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Dehydration of TFEA/water mixture through hydrophilic zeolite membrane by pervaporation

Hyoseong Ahn [a], Hyeryeon Lee [a], Soo-Bok Lee [b], Yongtaek Lee [a,*]

[a] *Department of Chemical Engineering, Chungnam National University, 220 Gungdong, Daejeon, Republic of Korea*
[b] *Advanced Chemical Technology Division, Korea Research Institute of Chemical Technology, 100 Jangdong, Daejeon, Republic of Korea*

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Abstract

Water was separated from water/2,2,2-trifluoroethyl alcohol (TFEA) mixtures by pervaporation using hydrothermally synthesized NaA and NaY zeolite membranes. The effect of a TFEA feed concentration and a temperature was studied on the permeation flux and the separation factor. The separation factors obtained with the NaA zeolite membrane were found to be 10 times higher than those obtained with the NaY zeolite membrane which were always no less than 1000 at all experimental conditions. The water flux through the NaY zeolite membrane was observed to be 1.2 times larger than that of the NaA zeolite membrane. The water flux increased significantly with increase of the temperature for both NaA and NaY zeolite membranes. The TFEA flux through NaA zeolite membrane was not much changed by the increase of the temperature when the TFEA concentration was below 0.8 mole fraction in a solution. On the other hand, the TFEA flux through the NaY zeolite membrane rapidly increased with increase of the temperature at the feed concentration below 0.8 mole fraction of TFEA. Long-term pervaporation tests showed a good stability since the total flux through the NaA zeolite membrane was stabilized at about 1250 g/m^2 h and the separation factor of 2.5×10^5 and total flux of about 1750 g/m^2 h and the separation factor of about 7×10^3 for the NaY zeolite membrane.

Keywords: Zeolite membrane; NaA zeolite; NaY zeolite; Dehydration; Pervaporation

1. Introduction

TFEA (2,2,2-trifluoroethyl alcohol) has been used as one of the chemicals for anesthetics and sedatives. It is also used for applications in waste heat recycling and air conditioning, an intermediate for organic synthesis, solvents, optical and electronic functional materials, fluorine containing esters and a base material for copolymers including fluorine. Especially, 3FMA (2,2,2-trifluoroethyl methacrylate) is a very useful ester for applications of contact lenses and paints since it shows not only a low refractive index and a high waterproof function but also easy ability of copolymerization with acrylate or methacrylate [1]. During synthesis of 3FMA, water is produced as a byproduct of the esterification process. An economic manufacturing process for 3FMA could be designed if an efficient water removal process is applied.

Pervaporation might have a great potential for application in various separation processes since it is not only an economic separation technology but also an environmentally clean technology [2,3]. Most organic compounds might have an azeotropic point with water, which leads to the difficulty of a fine purification by a conventional distillation. On the other hand, the pervaporation might be one of the alternatives for separation of water from water/organic mixtures and purification of organics from below an azeotropic point to the higher purity than the azeotropic point since the separation principle of the pervaporation is based on both the adsorption on the membrane and the diffusion in the membrane.

A hydrophilic membrane might be used for dehydration of water/organic mixtures by pervaporation. Hydrophilic polymer membranes could show a high separation factor for water but they were known to be very sensitive to the operational conditions such as a concentration and a temperature. Also their thermal, chemical and mechanical stabilities are not good enough for direct application to the conventional dehydration process. A zeolite membrane might be a good candidate for water

* Corresponding author. Tel.: +82 42 821 5686; fax: +82 42 822 8995.
E-mail address: ytlee@cnu.ac.kr (Y. Lee).

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pervaporation since it functions not only as a molecular sieve but also has a good physicochemical stability [4]. Therefore, the pervaporation using a zeolite membrane has been widely studied to separate either water from water/organic mixtures or organics from aqueous solutions [4–10]. Zeolite membranes such as NaA and NaY might be potentially applicable in a dehydration process because of their unique pore structure and an excellent hydrophilicity.

Kita et al. [5] synthesized a NaA zeolite membrane on the outside of α-alumina tube with a synthetic solution in which the molar ratio of components was $1SiO_2{:}1Na_2O{:}0.5Al_2O_3{:}60H_2O$. Their membrane showed the total flux of 2150 g/m^2 h and the separation factor of higher than 10,000 at 50–75 °C.

Kondo et al. [6] reported the preparation of the NaA zeolite membrane for ethanol/water pervaporation. Various supports composed of different alumina contents were tested for the economic synthesis of NaA zeolite membranes. They synthesized a thin film of the NaA zeolite on the porous support of 65 wt.% alumina, the price of which is 1/10 less than that of 100% alumina and it showed the total flux of 600 g/m^2 h and the separation factor of about 10,000 were obtained through their NaA zeolite membrane at 10 wt.% of water in the feed mixture and 50 °C.

Bhattacharyya and co-workers [7] studied the pervaporation of water from the aqueous alcohol solution with Mitsui Engineering and Shipbuilding's NaA zeolite membrane. They observed that the total fluxes were ranged between 1800 and 2100 g/m^2 h for the various aqueous solutions containing either methanol or ethanol. On the other hand, the separation factors were observed to be in the range from 140 to 2140 at the feed concentration of 30 wt.% of alcohols.

Kita et al. [8] synthesized NaY zeolite membranes for water/ethanol pervaporation. Their NaY zeolite membrane showed a permeation flux of 1590 g/m^2 h and a separation factor of 130 at 75 °C.

Xu et al. [9,10] successfully synthesized NaA zeolite membrane on a ceramic hollow fiber membrane (o.d. 400 μm, i.d. 200 μm, average pore radius 0.1 μm) and a home made α-alumina disk (30 mm diameter, 3 mm thickness, 0.1–0.3 μm pore radius, 50% porosity) using gel composition of $2SiO_2{:}Al_2O_3{:}3Na_2O{:}200H_2O$ by conventional hydrothermal synthesis (90 °C, 24 h) utilized with stainless steel autoclave. Their hollow fiber NaA membrane showed higher permselectivity of 3.66 (He/N_2) and 4.41 (He/Ar) than those of Knudsen diffusion 2.64 and 3.16, respectively. Also, they measured permselctivities of 20.1, 106 and 2.61 for H_2/N_2, $H_2/n\text{-}C_4H_{10}$ and O_2/N_2, which were much higher than those of the corresponding Knudsen diffusion ratios of 3.74, 5.39 and 0.96 for α-alumina disk membrane introducing seed crystals which have the uniform size of 1 μm and three times of repeating synthesis procedure.

Recently, Yang and co-workers [11,12] reported about the LTA membrane synthesis, the gas permeability, the pervaporation results and the membrane formation mechanism using so-called "in situ aging-microwave synthesis". Their LTA membranes showed the good pervaporation properties for alcohol/water mixtures and the gas permselectivities of 5.60 for H_2/N_2 and 9.17 for H_2/C_3H_8.

Many NaA and NaY zeolite membranes have been prepared on the outside surface of a porous tubular support and the aqueous solution has been fed to the outside of the tube to separate water in the early days. On the other hand, it might be necessary to prepare a tubular membrane where the water selective zeolite layer is grown on the inner surface of a tubular support since there are many equations were already established well which clearly describe the relationship between liquid flow pattern and mass transfer and those equations are easily incorporated into the equations to carry out the numerical analysis of pervaporation process. Both the separation and the concentration might be obtainable more rigorously during the numerical analysis when the feed liquid flows inside of the tube rather than it flows outside of the tube because the liquid side mass transfer is more important than the mass transfer in vacuum side for a pervaporation process.

In this study, a thin film of either the NaA or the NaY zeolite was prepared by growing crystals on the inside of a support and used as a water selective membrane to separate water from an aqueous feed solution containing TFEA which is a possible mixture during the manufacture of 3FMA. The separation characteristics were investigated and compared through both the NaA and the NaY zeolite membranes. In particular, the effect of a temperature on the water/TFEA separation was intensively investigated. In order to check the stability of the NaA and NaY zeolite membranes, long-term experiments for 1 week were carried out and its results are presented.

2. Experimental

2.1. Preparation and analysis of membrane

NaA and NaY zeolite membranes were synthesized from liquid mixtures in which the chemical compositions were $2SiO_2{:}1Al_2O_3{:}4Na_2O{:}120H_2O$ and $10SiO_2{:}1Al_2O_3{:}14Na_2O{:}840H_2O$, respectively. Sodium silicate solution (Samchun, Korea) was used as a source material for Si; sodium aluminate (Wako, Japan) and sodium hydroxide (Daejung, Korea) were used as source chemicals for Al and Na, respectively. After preparing a Si solution and an Al solution, a Si solution was added to an Al solution and mixed for 1 h for aging gel. Both ends of the support tube (α-alumina tube, USF/Schmacher, o.d. 10 mm, i.d. 7 mm, length 47 mm, mean pore size 0.2 μm, porosity 0.33) were glazed 10 mm to give the sealed area for O-ring. Molecular sieve 4A (mean particle size: ≤5 μm, Aldrich, USA) and molecular sieve NaY (mean particle size: ≤5 μm, Aldrich, USA) powders were used as seed crystals. They were rubbed on the inside surface of a support with sponge brush. The seeded support and an autoclave were preheated at 40 °C for 1 h. The mixed solution was carefully poured into the inside of the support to prevent attaching air bubbles at the inside wall of the tube. Then, the support was wrapped with teflon tapes to prevent not only growing crystals on the outside of the support but also leaking out of solution. After that, the wrapped support was placed vertically in the autoclave. NaA and NaY zeolite membranes were synthesized under the reaction temperature of 90 °C and the reaction time of 6 h for NaA zeolite membrane and