrane on the bulk disk or tubular support. This was possibly caused by the thinner wall thickness of the ceramic hollow fiber support than the bulk disk or tubular support, and therefore the formation of fewer zeolite crystals in the pores of the ceramic hollow fiber support than in the pores of the bulk disk or tubular support.

4. Conclusion

NaA zeolite membrane was successfully synthesized on a ceramic hollow fiber. A continuous NaA zeolite membrane formed on the hollow fiber support after a three-stage synthesis and the membrane thickness was about 5 μm. Gas permeation results indicated that only after a three-stage synthesis did a high quality NaA zeolite membrane formed on the hollow fiber support. Further increasing the synthesis-stage to four stages deteriorated the quality of the NaA zeolite membrane.

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