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High Performance Zeolite LTA Pervaporation Membranes on Ceramic Hollow Fibers by Dipcoating−Wiping Seed Deposition

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Bioethanol is considered a renewable and sustainable fuel for automotives. One key step in bioethanol production is the removal of a large amount of water from the dilute (<10%) ethanol solution generated by the fermentation process. The current process used for this purification is distillation that is energy intensive and thus negatively impacts the economic viability of bioethanol.[1] Zeolite membrane separation has been considered an attractive alternative to distillation.[2,3]

Zeolite membranes have been intensively investigated for the past two decades[2,4] and shown to have interesting properties in gas permeation and pervaporation (PV).[5−7] The hydrophilic zeolite LTA membrane is extremely selective for removal of water from organic solutions by PV or vapor permeation and can be used, therefore, for the production of water-free ethanol (>99 wt % ethanol) for biofuel application. Mitsui Engineering and Shipbuilding Co. Ltd. in Japan adopted Kita group's technology and developed the first large scale PV plant in 1998 using tubular LTA membranes for dehydration of organic solvents.[3] In 2003 Bussan Nanotech Research Institute Inc., a 100% subsidiary of Mitsui & Co. Ltd. Japan, tested successfully the dehydration of bioethanol on a pilot scale by using LTA membranes for vapor permeation in Brazil. Despite their excellent water/ethanol separation factor and reasonable flux, the critical drawback shared by the two LTA membranes mentioned above is the large diameter of their tubular supports (i.e., 12 and 16 mm, respectively). This large diameter translates into low membrane area per unit volume, which in turn leads to large inefficient modules. It is also highly desirable to increase the reproducibility of zeolite membranes with high performance and increase the water flux so that the module volume can be further reduced.

In this communication, we demonstrate for the first time that, by one single hydrothermal synthesis, zeolite membranes with high PV performance and high reproducibility on ceramic hollow fiber (HF) supports can be obtained using a dipcoating−wiping seeding method. We are interested in using ceramic HFs as supports, because of their high packing density (membrane surface area/volume ratio > 1000 m^2/m^3, if the outer diameter is smaller than 4 mm) and thinner wall. Ceramic supports are also known for their chemical and thermal stability. Xu et al.[8] reported that a zeolite LTA membrane was successfully synthesized on a ceramic HF. The synthesis had to be repeated three times to obtain high quality zeolite LTA membranes. Only gas permeation results were shown; no dehydration performance was reported.

Zeolite LTA membranes were usually synthesized by a seeded growth method.[5,6] The seeding on the supports has been recognized to be a crucial processing factor to obtain high quality zeolite membranes.[9,10] Many seeding methods have been reported, such as dip-coating,[10] vacuum method,[11] and rubbing.[12,13] Nakao et al.[12] and Pina et al.[13] covered the porous support by directly rubbing the powdered seed crystals on it. The properties of alumina HF and mullite tube (MT) supports used in this study are shown in Table 1 and Supporting Information, Figure S1. HF supports are too slender and brittle for rubbing powdered seed crystals directly onto them by hand. We made three zeolite LTA membranes on HF supports by direct but very careful rubbing of powdered seed crystals (average size 0.8 μm, from Mizusawa Chemical Co. Ltd., Japan) onto them. The separation properties of zeolite LTA membranes were characterized by PV experiments (Figure S2). Only one sample showed good separation performance (Table S1). It is also expected to be very difficult to automate the direct rubbing of powdered seed crystals on HF supports in eventual commercial practice. We also attempted to cover the alumina HF supports with LTA seed crystals by only the dip-coating method in the present study. However, the LTA membranes made by this method were of low quality. Their water/ethanol separation factor (α) in PV characterization was lower than 1000. Dip-coating produces a mostly uniform seed layer, but there are still gaps (Figure 1a) that lead to poor coverage of zeolite membranes (Figure 1b). We discovered that high quality LTA membranes with high reproducibility were synthesized by one single hydrothermal synthesis after wiping the seed dip-coated supports. After wiping, a much smaller amount of seeds (<0.1 g/m^2) was on the surface of the hollow fiber supports (Figure 1c) compared with just after dip-coating (ca. 1.1 g/m^2) (Figure 1a); however, a dense membrane was produced (Figure 1d). Zeolite LTA membranes synthesized by the dipcoating−wiping seeding method showed high PV performance (α > 10 000, Table 1), indicating the amount of seeds is not the critical factor for obtaining high quality membranes on these kind of supports.

Table 1. Support Properties and PV Results of the Corresponding Zeolite LTA Membranes

S[a]	O.D. (mm)	I.D. (mm)	A.P.S.[b] (μm)	M.T.[c] (μm)	flux (kg/m²h)	α[d]
HF	1.2	0.6	0.3	3.0	6.2	12 500
MT	12.0	9.0	1.0	5.0	1.8	5192

[a] HF, hollow fiber; MT, mullite tube. [b] A.P.S., average pore size. [c] M.T., membrane thickness. [d] α, water/ethanol separation factor. Pervaporation conditions: 90 wt % ethanol aqueous solution at 75 °C.

A very recent study[14] suggested that even amorphous "seeds" may play an important role in the early stages of nucleation and growth of zeolite crystals. Here, we hypothesize that wiping led to the contact of the seed crystals with the support surface leaving possibly a trace amount of "seeds" everywhere including support defects (Figure S3). We thus performed an experiment using a zeolite membrane coated hollow fiber to rub the surface of a blank support and then exposing the support to synthesis. This has led to the selective growth of a zeolite coating line (Figure 1f), although no clear seed line can be seen (Figure 1e and inset). Therefore,

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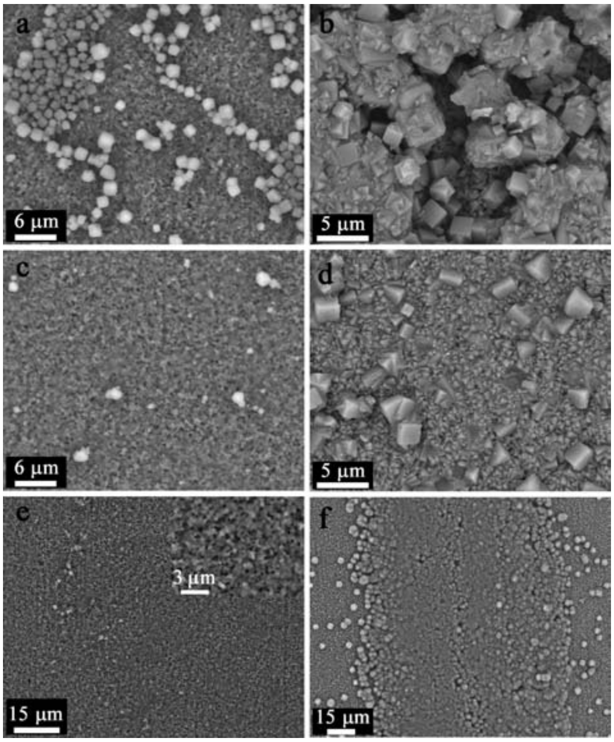

Figure 1. SEM images of seeded supports (a, c, e) and zeolite membranes (b, d, f): (a) only dip-coating, (c) dipcoating−wiping, (e) chalking, and (b), (d), (f) zeolite membranes synthesized at 100 °C for 3 h on corresponding supports.

wiping the seed dip-coated supports appears to make seeds become more uniform and possibly enter into the defects on the surface of the support. Xu et al.[8] mentioned that only after the hydrothermal synthesis was repeated three times did a high quality zeolite LTA membrane form on the HF. Since the composition of the synthesis solution used in this study is similar to the one used by Xu et al., this suggests the differentiating factor is the dipcoating−wiping method used in this study. It was also found that the thinner zeolite membranes were obtained by wiping the seed dip-coated supports compared with only dip-coating because of the thinner seed layer obtained by the former method. Therefore, the wiped seed dip-coated HF supports were always used in this study. However, the defects on the MT supports (Figure S3) seem to be too large for the dipcoating−wiping to work. The water/ethanol separation factor of zeolite LTA membranes on MT supports was much lower than that on HF supports (Table 1).

XRD analysis on the surface of the membrane prepared confirmed the formation of a zeolite layer of LTA structure on the HF support (Figure S4). Cross-sectional SEM analysis shows a zeolite layer thickness of 3−4 μm (Figure S5). As shown in Table 1, the flux of the zeolite LTA membrane on the HF support is much higher than that on the MT support, although the porosity of two types of supports is the same (35%). The flux on MT supports is similar to what is previously reported.[5] These results indicate that the properties of the supports strongly influence the flux of the zeolite membranes. It is possible that the lower flux of the zeolite membrane on the MT support is due to the thicker wall of the support. The thinner thickness of zeolite membranes on HF supports is also probably one of the reasons.

Another finding in this study is that the flux of the membranes increased with the porosity of HF supports dramatically (Figure 2). A flux of 9.0 kg/m^2 h was obtained when the HF support with a porosity of 50% was used. We believe that this is the highest value reported in literatures under the same PV conditions (Table S2). From the curve in Figure 2, a flux higher than 10.0 kg/m^2 h is possible, if the HF support with a porosity higher than 60% can be made.

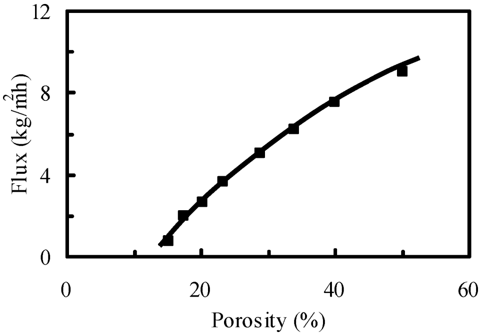

Figure 2. Relationship between the flux of zeolite membrane and the porosity of HF support.

In summary, we have demonstrated for the first time that, by one single hydrothermal synthesis, a zeolite LTA membrane with a high flux of 9.0 kg/m^2 h and high water/ethanol separation factor of 10 000 could be formed on a ceramic hollow fiber that is known for its ability to form a compact module. The flux is the highest reported in literatures.[5,15] A novel seeding method, dipcoating−wiping, is key to obtaining zeolite membranes with high separation performance because it reproducibly produces a uniform and trace seed layer on the support. This new seeding method is expected to have serious implications for making defect-free zeolite films and membranes for many applications. The membranes reported here have the potential to solve the key problems that have prevented zeolite membranes from widespread use for biofuel production.

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Supporting Information Available: Experimental methods, Tables S1−S2, Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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