High-performance silicalite-1 membranes on porous tubular silica supports for separation of ethanol/water mixtures

Kyohei Ueno [a], Hideyuki Negishi [b], Takuya Okuno [c], Takahiro Saito [c], Hiromasa Tawarayama [c], Shinji Ishikawa [c], Manabu Miyamoto [d], Shigeyuki Uemiya [d], Yoshiharu Sawada [e], Yasunori Oumi [e,*]

[a] Graduate School of Engineering, Gifu University, 1-1 Yanagido, Gifu, Gifu 501-1193, Japan
[b] Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST), AIST Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
[c] Optical Communications Laboratory, Sumitomo Electric Industries, Ltd., 1, Taya-cho, Sakae-ku, Yokohama, Kanagawa 244-8588, Japan
[d] Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu, Gifu 501-1193, Japan
[e] Life Science Research Center, Gifu University, 1-1 Yanagido, Gifu, Gifu 501-1193, Japan

ABSTRACT

Production of bioethanol, a renewable energy source, is limited by the costly, energy-consuming concentration processes involved. Membrane separation techniques have emerged as promising alternatives to overcome these limitations. In this study, silicalite-1 zeolite membranes with high pervaporation (PV) performance were prepared on porous tubular silica supports by a secondary growth method. The effects of the deposited seed amount on the support and synthesis parameters, namely, the tetra-n-propylammonium concentration (TPA$^+$/Si), alkalinity (OH$^-$/Si), and crystallization time, were investigated. A dense zeolite layer was formed between the typical columnar crystal layer of silicalite-1 membranes and the silica support. The PV performance was mainly dependent on the thickness of the dense layer: as the thickness increased, the separation factor increased. The silicalite-1 membrane prepared using a synthesis solution with a molar composition of $1SiO_2$:$0.05TPABr$:$0.08NaOH$:$75H_2O$ at 433 K for 8 h exhibited the highest separation performance with a separation factor of 92 and a flux of $3.00 \text{ kg m}^{-2} \text{ h}^{-1}$ for 10 wt% ethanol/water mixtures at 323 K, which is the best result reported to date for tubular supports. Thus, silica supports proved to be suitable for the preparation of high-performance silicalite-1 membranes for ethanol/water mixture separation.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Bioethanol is a clean and renewable industrial raw material produced by biomass fermentation, and it has attracted considerable attention as an alternative to other energy sources [1]. Because the fermentation broth contains only about 10 wt% of bioethanol, extraction and concentration processes are necessary for its industrial application. However, these production steps require large amounts of energy and represent an economic limitation, preventing the widespread use of bioethanol [2]. Compared with conventional separation methods such as distillation and adsorption, membrane-based pervaporation (PV) is a highly effective and economic technique for liquid mixture separation because of its efficiency in separating azeotropic, close-boiling mixtures or isomers and heat-sensitive compounds; moreover, it has the advantages of low energy consumption, simple operation, cost-effectiveness, and low environmental impact [3,6].

Concentration processes of organic aqueous solutions using only membrane separation techniques provide a high energy-saving effect. The separation of organic/water mixtures by PV is performed by a combination of water- and organic-selective membranes (with hydrophilic and hydrophobic properties, respectively). Hydrophilic membranes are used for the dehydration of organic solutions containing small amounts of water, and they have been applied to industrial processes [7]. Hydrophobic membranes are employed for removing traces of organic compounds from diluted aqueous solutions. During the past decades, many efforts have been made to develop hydrophobic organic

membranes and organic-inorganic hybrid membranes for ethanol separation from fermentation broths [8,9]. However, organic-based membranes generally have a low separation factor for ethanol/water mixtures and are therefore not suitable for industrial applications. As compared to polymeric membranes, zeolite membranes have greater potential for use in separation techniques due to their superior thermal, mechanical, and chemical properties. Zeolites are crystalline aluminosilicates with uniform molecular-sized pores and unique physical and chemical properties, such as hydrophilic-hydrophobic properties and solid acidity; thus, separation by zeolite membranes is achieved by a combination of molecular sieving, selective adsorption (hydrophilic-hydrophobic properties), and differences in diffusion rates [4–6]. The degree of hydrophobicity of zeolites is dependent on the amount of Al atoms incorporated into the zeolite framework (Si/Al ratio) and it increases with increasing Si/Al ratios. In particular, siliceous mordenite framework inverted (MFI)-type zeolite, called silicalite-1, has attracted great interest because of its hydrophobicity, uniform pore structure, and high thermal stability. Silicalite-1 membranes have been extensively studied for the removal of organic compounds from diluted organic aqueous solutions by PV [10–36], which results from their selective adsorption on the surface of silicalite-1 zeolite. The separation selectivity for organic compounds increases with increasing hydrophobicity of the silicalite-1 membrane.

However, during the preparation of silicalite-1 membranes by hydrothermal synthesis on conventional supports, such as α-Al$_2$O$_3$ and mullite, Al atoms leach out from these supports because of the high pH of the growth gel and are incorporated into the zeolite framework, resulting in a decrease in hydrophobicity [10,24,32]. Except for a few studies, the separation factors of MFI-type zeolite membranes toward ethanol/water mixtures have been reported to be around 60 [10–36]. Thus, silicalite-1 membranes on Al-free supports, such as stainless steel and pure silica, are preferred. Several groups have prepared silicalite-1 membranes on stainless steel [10–12,16–18] and silica [13,14,36–39] porous supports; however, cracks were easily formed on stainless steel supports during calcination because stainless steel has a higher thermal expansion coefficient than silicalite-1 zeolite [40]. There have been a few reports of silicalite-1 membranes prepared on a silica support for the separation of ethanol/water mixtures [13,14,36]. Chen et al. [13,14] reported the preparation of a silicalite-1 membrane by a solution-filling method on a porous tubular silica support. The silica support was prepared by a casting method using a slurry of silica powder and clays as a binder containing a small amount of Al atoms, which were incorporated into the framework of the membrane (Si/Al = 100). As compared with silicalite-1 membranes on α-Al$_2$O$_3$ supports, the prepared membrane showed higher ethanol selectivity for the separation of ethanol/water mixtures, but a lower permeation flux because of the larger thickness of the membrane layer (about 30 μm). Moreover, Elyassi et al. [36] reported that the silicalite-1 film prepared by gel-free secondary growth on a disk-type silica support with a Stöber silica-modified surface gave a high separation performance with a separation factor of 85 and a flux of 2.1 kg m^{-2} h^{-1}. Unfortunately, this method cannot be applied to the preparation of silicalite-1 membranes on tubular-type porous silica supports with a large surface area because of the difficult preparation of the support requiring special silica particles; thus, this synthetic method was specific for disk-type supports. To the best of our knowledge, there have been no reports of silicalite-1 membranes on tubular-type pure silica supports with a high separation performance and their application for the separation of ethanol/water mixtures by PV.

It is known that the permeability of zeolite membranes is related to the transport resistance of the zeolite layer and porous support; thus, a decrease in the thickness and increase in porosity of the support result in an improved permeation flux [29,41–43]. Recently, porous ceramic hollow fibers such as α-Al$_2$O$_3$ and yttria-stabilized zirconia (YSZ) hollow fibers have been successfully used as supports for zeolite membranes, which showed high permeability due to the very low thickness [41,42]. However, MFI zeolite membranes supported on α-Al$_2$O$_3$ hollow fibers were unavoidably contaminated by aluminum atoms from the support [18,34], giving a very high flux of 9.8 kg m^{-2} h^{-1} but a separation factor in the average range (α = 58) [34]. Silicalite-1 membranes on YSZ hollow fibers showed a high flux of 7.4 kg m^{-2} h^{-1} but a separation factor (α = 47) lower than that of α-Al$_2$O$_3$-supported membranes [33]. Moreover, these hollow fiber supports have a multilayer asymmetric structure and high production cost. For these reasons, the flux of previously reported MFI membranes on tubular-type supports was <2.0 kg m^{-2} h^{-1} with a high separation factor above 60 for ethanol/water mixtures, except for the reports by Kita's group [16,25,27]. To date, silicalite-1 membranes with high separation performance (high separation factor and high flux) that can replace distillation for ethanol concentration have not been synthesized. A suitable support and fabrication method are crucial for the synthesis of silicalite-1 membranes with both high separation factor and permeation flux.

In this study, we prepared silicalite-1 membranes on tubular porous silica supports by secondary growth method. This support is composed of pure silica and has a low thickness and high porosity; therefore, it was envisioned to provide a high separation factor and high flux. In addition, the effect of support dissolution, amount of deposited seed crystal, composition of the synthesis solution (TPA$^+$/Si and OH$^-$/Si ratios), and crystallization time on membrane morphology and separation performance was investigated. The prepared silicalite-1 membranes were applied for the separation of ethanol/water mixtures by PV.

2. Experimental

2.1. Preparation of silicalite-1 seed crystals

Silicalite-1 seed crystals were prepared by hydrothermal synthesis. The synthesis solution consisted of tetra-*n*-propylammonium bromide (TPABr) (Tokyo Chemical Industry Co., Ltd., Japan, >98.0%) as the organic structure-directing agent, colloidal silica (CATAROID SI-30, JGC Catalysts and Chemicals Ltd., Japan, SiO$_2$: 30.7%, Na$_2$O: 0.42%, H$_2$O: 68.88%), sodium hydroxide (Merck, Germany, 99%), and distilled water with a SiO$_2$:TPABr:NaOH:H$_2$O molar ratio of 1:0.1:0.2:40. The resulting hydrogel was stirred at room temperature for 24 h and then at 373 K for 144 h. The obtained particles (average diameter; about 1 μm) were washed with distilled water and dried at 333 K overnight (Figs. S1 and S2).

2.2. Seeding by electrophoretic deposition

The seed crystals were deposited on the tubular silica support (length: 80 mm, outer diameter: 10 mm, inner diameter: 8.4 mm, porosity: 64%, pore size: 0.5 μm; Sumitomo Electric Ind., Japan) using electrophoretic deposition (EPD) as a seeding technique (i.e., a seed layer formed on the outer surface of the support) (Fig. S3). Acetone, a stainless steel rod, and a stainless steel mesh were used as a dispersion solvent, deposition electrode, and opposite electrode, respectively. The electrode distance was about 15 mm. The EPD bath was prepared by adding the seed crystals to the solution to obtain a concentration of 5 g L^{-1} followed by dispersion via ultrasonic vibration for 30 min. EPD was carried out using an electrochemical cell. A stainless steel rod in the center