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ZIF-8 membranes prepared at miscible and immiscible liquid–liquid interfaces

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ABSTRACT

ZIF-8 membranes are currently attracting attention for the separation of propylene/propane based on the molecular sieve effect. We have recently reported the preparation of ZIF-8 membranes using the counter-diffusion method, which is advantageous in reducing defects in the selective layer. In the present study, ZIF-8 membranes were prepared at the interface of miscible and immiscible pairs of solvents such as water/methanol and water/1-octanol, respectively. ZIF-8 membranes prepared from the immiscible pair of water and 1-octanol showed a propylene permeance of 5.2×10^{-9} mol m^{-2} s^{-1} Pa^{-1} and a propylene/propane permselectivity of 7.2 at 25 °C. As for the ZIF-8 membrane prepared by the initial reaction using the immiscible pair of water/1-octanol and the successive reaction using the miscible pair of water/methanol mixture, the average propylene permeance and average propylene/propane permselectivity increased to 1.2×10^{-8} mol m^{-2} s^{-1} Pa^{-1} and 20 at 25 °C, respectively. The successive reactions in water/1-octanol and water/methanol mixtures successfully decreased the defects in the ZIF-8 selective layer, resulting in high propylene permeance and high permselectivity for propylene/propane. The structure and gas permeation properties were also thoroughly characterized.

1. Introduction

Separation of a propylene/propane mixture by distillation is acknowledged as one of the most energy-consuming processes in the petrochemical industry [1,2]. Membrane separation processes are recognized as an attractive alternative as they have the potential to significantly reduce energy consumption.

Among the several varieties of materials for propylene/propane separation membranes, the zeolitic imidazolate framework-8 (ZIF-8) is one of the most promising [3]. ZIF-8 is composed of zinc atoms with 2-methylimidazole as a ligand that form a sodalite zeolite structure having large cavities, which are connected through a small pore aperture [4]. Zhang et al. reported that the diffusivity of propylene was approximately 100 times higher than that of propane [5]. They concluded that the effective aperture size of ZIF-8 for molecular sieving was between 0.40 and 0.42 nm, which corresponded to the van der Waals diameter of propylene and propane, respectively. Therefore, ZIF-8 is now recognized as a promising material for the separation of propylene/propane based on the difference of the molecular size. ZIF-8 is also focused for such applications as hydrogen separation, carbon dioxide separation, and alcohol dehydration [3].

Several preparation methods for ZIF-8 membranes have been reported, such as the in situ growth method [6–10], the secondary growth method [11–18], and the counter-diffusion method [19–21]. Pan et al. first described the effective separation of propylene/propane using ZIF-8 membranes prepared from the secondary growth method with selectivity up to 50 for an equimolar mixture of propylene/propane [22]. Successively, Kwon and Jeong [18] and Liu et al. [16] also reported ZIF-8 membranes with comparable propylene/propane separation performances. Recently, the counter-diffusion method has attracted attention because it facilitated the preparation of the ZIF-8 selective layer with fewer defects through a simple preparation procedure. Using this method, the ZIF-8 layer is directly prepared at the interface of two solutions, zinc nitrate and 2-methylimidazole. In the preparation, 2-methylimidazole and zinc ions interdiffuse at the interface, and the crystallization occurs simultaneously until the entire path through the ZIF-8 layer becomes "plugged." Kwon and Jeong reported the counter-diffusion preparation method and the permeation properties of ZIF-8 membranes with a selectivity of up to 55 for an equimolar mixture of propylene/propane [19]. We reported the preparation of ZIF-8 membranes with propylene/propane permselectivity of 59, for

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which a ZIF-8 layer was prepared within the pores of an alumina porous substrate using the counter-diffusion method [20].

For the practical use of ZIF-8 membranes, Brown et al. recently reported the scalable preparation of ZIF-8 membranes with the ZIF-8 layer being formed on the inner surface of polymeric hollow fibers using microfluidic membrane processing (IMMP) based on the counter-diffusion concept [21]. They prepared the ZIF-8 membranes at the interface of the immiscible pair of water and 1-octanol solutions, and reported a propylene/propane selectivity as high as 12. It was reported that the ZIF-8 membranes with selective layer formed on the unexposed inner surfaces of hollow fibers had an advantage in avoiding possible defects during synthesis. In the counter-diffusion method, various conditions such as solvent species, concentration, and temperature can affect the structure and the resultant permeation properties [23]. A major factor that determines the reaction occurrence and the diffusion in the liquid–liquid interface, for the counter-diffusion method, is the compatibility of the two employed solutions. In the previously mentioned study, ZIF-8 membranes were prepared using polymeric hollow fibers for the purpose of scaling up the process using an inexpensive substrate, where gas permeation properties should be significantly influenced by the flexibility of the polymeric substrate [21]. An alternative for the development of the ZIF-8 membrane is to estimate the structure and gas permeation properties independently, without the involvement of the flexible polymeric substrate. Therefore, the preparation of ZIF-8 membranes using the miscible and immiscible liquid–liquid interface should be further investigated using a rigid substrate such as the α-alumina substrate.

In the present study, we focused on the preparation of ZIF-8 membranes at miscible and immiscible liquid–liquid interfaces as well as their analysis. ZIF-8 membranes were prepared by the counter-diffusion method using a porous α-alumina hollow capillary substrate. The zinc nitrate aqueous solution was supplied from the inner part of the substrate, and the 2-methylimidazole solution in 1-octanol was supplied from the outer part of the substrate. In order to investigate the miscibility effect of the solutions, ZIF-8 membranes were also prepared using a 2-methylimidazole solution in methanol. The structure of the ZIF-8 membranes, the single component gas permeation properties obtained for helium, hydrogen, carbon dioxide, oxygen, nitrogen, methane, propylene, propane are comprehensively discussed.

2. Experimental

2.1. Membrane preparation

A porous α-alumina hollow capillary substrate with a diameter of 3 mm, an average pore diameter of 150 nm, a porosity of 46%, and a thickness of 350 μm was obtained from NOK Corporation. The substrate was cut into 45-mm-long pieces, washed with acetone, and then dried under vacuum. Methanol, 1-octanol, and zinc nitrate hexahydrate were purchased from Wako Chemicals, Japan, 2-methylimidazole was purchased from Sigma–Aldrich; and all compounds were used as received.

ZIF-8 membranes were prepared by the counter-diffusion method as shown in Fig. 1. One end of the substrate was sealed with molten glass to separate its inner and outer compartments. The substrate was then completely immersed in a 0.4 M zinc nitrate aqueous solution in a glass vial. The glass vial was then placed under vacuum at 0.01 MPa for approximately 60 s in order to remove any bubbles from the pores of the substrate. A plastic plug was placed on the open top end of the substrate in order to seal the inner part. The entire substrate was then immersed in a 0.8 M 2-methylimidazole solution in 1-octanol preheated at 50 °C. The glass vial was sealed and maintained at 50 °C for 1 h to generate the first membrane, M1, for 72 h for M2. M3 was obtained after successive immersions in 1-octanol solution for 1 h and in 0.8 M 2-methylimidazole solution in methanol for 72 h. M4 was prepared by immersion in a 0.8 M 2-methylimidazole solution in methanol for 72 h at 50 °C. The glass vial was allowed to cool to room temperature, and the obtained ZIF-8 membranes were washed with methanol at 50 °C for 24 h in order to remove unreacted zinc nitrate and 2-methylimidazole. Then, ZIF-8 membranes were dried at 60 °C for 12 h in a vacuum oven.

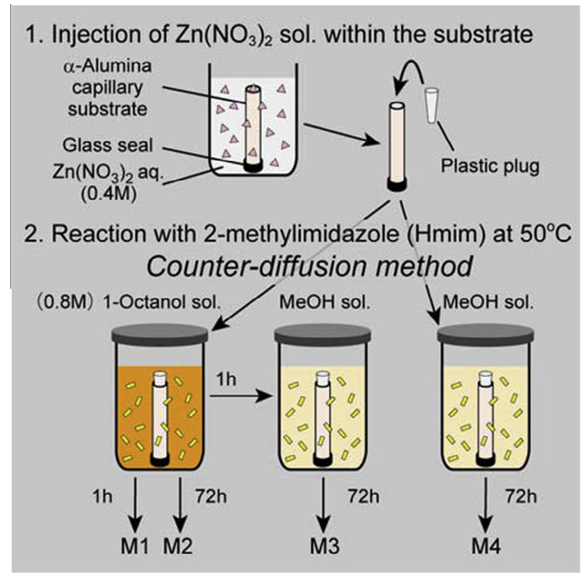

Fig. 1. Schematic illustration of the counter-diffusion method used in this study.

The preparation of the ZIF-8 membranes was gravimetrically characterized from the loading capacity (wt%) using the equation given as Eq. (1):

$$\text{Loading capacity} = 100 \times \frac{w_m - w_s}{w_s}, \qquad (1)$$

where w_m (g) is the weight of the ZIF-8 membrane and w_s (g) is the weight of the substrate.

2.2. Analysis

The crystal structures of the ZIF-8 membranes were determined by XRD analysis with Cu-Kα radiation, using a Bruker D8 Advance instrument. The membranes were sliced into small pieces and placed on the plastic cell for measurement. Diffraction patterns were measured at room temperature with 2θ ranging from 5° to 40°.

The surface and the cross-sectional structures of the ZIF-8 membranes were analyzed by scanning electron microscopy (SEM) with an energy dispersive X-ray (EDX) analyzer using an S-3400N instrument (Hitachi High-Technologies Corporation).

2.3. Gas permeation measurements

The single-component gas permeation properties of the ZIF-8 membranes were evaluated using helium, hydrogen, carbon dioxide, oxygen, nitrogen, propylene, and propane. The analyses were conducted at 25 °C using a high-vacuum time-lag method under a pressure difference of 0.1 MPa [24]. Before the permeation analyses, the membranes were vacuum-dried at 25 °C for more than 12 h to remove any residual water and gas molecules. Both the feed