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Fabrication of high-performance silicalite-1 membrane by a novel seeding method using zeolite-dispersed polymer film

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ABSTRACT

A highly reproducible silicalite-1 membrane with high pervaporation performance was successfully prepared on a tubular silica support by a novel seeding method using a zeolite-dispersed polymer film. The proposed seeding method (film seeding) allowed for the formation of a uniform and continuous zeolite seed layer with high reproducibility on the support surface in a single seeding step, resulting in a membrane with high separation performance. The synthesized membrane had a continuous and dense zeolite layer with a thickness of approximately 12 μm and exhibited an ethanol/water separation factor of 120 and flux of 3.16 kg m^{-2} h^{-1} for 10 wt% ethanol/water mixtures at 323 K by pervaporation. This novel seeding method should lead to the development of new processes for synthesizing zeolite membranes that show both high performance and reproducibility. Moreover, given the simplicity and effectiveness of the method, it has immense potential for use in the commercial production of various types of zeolite membranes.

1. Introduction

Zeolites are crystalline aluminosilicates that have uniform molecular-sized pores and exhibit unique physical and chemical properties, such as hydrophilicity, hydrophobicity, and solid acidity, and are thus employed widely in various industrial processes. Zeolite membranes have great potential for use in separation and catalysis processes owing to their unique pore structure, adsorption properties, and high thermal, mechanical, and chemical stabilities, which are superior to those of polymeric membranes [1,2]. Membranes of pure silica mordenite framework inverted (MFI) type zeolite (called silicalite-1) have attracted interest owing to their hydrophobicity, uniform pore structure, high thermal stability, and potential for use in the separation of organic molecules from organic/water mixtures [3–19].

The two primary methods available for the synthesis of zeolite membranes on supports are in-situ crystallization and secondary (seeded) growth. In-situ crystallization is the simplest method but lacks reproducibility. The secondary growth method consists of two processes: first, the support surface is coated with a layer of seed crystals. This is followed by a hydrothermal synthesis process to grow the zeolite seed layer into a continuous zeolite membrane layer. The use of seeds is an easy way of growing a zeolite membrane layer on a support with high reproducibility. Therefore, zeolite membranes are usually synthesized by the secondary growth method. The process of forming a seed layer on the support plays an important role in determining the quality of the zeolite membranes [17–22]. Several seeding methods for coating seed crystals on the support surface have been reported, such as dip coating [7–9,23,24], rub coating [5,10,25,26], vacuum seeding [6,27,28], spin coating [29,30], filtration seeding [31,32], electrophoretic deposition [4,17–19,33], and a cationic polymer treatment [34]. However, the ideal seeding method for preparing high-quality zeolite membranes remains to be developed, because it is difficult to form a uniform and continuous seed layer with high reproducibility on the support surface. The dip-coating method, which depends on the capillary force of the support channels, is the one used most widely to synthesize the seed layer on tubular supports. However, this method generally requires a very smooth and uniform support surface. Further, multiple steps are needed to ensure that the support is covered

Abbreviations: MFI, mordenite framework inverted; PMMA, Polymethylmethacrylate; XRD, X-ray diffraction; SEM, scanning electron microscopy; PV, pervaporation; PSI, pervaporation separation index

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completely [15]. Moreover, large zeolite seeds or support pores can reduce the efficiency because of the negative effects of the resulting increase in the gravitational force or the weakening of the capillary force [35]. Therefore, the reproducibility of this method is low for supports with large pores (> 1.0 μm) [36]. The rub-coating method is an easy one to perform; however, it is difficult to form a uniform seed layer on the support using this method even by repeating the coating steps [37]. Although vacuum seeding allows for the formation of seed layers of different thicknesses in a controllable manner [27], the small zeolite crystals are readily dispersed into the macroporous support even at low pressure differences. Similarly, the other seeding methods available are not used frequently owing to their complexity or poor reproducibility with respect to tubular supports. As mentioned above, in the case of the conventional seeding methods, it is difficult to form a uniform and continuous seed layer on the support because the morphology of the seed layer depends on the pore size and surface morphology of the support as well as the size of the seed crystals. Hence, the low reproducibility of seeding methods is a major problem with respect to their industrial large-scale production. A composite seeding method called dip-coating—rubbing—dip-coating [35], which shows high reproducibility, was reported recently. However, this seeding process is too complex and time consuming to be suitable for practical applications. Therefore, a simple and effective seeding method that also shows high reproducibility is desired.

In this study, we report, for the first time, a novel seeding method with high reproducibility that uses a zeolite-dispersed polymer film to form a uniform and continuous seed layer on the support. In this method, first, the polymer film with dispersed zeolite seed crystals are prepared. Next, the seed crystal layer is formed by wrapping the polymer film around the outer surface of the tubular support. Therefore, seeding can be carried out irrespective of the pore size of the support and the size of the seed crystals. Further, the dispersion of the seed crystals into the support pores is prevented. Moreover, the amount of seed crystals deposited on the support can be controlled by varying the amount of zeolite added to the film. Thus, it is possible to form a uniform and continuous seed crystal layer in a single step. The silicalite-1 membranes synthesized using seeded supports prepared using this method exhibited high separation factors and fluxes with respect to the separation of ethanol/water mixtures by pervaporation.

2. Experimental

2.1. Preparation of zeolite-dispersed polymer film

The zeolite-dispersed polymer film was prepared as follows (for additional details, see Supporting Information). Polymethylmethacrylate (PMMA, Mw = 350,000) and chloroform (99.9%) were used as the polymeric material and solvent, respectively. Silicalite-1 crystals (for details, see Supporting Information, Figs. S1 and S2) and chloroform were mixed and distributed by ultrasonication. PMMA was added to this mixture and stirred. The solution was then cast on a flat glass substrate. The thus-obtained film was used as the zeolite-dispersed polymer film.

2.2. Preparation of the seeded support

The process of seeding by coating this zeolite-dispersed polymer film on the outer surface of the support (length: 80 mm, outer diameter: 10 mm, inner diameter: 8.4 mm, porosity: 64%, pore size: 0.5 μm, Sumitomo Electric Ind., Japan) was as follows (Fig. 1). The support was first dipped in acetone (Wako chemical, 99.5%) for 1 min. As soon as the support was removed from the acetone, the zeolite-dispersed polymer film became wrapped around its outer surface. Because the PMMA film was soluble in acetone, the zeolite-dispersed polymer film adhered onto the support surface containing acetone. After the polymer film had been coated on the support, the film-coated support was dried at room temperature for 30 min and then calcined at 773 K for 3 h, so that the polymer layer was removed and only the seed crystals remained on the support surface.

2.3. Preparation of the silicalite-1 membrane

The silicalite-1 membrane was prepared on the seeded support by the secondary growth method in a precursor gel with a molar composition of $1SiO_2$:0.05TPABr:0.08NaOH:$75H_2O$ for 8 h at 433 K, as described in Supporting Information.

2.4. Characterization

The prepared samples were characterized by X-ray diffraction (XRD) analysis (AXS D8 Advance, Bruker, Germany). The morphologies of the obtained samples were observed by scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The pervaporation performances of the obtained membranes were evaluated using 10 wt% ethanol/water mixtures at 323 K (for details, see Supporting Information).

3. Results and discussion

3.1. Seeded support

SEM images and photographs of the tubular silica support and the seeded support before and after calcination are shown in Fig. 2 and Fig. S3, respectively. It can be seen that the top surface of the support is smooth after being covered with the zeolite-dispersed polymer film (Fig. 2b and Fig. S3b). Moreover, the dispersion state of the zeolite particles after the coating of the polymer film could not be observed from the SEM images. After the calcination step, the top surface of the support was completely covered with the zeolite seed crystals (Fig. 2c), and the thickness of seed layer on the support was approximately 2.5 μm (Fig. 2d). During calcination, the polymer film was removed, resulting in a dehydration reaction between the surface hydroxyl groups of the seed crystals and the support. As a result, strong bonds were formed between the seed crystals and the support surface, leading to strong adhesion between them. In this manner, the seed crystals were immobilized on the support. Thus, it can be concluded that a uniform and continuous seed layer can be formed readily using the proposed seeding method based on a zeolite-dispersed polymer film. We had previously reported that the optimal seed amount per unit outer surface area of the support is approximately 2 g m^{-2} for preparing a silicalite-1 membrane on the same silica support by the secondary growth method [18]. Therefore, in this study, the amount of seed crystals supported on the support was adjusted to be 2 g m^{-2} after the removal of the zeolite-dispersed polymer film by calcination.

3.2. Silicalite-1 membrane

Fig. 3 shows the XRD patterns of the seeded support after calcination and the silicalite-1 membrane synthesized using the seeded support. No XRD peaks assignable to the support were observed because the silica support consisted of amorphous silica. The XRD pattern of the synthesized membrane (Fig. 3b) exhibited peaks typical of an MFI-type zeolite structure, and MFI-type zeolite was only the crystalline phase present, with the peak intensities being higher than those in the case of the seeded support (Fig. 3a), indicating that the silicalite-1 membrane layer was formed on the support after the hydrothermal synthesis process. Further, the SEM images of the synthesized silicalite-1 membrane (Fig. 4) indicated that the top surface of the membrane consisted of well-grown interconnected particles. The cross-sectional SEM image also showed that a continuous and dense zeolite layer with a thickness of approximately 12 μm was formed on the support surface. Considering that a continuous and dense silicalite-1 membrane layer was not formed when a non-seeded support was used, it can be surmised