

Silicalite Membrane for Separation of Acetic Acid/Water Mixture

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The polycrystalline silicalite membrane was prepared on a porous sintered stainless steel support and its pervaporation performance was investigated using an acetic acid/water mixture as a feed. The silicalite membrane selectively permeates acetic acid in the concentration of the feed acetic acid in the region of 5 to 40 vol%.

Zeolite has recently been focused on as one of the materials for inorganic membranes because of its high chemical and thermal stability as well as molecular sieving.¹ More recently, we have also studied the liquid separation potential of the zeolite membrane and reported a high pervaporation performance of the silicalite membrane for the separation of alcohol/water mixtures.² The fact that the silicalite membrane selectively permeates alcohols leads possibility that the membrane might be applicable to the separation of organic liquid mixtures.

It is well known that among the organic liquids, acetic acid is one of the most important intermediates in the chemical and the food industries. For the separation of the acetic acid/water mixture normally techniques such as fractionation distillation, azeotropic distillation, supercritical extraction and freeze concentration are used. Since these techniques consume too much energy, it is desirable thus to develop a new separation process and the pervaporation membrane separation technique is a potential candidate for this purpose. So far, many papers have dealt with studies on the pervaporation performance of organic membranes for the dehydration of acetic acid/water mixture.³ Very recently, the preferential pervaporation of acetic acid through a few organic membranes was also found.⁴ In contrast, the separation of acetic acid/water mixture using inorganic membranes has received relatively little attention. From these standpoints, we have investigated the ability of the separation of acetic acid from aqueous acetic acid solution through the silicalite membrane and describe our results in this paper.

The hydrothermal synthesis of a silicalite membrane was performed as follows.² Colloidal silica (Cataloid SI-30 from Shokubai Kasei Co.; 30.4 wt% SiO₂, 0.38 wt% Na₂O, 69.22 wt% water) was added to a stirred mixture of tetrapropylammonium bromide (TPABr) and sodium hydroxide in solution, to give a hydrogel with a composition of 0.1TPABr-0.05Na₂O-SiO₂-80H₂O. Then the hydrogel was transferred to a 300 ml stainless steel autoclave. A porous support of sintered stainless steel disc (5 cm diameter) with an average pore diameter of ca. 2 μm was placed on the bottom of the autoclave. The autoclave was placed in an air-heated oven at 170°C for 48 h. After the completion of crystallization under autogenous pressure without stirring, the autoclave was cooled down, and the support was recovered. The silicalite membrane on the support was washed with deionized water and dried at 100°C. After then the silicalite membrane was calcined at 400°C for 20 h in order to decompose the organic amine occluded in the

zeolite framework. The identification of the membrane was achieved by X-ray diffraction. The membrane thickness measured by scanning electron microscopy was about 460 μm. The pervaporation measurements using acetic acid/water mixtures as a feed were performed on a standard pervaporation apparatus.² Liquid nitrogen was used as a cooling agent for the cold trap. The compositions of the feed and the permeate were determined by gas chromatography.

A few introductory experiments were carried out to investigate the influence of the feed concentration on the pervaporation performance. Figure 1 illustrates the permeate rate (flux) and the acetic acid concentration of the permeate as a function of the feed acetic acid concentration. The flux

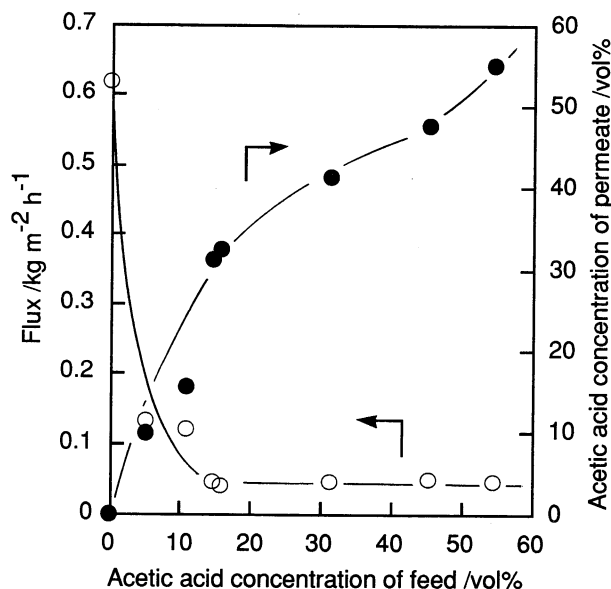


Figure 1. Influence of feed acetic acid concentration on pervaporation performance
 Feed temperature : 30°C

decreased rapidly by adding acetic acid to water and then reached constant. The acetic acid concentrations of the permeates were higher than those of the feeds. Although the degree of the concentration was not so high, it is found that the silicalite membrane selectively permeates acetic acid in the concentration of the feed acetic acid in the region of 5 to 40 vol%. Of course, the acetic acid selectivity of pervaporation was higher than that of distillation. To my knowledge, there are few reports concerning to inorganic membranes which permeates acetic acid preferentially. Although a transport mechanism in pervaporation through the silicalite membrane is not clear at the present time, the high acetic acid permselectivity seems to be

attributable to the high hydrophilic properties of silicalite.² Figure 2 shows the effect of the feed temperature on the pervaporation performance. The pervaporation measurements

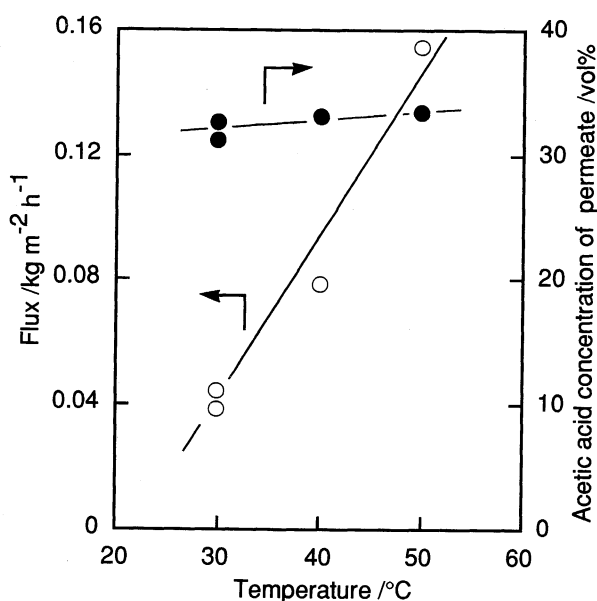


Figure 2. Effect of feed temperature on pervaporation performance
Feed acetic acid concentration : 15 vol%

Table 1. Concentration of Vinegar Using Silicalite Membrane

Component	Feed	Permeate
Acetic acid /vol%	14.0	35.3
Alcohols /vol%	0.32	0.49
Pyroglutamic acid /mg 100ml ⁻¹	0.68	n.d.
Lactic acid /mg 100ml ⁻¹	0.13	1.16
Pyruvic acid /mg 100ml ⁻¹	0.12	n.d.
Citric acid /mg 100ml ⁻¹	4.05	n.d.
Succinic acid /mg 100ml ⁻¹	3.99	n.d.
α -Ketoglutaric acid /mg 100ml ⁻¹	0.20	n.d.
Malic acid /mg 100ml ⁻¹	0.02	n.d.

Feed temperature : 30°C

n.d. : not detect

were conducted at 30°C using the aqueous acetic acid solution of 15vol% as a feed. The flux increased linearly with the feed temperature, while the acetic acid concentration of the permeate was hardly dependent on the temperature.

As the pervaporation process is much more attractive for the extraction of a minor component in a solvent, the silicalite membrane seems to be applicable to the condensation process in the production of vinegar via fermentation of biomasses. Therefore, the transport property of the membrane was tested against the vinegar containing small amounts of components such as alcohols and organic acids. The representative result is presented in Table 1. The permeate rate was 0.020 kg m⁻²h⁻¹. The solution was concentrated to over two times of the original concentration. Except for alcohols and lactic acid, the organic acids were hardly detected in the concentrated solution.

From above results, it was concluded that although the silicalite membrane prepared here is polycrystalline, the membrane permeates acetic acid in preference to water from an aqueous acetic acid solution.

References and Notes

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