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High-Performance Zeolite NaA Membranes on Polymer−Zeolite Composite Hollow Fiber Supports

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Zeolite NaA membranes are hydrophilic and have shown high selectivity for removal of water from organic solutions[1−4] and especially in alcohol dehydration, a necessary and expensive step in the production of biofuels. Zeolite membranes have usually been synthesized by a seeded growth method. Seeding on the supports has been recognized as a crucial processing factor for obtaining high-performance zeolite membranes.[5−7] Many seeding methods have been reported to date.[4] However, none of them is a perfect seeding method for synthesizing zeolite membranes with high pervaporation (PV) performance, mainly because of the difficulty in forming a uniform seed distribution on the surface of the supports. On the other hand, zeolite membranes supported on large-diameter (12 mm) ceramic tubes have been commercially used in Asia and Europe,[1a] but the ceramic tubes are large and expensive, and the membranes have low flux.[1b] The large diameter and the low flux together lead to large module size. Very recently, we reported a new seeding method, dipcoating−wiping deposition, which is very useful for obtaining high-performance zeolite NaA membranes on ceramic hollow fiber (HF) supports.[7] The high-performance ceramic HF-based zeolite membranes are expected to reduce the module size dramatically, but the cost of producing ceramic HF is still of concern, and the seeding process is still needed.

Here, we report a new strategy: use of polymer−zeolite composite hollow fibers (CHFs) as supports. The zeolite crystals embedded in the polymer HFs serve as seeds for the zeolite membrane growth, and they also "anchor" the zeolite membrane to the support to increase the adhesion of the zeolite membrane. Therefore, a separate and often complex seeding process can be omitted. A very uniform crystal distribution can be obtained easily, so continuous zeolite membranes can be prepared with high reproducibility. These CHFs can be produced simply by blending zeolite crystals into the polymer feed before the HF extrusion and thus are expected to be inexpensive. We estimate that by using CHFs to replace the large ceramic tubes, we can reduce the size of the separate module by a factor of 30 and the cost by a factor of >30.

Polyethersulfone (PES)−zeolite NaA CHF supports were prepared by spinning a PES solution containing suspended zeolite NaA powders into a HF precursor, which was then washed in water and dried at 60 °C, according to the literature.[8,9] The top and cross-sectional views of the CHF supports were examined by scanning electron microscopy (SEM) (Figure 1). The outer diameter of the HF is ~2.2 mm, and the inner diameter ~1.0 mm (Figure 1a). The zeolite particles are uniformly distributed inside the polymer wall (Figure 1b). The X-ray diffraction pattern of the CHF support is consistent with the structure of zeolite LTA (Figure S1a in the Supporting Information), indicating that no damage to the zeolite crystals occurred during preparation of the CHF supports. If zeolite NaA crystals were added to the feed for making ceramic HFs, they would be damaged because ceramic HFs must be sintered at high temperature (>1400 °C).

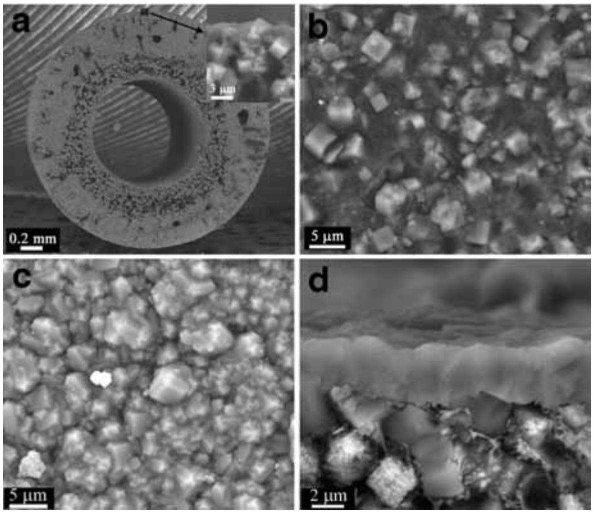

Figure 1. SEM images of (a, b) the CHF support and (c, d) the zeolite membrane on it: (a, d) cross-sectional views; (b, c) top views. Zeolite membrane was synthesized at 100 °C for 4 h by in situ hydrothermal crystallization.

Table 1. Effects of Synthesis Time on Membrane Properties

membrane no.	*t* (h)[a]	*D* (μm)[b]	*J* (kg m^{-2} h^{-1})[c]	α[d]
1	2	1.0	8.0	1000
2	3	2.0	9.3	>10000
3	4	3.0	9.2	>10000
4	5	3.5	8.1	>10000

[a] *t*, synthesis time. [b] *D*, membrane thickness. [c] *J*, flux. [d] α, separation factor. Pervaporation conditions: 90 wt % ethanol solution at 75 °C.

The XRD patterns of zeolite membranes obtained on all the supports were consistent with the zeolite LTA structure (Figure S1b), indicating that zeolite LTA was the only crystalline phase formed during the hydrothermal synthesis. Their peak intensities were higher than those of the parent CHF supports (Figure S1a). The morphology and thickness of the as-synthesized membranes were examined by SEM (Figure 1c,d). The zeolite crystals were found to be so well intergrown that they formed a dense layer on the supports, and the typical cubic morphology of zeolite NaA crystals was hardly seen (Figure 1c). The cross-sectional SEM image also showed a uniform zeolite layer on top of the CHF support with a thickness of ~3.0 μm (Figure 1d).

PV performance results for the zeolite membranes were obtained, and as shown in Table 1 (membrane 3), the separation factor (α) of the zeolite NaA membrane after the 4 h synthesis on CHF supports

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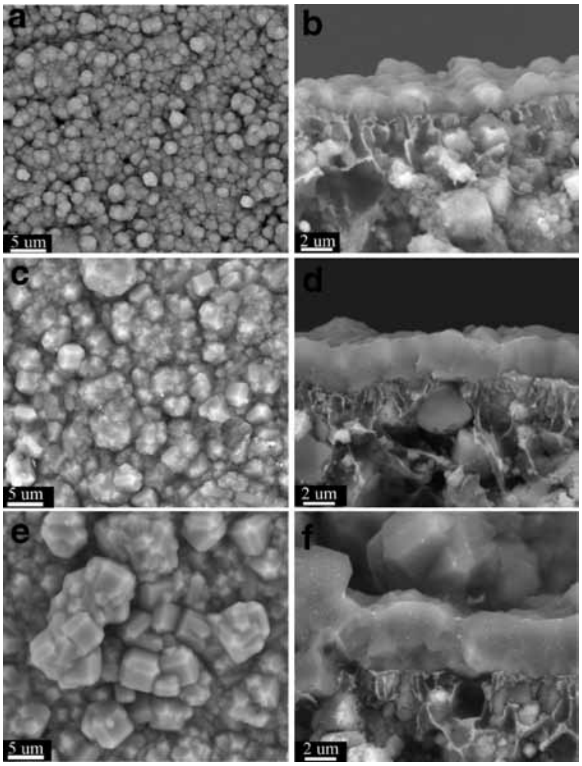

Figure 2. SEM images of zeolite membranes on CHF supports synthesized at 100 °C for (a, b) 2, (c, d) 3, and (e, f) 5 h: (a, c, e) top views; (b, d, f) cross-sectional views.

was very high (>10 000), indicating that the zeolite NaA membrane on the CHF support prepared by a single in situ hydrothermal synthesis was continuous and well-intergrown. The flux of this zeolite membrane on the CHF support was 9.2 kg m^{-2} h^{-1}, which is much higher than those reported in the literature for zeolite membranes on ceramic tube supports[1] and polymer−zeolite mixed-matrix membranes (MMMs).[10] This is probably due to the higher porosity of the PES−zeolite CHF supports than of ceramic tube supports (∼40%) and polymer−zeolite MMMs (thought to be a dense membrane) and the smaller wall thickness of the CHF supports (0.6 mm) than of ceramic tube supports (∼1.5 mm). Also, all three zeolite membranes on the CHF supports after the 4 h synthesis (Table S1, membranes 3a−c) showed similar high PV selectivities ($\alpha > 10\,000$), indicating the high reproducibility of the synthesis of zeolite membranes on CHF supports. This shows the advantage of having uniformly embedded zeolite crystals in polymer HF supports. The slight difference in the fluxes of these three membranes is possibly due to subtle differences in the support porosity.

As mentioned above, zeolite membranes with high PV performance can readily be obtained in high yield using PES−zeolite CHFs as supports. From the point view of large-scale commercial production, therefore, the reproducibility of the synthesis of zeolite membranes can be increased by using CHF supports. From the viewpoint of basic research, by omission of the seeding process, the effects of the synthesis conditions and composition can easily be elucidated. These studies are ongoing in our laboratory. Here we focus only on the effects of the synthesis time on the quality of the zeolite membranes. Zeolite membranes were synthesized in 2−5 h. No significant difference could be found in the morphology of zeolite on the surface of the membranes (Figure 2). There were some pinholes found on the surface of the membrane synthesized at 2 h and a second layer on the surface of the membrane synthesized at 5 h. From the cross-sectional SEM view, the thickness of zeolite membranes was found to increase from 1.0 to 3.5 μm with the synthesis time (Table 1). Although the α value of 2 h-synthesized membrane was low (Table 1, membrane 1), the α values of the zeolite membranes synthesized in >3 h are very high (Table 1, membranes 2−4). Zeolite membranes with thicknesses of 2 μm synthesized in 3 h were already good enough for dehydration of ethanol solution. The fluxes were 8.0−9.3 kg m^{-2} h^{-1}. The effects of the thickness of the zeolite membrane on the flux in this range could not be seen (Table S1). The difference in the flux is possibly due to the difference of the support porosity. XRD patterns of the powders from the same autoclave as for making the membranes in 3 h (Figure S2) did not show zeolite LTA, but it did appear in syntheses longer than 4 h, indicating that the continuous layer of zeolite NaA was mainly produced from the seeds in the CHF supports and the second layer mainly from the synthesis mixture.

In conclusion, zeolite membranes with high PV performance have been synthesized on PES−zeolite CHF supports by a single in situ hydrothermal crystallization with good yield, because the CHF supports provided uniform zeolite seed particles on their surfaces. The composite support approach is likely to open up a completely new route without a separate seeding process to prepare high-performance, low-cost, reproducible zeolite membranes. Polymer−zeolite CHF supports are also expected to have serious implications for preparing zeolite membranes on their inner surfaces because they also provide a very uniform zeolite seed crystal distribution on their inner surfaces. Zeolite membranes on the inner surfaces of hollow fiber supports can reduce pressure loss during the PV process and provide significant processing advantages as the membranes are naturally protected by the support during handling. The mechanical stability of CHF supports can be improved by making polymer−zeolite composite monoliths with multiple channels. These efforts are ongoing in our laboratory and will be published in the near future.

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Supporting Information Available: Main contributions, experimental methods, Table S1, and Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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