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# Zeolite Membrane for Dehydration of Isopropylalcohol–Water Mixture by Vapor Permeation

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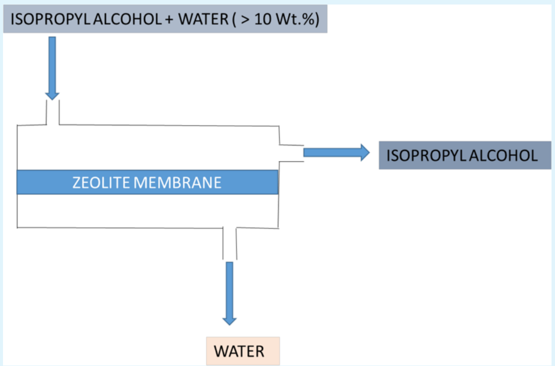
*Supporting Information*

**ABSTRACT:** Highly stable FAU-type zeolite membrane for the separation of isopropanol (IPA)-water mixture by pervaporation is described. FAU membrane showed high water permselectivity and permeance. Comparison of FAU membrane with a conventional LTA-type zeolite membrane revealed superior stability of FAU zeolite membrane in a mixture containing a large water content.



**KEYWORDS:** *zeolite membrane, pervaporation, vapor permeation, separation and purification*

Combining distillation and membrane separation units hold great potential to reduce energy demands of separation units in chemical and petrochemical industries.[1,2] Pervaporation of liquids through a membrane is a process used to separate azeotropic liquids and liquids with close boiling points. Several types of polymeric membrane are used in the pervaporation process. However, they suffer from disadvantages such as swelling, concentration polarization and poor chemical and thermal stability. On the other hand, zeolites (with micropores in the range of 0.4–1.3 nm) are promising membrane material due to their relatively high chemical and thermal resistance. Strongly hydrophilic LTA type zeolite membrane is the only zeolite membrane that has been commercialized, so far, for the dehydration of various water–alcohol mixtures.[3−5] The currently used LTA membrane is effective only with mild organic solvents containing a small amount of water (up to 10%) in the mixture.

Isopropyl alcohol (IPA) is used extensively in semiconductor and pharmaceutical industries. IPA-water system forms an azeotrope when the water content of the mixture is about 14%. Thus, current production process of IPA involves an azeotropic distillation step that consumes about 35% of the energy demand of the whole production process. Replacing this energy-intensive azeotropic distillation step with a membrane-based dehydration unit would reduce energy consumption of the whole process significantly.

FAU-type zeolite is a large pore zeolite with a strong hydrophilic nature and has a relatively high resistance to water. Although different approaches such as in situ crystallization, dry gel transfer, and secondary growth have been used to prepare zeolite membrane, FAU-type zeolite membranes have been synthesized by a secondary growth method using seed crystals.[6−17] Kita et al. first prepared a FAU-type membrane from an aluminosilicate gel, and studied its dewatering behavior in an ethanol–water mixture by pervaporation.[6] Kumakiri et al. proposed a different strategy that involves the preparation of a well-aligned seed layer followed by a hydrothermal growth in a clear solution of aluminosilicate.[7] In most of the previous studies, membrane degraded in the presence of a large content of water (in the separation mixture), thereby limiting their application to streams with a low water content. Herein, we report, the preparation of a compact FAU type zeolite membrane that is useful in the dehydration of alcohol–water mixture containing a large fraction of water (>10%).

In this report, we demonstrate a two-step crystallization method to get a compact FAU type zeolite layer, with improved separation property and stability. FAU type zeolite membrane was synthesized onto a porous $\alpha$-alumina tubular support (inner diameter = 7 mm, outer diameter = 10 mm, length = 30 mm, average pore size = 0.15 $\mu$m) by a two-step secondary growth method (detailed experimental procedure is described in the Supporting Information). The first step of this process

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consisted of a seed crystallization onto a porous support from an aluminosilicate gel, followed by a hydrothermal step, in a clear solution of aluminosilicate, for further crystal growth. The second step also improved the compactness of the membrane thereby reducing the nonzeolitic pores.

We compared the stability of LTA and FAU zeolite membrane, in IPA-water mixture containing a large water content. LTA membrane was prepared on the same porous support by following a previous literature.[3−5] In order to investigate the membrane stability, these membranes were immersed in a 50/50 (by weight %) water/IPA mixture at 403 K for 42 h in an autoclave, or exposed to vapor produced from 50/50 (by weight %) water/IPA mixture at 403 K under an autogenous pressure for 42 h (see the Supporting Information, Figure S1).

Figure 1 compares the typical FE-SEM images of LTA type and FAU type membranes before and after the stability tests.

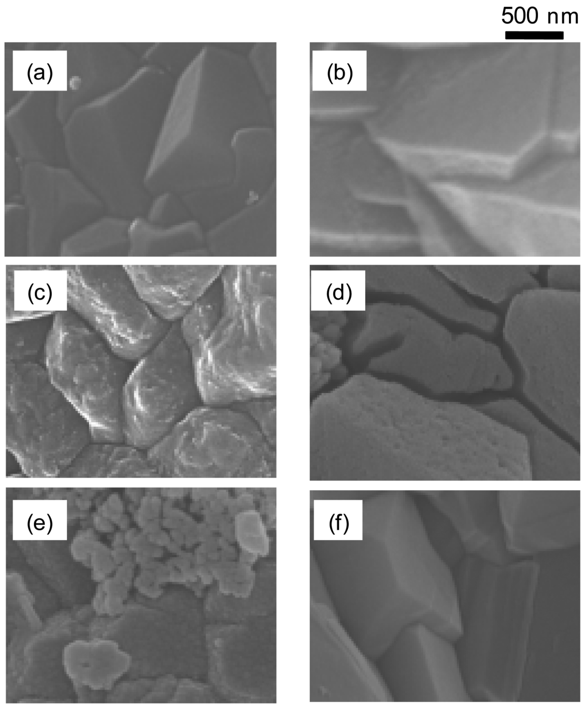

**Figure 1.** Typical FE-SEM images of the surface of zeolite membranes before and after stability tests: (a) Fresh LTA membrane, (b) fresh FAU type membrane, (c) LTA type membrane after the stability test in liquid phase, (d) FAU type membrane after the stability test in liquid phase, (e) LTA type membrane after the stability test in vapor phase, and (f) FAU type membrane after the stability test in vapor phase.

Comparison of surface FE-SEM images of fresh FAU and LTA type membranes, before (Figure 1a, b) and after (Figure 1c, d) immersion test, clearly indicates that the surfaces of both types of membrane were seriously eroded and voids were formed along crystal boundaries after the immersion of membranes in IPA-water mixture. On the contrary, comparison of FE-SEM images before (Figure 1a, b) and after (Figure 1 (e) and (f)) exposure to water/isopropanol vapors reveals the following. Vapor exposure of LTA type membrane resulted in the formation of a large number of small particles, probably amorphous aluminosilicate particles, on the membrane surface, as seen in Figure 1e. However, no obvious changes were observed for the FAU membrane (Figure 1f) after the exposure to the water/IPA-mixed vapor.

The XRD patterns of the FAU membrane did not show any change after the exposure see the Supporting Information, Figure S2) to water vapor, indicating the absence of any deterioration in the crystallinity of FAU membrane. On the other hand, after the water vapor exposure, a reduction in the diffraction peak intensities of LTA membrane was noticed. This suggests a degradation in the crystallinity of LTA membrane in addition to the morphological changes (see the Supporting Informationj, Figure S2). Generally, the steaming stability of zeolites increases with increasing Si/Al ratio in zeolite framework, trading-off its hydrophilic nature. The EDX measurement of the surface of LTA and FAU membranes revealed that Si/Al ratios of LTA zeolite and FAU zeolite were 1 and 1.4, respectively. Relatively higher stability of FAU type membrane would be due to its lower hydrophilicity compared to LTA type membranes as evidenced by a higher Si/Al ratio of the FAU type membrane (Si/Al = ca. 1.4−1.5) compared to LTA type membrane (Si/Al = 1). Therefore, considering the results of stability tests, FAU type membranes were further evaluated for the vapor phase permeation and separation of IPA-water mixture with a high water content. LTA Type membrane was not evaluated as they were unstable under such water rich condition as shown by the stability tests.

Vapor permeation and separation measurements were performed using a stainless steel tube module cell, as described in the Supporting Information (Figure S3). Figure 2 shows the temperature dependency of the permeances of water and IPA through the FAU type membrane. In a binary system of 20/80 (by wt %) water/IPA mixture, the permeance of water was almost constant at ca. $5 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$, whereas the permeance of IPA largely increased from $3.4 \times 10^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ to $6.2 \times 10^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ with increasing temperature from 373 to 423 K. Therefore, the water permselectivity, $\alpha_{\mathrm{Water/IPA}}$, was larger at lower temperature and exceeded 1000 at 373 K. Because kinetic diameters[18] of water (0.30 nm) and IPA (0.47 nm) are smaller than the size of FAU pores (0.74 nm), both water and IPA can enter FAU pores. However, hydrophilic nature of FAU should contribute to preferential adsorption of water against IPA. In addition, diffusion of a smaller molecule, or water, should be faster than a larger molecule, or IPA. Even in an unary system, the permeation of IPA was considerably small, compared with

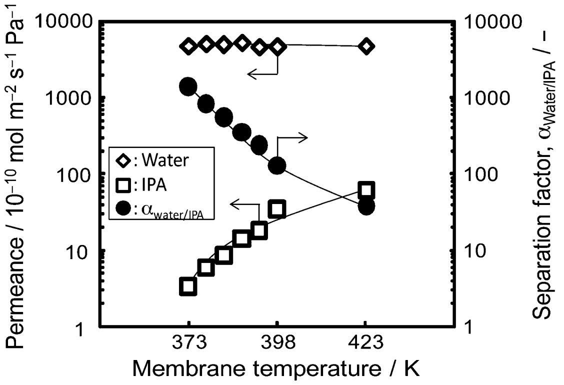

**Figure 2.** Effect of membrane temperature on vapor phase separation property of a FAU membrane in the binary system of 20/80 (by wt %) water/IPA mixture.

that of water (see the Supporting Information). At 423 K, the permeance of IPA in the unary system was 1.4 × $10^{-8}$ mol $m^{-2}$ $s^{-1}$ $Pa^{-1}$, whereas that of water was ca. 6 × $10^{-7}$ mol $m^{-2}$ $s^{-1}$ $Pa^{-1}$. The thermogravimetric (TG) analysis (see the Supporting Information, Figure S4) indicated that FAU type zeolite (Si/Al = ca. 1.4, Na-type) held 54 mg $g^{-1}$ of water (corresponding to 40 water molecules per unit cell) even after heating at 423 K. The TG analysis indicates that nearly all the preadsorbed water were removed at 873 K. The lower permeance of IPA in unary system is attributed to the presence of water molecules, remaining in the FAU membrane, narrowing the zeolite pores thereby inhibiting the permeation of IPA.

Figure 3 shows the permeances of water and IPA as a function of water content through the FAU type membrane. The permeance of water was almost constant (ca. 5 × $10^{-7}$ mol $m^{-2}$ $s^{-1}$ $Pa^{-1}$) in the range of water weight fraction from 10 to 50 (by weight %). On the other hand, the permeance of IPA decreased from 2.4 × $10^{-9}$ to 5.8 × $10^{-11}$ mol $m^{-2}$ $s^{-1}$ $Pa^{-1}$ when the water content in the mixture was increased from 10 to 50%, suggesting that the presence of water strongly inhibited the permeation of IPA. As a result, water permselectivity increased with increasing water weight fraction.

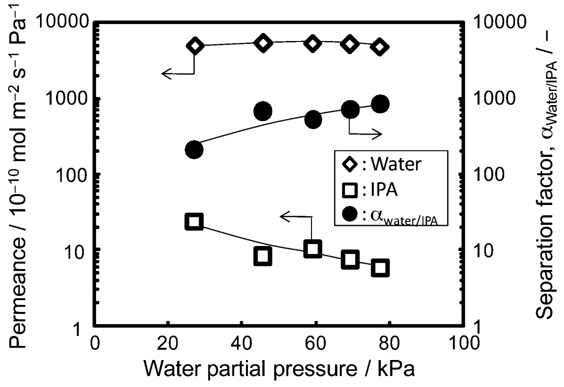

**Figure 3.** Effect of water partial pressure in feed on vapor phase separation property of a FAU type membrane at 373 K.

In conclusion, the FAU type membrane prepared in this study effectively separated water from water/IPA mixtures in vapor phase. The separation factor of water/IPA increased at lower temperature and higher water content. The FE-SEM and XRD results suggested high water resistance of the FAU type membrane, in comparison with a LTA type membrane. The result of this study suggests that FAU type membrane seems promising for vapor phase dewatering of alcohol with large water contents.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Detailed experimental procedure describing membrane preparation and evaluation. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b04085.

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### Notes

The authors declare no competing financial interest.

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