



Synthesis, reproducibility, characterization, pervaporation and technical feasibility of preferentially *b*-oriented mordenite membranes for dehydration of acetic acid solution

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ABSTRACT

This paper describes the development of mordenite membranes for industrial purpose to apply in dehydration processes of acetic acid (AAc) aqueous solution under high-temperature and high-pressure conditions. The membrane formation process is clarified as a function of synthesis time by investigation of the properties of permselective, crystalline state and surface morphology in the synthesized polycrystalline thin film. The crystallographic development from the random orientation to the preferred orientation of *b*-axis was observed in the synthesized membranes with increasing of crystallization times. The membrane performance in pervaporation was measured in a feed mixture of water (50 wt.%) / AAc (50 wt.%) to be $10.9 \text{ kg m}^{-2} \text{ h}^{-1}$ for permeate flux and to be $0.77 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for water permeance with separation factor (α) of 500 at 130°C .

A technical feasibility study was undertaken for a hybrid pervaporation–distillation system to produce acetic acid with 1 wt.% of water content from a feed flow with water (55 wt.%) / AAc (45 wt.%) for 1000 kg h^{-1} . It was a case in which dehydration from 55 wt.% to 40 wt.% water content was processed in a feed flow before distillation by pervaporation at 110°C . Two values of (1) the energy saving ratio compared with a case of distillation alone and (2) the required membrane area were calculated to be 34% and 55 m^2 , respectively, using the experimentally determined values of membrane performance. This size of the membrane module for the 55 m^2 membrane area could be a realistic scale for industrial utilizations. Therefore, the present fabrication method for mordenite membrane deserves to further technological developments of large-scale membranes and mass-production.

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1. Introduction

The recent economical and political situation related with global environmental problems such as the global warming issue induces the industry to reduce the energy-consumption not only because of the point of cost-reduction but also because of reduction of CO_2 emission. It is a case in Japan that the chemical industry consumes 15% of the energy-consumption in the entire industrial field, and 40% of such energy is consumed in separating operations by distillation processes [1]. Similar situation should be found in the almost industrial nations. Membrane separation is expected to be an alternative separation process to conventional energy-intensive separating processes because the utilization of membrane technology will contribute to the achievement of significant energy savings.

Dehydration is the most important and prevailing separating process in the chemical industry. Membrane separation can

be utilized for dehydration of azeotropic systems, because those processes are applied by conventional distillation which has a typical energy-consuming feature. Many studies are reported on polymeric membranes for separation of water and solvents [e.g., 2–6]. Almost utilization of polymeric membranes, however, is limited in rather lower temperatures than 100°C because of their insufficient thermal, mechanical and chemical resistance. For practical utilizations in industrial processes, the membrane separation unit should be installed in a series of process flow operated at high-temperature and high-pressure conditions. The properties of thermal- and mechanical-resistance are required for membrane materials that should be used for the chemical processes. Zeolite membranes have been studied and developed for 20 years for utilizations, in particular, NaA type zeolite membranes have been studied [e.g., 7–13] and commercially developed [14,15]. It has been demonstrated in a plant for ethanol dehydration that a hybrid distillation–membrane system can replace the conventional azeotropic distillation processes [15]. In the case of hybrid system for purification of hydrous ethanol, conventional distillation column and membrane unit are integrated (Fig. 1a).

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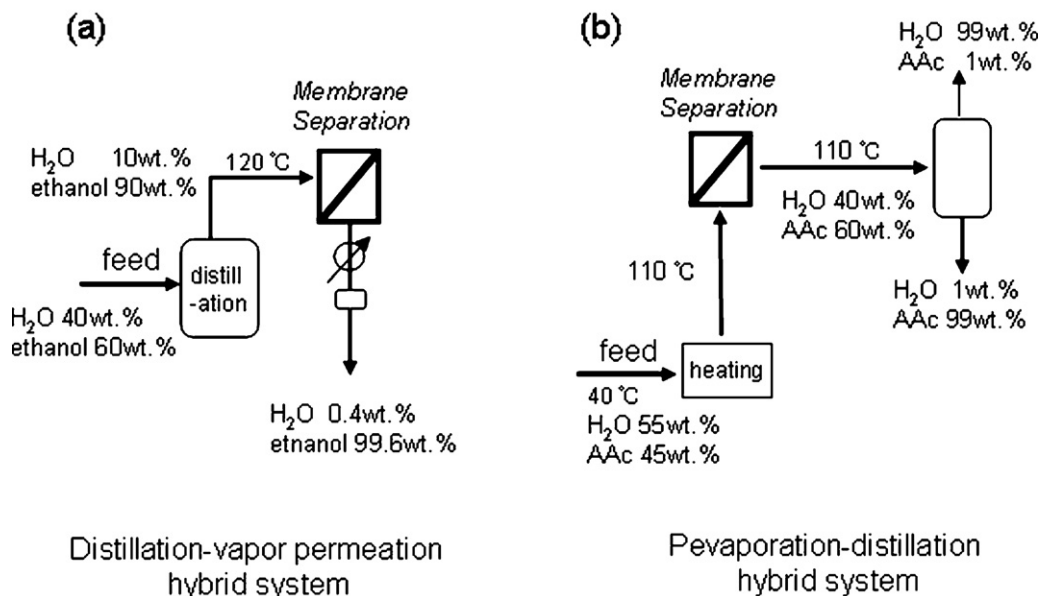


Fig. 1. The configuration of membrane–distillation hybrid systems: (a) a distillation–vapor permeation hybrid system for ethanol dehydration and (b) a pervaporation membrane–distillation hybrid system for acetic acid dehydration.

The NaA type zeolite membranes exhibit higher dehydrating performance, however, those have limits to particular processing conditions. It was reported that the membrane performance of NaA type zeolite membranes could be unstable under higher water feed concentrations [16] or under acidity conditions [17]. The NaA zeolite membranes cannot cover such conditions with acidic or high-water contents. However, a potential demand for membrane separation units working under acid conditions is recognized in the chemical industry. Dehydration of acetic acid aqueous solution is an example of the membrane separation for energy savings. Because separation of acetic acid from water in the distillation is an energy-consuming process due to that the evaporating heats for both of acetic acid and water are high.

A certain degree of energy saving is expected in dehydration of acetic acid aqueous solution with a hybrid membrane–distillation system [18]. It is a case of our concern that the membrane process would be placed before distillation in a case of acetic acid dehydration where the feed contains high-water content of 55 wt.% is purified into the product of acetic acid with 1 wt.% water content (Fig. 1b). This configuration of the pervaporation–distillation system can take advantage of benefit of membrane separation because such the higher driving force by the higher water vapor pressure through membranes is available for the permeate flux. To realize these dehydration processes, we have to prepare an appropriate membrane that can be operated under such higher temperatures as over 100 °C, strong acidic conditions as pH < 3, and high-water content conditions.

Mordenite membrane is a candidate for dehydration of acetic acid aqueous solution because of the property of acid-resistance. Many studies on fabrication methods and permeating properties of mordenite membrane have been reported [19–25]. In particular, the research group of Matsukata and coworkers reported in the series of studies [26–29] on highly water-selective mordenite membranes. Those mordenite membranes [26] exhibit higher permeate fluxes than other mordenite membranes in other previous studies, suggesting that this synthesis method should be developed for our purpose of the practical utilization of acid-proof membrane.

High membrane performance and high reproducibility are required in fabrication of zeolite membranes for industrial purpose. It was indicated that zeolite membranes with high performance could be fabricated by a secondary growth method [e.g., 7–9,12,13,26,30,31]. Furthermore, the advantage of this method has been verified by the studies that up-scaled zeolite membranes were fabricated with the seeded growth method for NaA type and faujasite with higher performance for industrial purpose [8,15,32]. Addition to the secondary growth method, an employment porous substrate with a larger average pore size (~1.0 μm) to ensure higher fluxes was a significant feature in the industrial zeolite membrane fabrication [15,31]. The both of seeded growth method and utilization of substrate with a larger average pore size ~1.0 μm will be employed in mordenite membrane fabrication method in this study.

Membrane formation is caused by crystal growth of zeolite on the substrate. The crystal growth is sequential results of crystallization with synthesis time. The crystallization time is a key factor in determining properties in synthesized membranes. Hence, it is required to investigate changes of properties of perselective, crystallographic, morphological and microstructure as a function of synthesis time. Particularly, the relation of reproducibility and synthesis time has to be clarified. The series of synthesis of membranes with time would contribute not only to optimize the synthetic condition but also to give information about formation mechanism of the membrane.

A study of technical feasibility on the fabricated mordenite membrane has to be undertaken before developments on the large-scale fabrication and mass-production of the membranes. Namely, it is required to estimate the required membrane area and the energy-saving efficiency in a case of dehydration of acetic acid aqueous solution for the present mordenite membrane. Then, we have to judge that the required membrane area could be realistic for industrial cases.

The purpose of this study is (1) to synthesize mordenite membrane in a lab-scale with higher performance and reproducibility as a function of synthesis time, (2) to observe the development of microstructure in membranes, (3) to measure performance in

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