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Silicalite Pervaporation Membrane Exhibiting a Separation Factor of over 400 for Butanol

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Bio-butanol is expected to be useful as a liquid fuel because the energy density of butanol is higher than that of ethanol. We developed a separation membrane that yielded an butanol concentration of 81.8 wt % from 1 wt % butanol solution by a pervaporation method. The membrane is a silicone-rubber-coated silicalite on a porous support tube. The butanol concentration process will be simplified greatly by the development of this membrane. Refining the butanol from 1 wt % butanol solution takes 13% of the amount of energy yielded by the butanol.

Butanol is considered potentially more useful than bio-ethanol. It has a higher energy density than ethanol: the heating value of butanol is 34 MJ kg^{-1} and that of ethanol is 27 MJ kg^{-1}. Therefore, bio-butanol is expected to be useful as a liquid fuel substitute for oil.[1] The process of acetone, butanol, and ethanol (ABE) fermentation has been known since the beginning of the 20th Century,[2] and ABE fermentation for butanol production has been attracting attention for the production of chemical feedstocks and liquid fuels.[3] Universally, the butanol concentration in fermentation liquid is low, at ca. 0.5% to 1.5%.[4] At these concentrations, the energy of the butanol purified by distillation is less than that needed for the distillation process.[4]

Membrane separation is one way of refining butanol and is expected to conserve energy. With this method a hydrophobic membrane is needed to separate the butanol selectively, as the case with the separation of ethanol. Such devices as silicone-rubber membranes and silicalite-powder-mixed silicone-rubber membranes have been used as films for the separation of butanol concentrate.[1,5] One study obtained a maximum butanol concentration of 52.9% at 50 °C from 1 wt % aqueous butanol solution.[6] At this concentration the butanol solution causes phase separation. When the concentration of butanol is between about 8 and 80 wt %, it separates into two layers (a butanol-rich solution and a water-rich solution).[7] To collect all the butanol in the permeate, not only is the butanol concentration needed for each layer, but also the total system becomes complex. A lot of energy is needed for this system, and only a little energy can be produced. Therefore, it is important that a butanol concentration of over 80% is obtained from solutions that have butanol concentrations of less than 1%.

Silicalite is a zeolite that does not contain aluminum and is therefore more hydrophobic than any of the other zeolites. Silicalite membranes have been synthesized under various conditions, and the separation performances of a water–organic material mixture using the pervaporation (PV) process have been reported.[8,9] We also reported the concentrations of ethanol by using silicalite membranes.[10] Silicalite membranes were prepared by hydrothermal synthesis with electrophoretic deposition (EPD) as a seeding technique.[10] At 60 °C the *flux* from 5 vol % aqueous ethanol solution was 1.3 kg m^{-2} h^{-1} and the separation factor α was 70. We aimed at a separation performance that would give a butanol concentration of over 80 wt % from a 1 wt % aqueous butanol solution. This meant a separation factor of over 400. A membrane with high separation performance was necessary to achieve this target, and we considered adequate crystalline growth indispensable to preparing such a membrane: when the seed crystals grow they fill the spaces between the particles and ensure that the membrane does not have defects. We controlled the temperature and the timing of hydrothermal synthesis for which we controlled the solution composition and aging time. Aging temperature also has a significant influence on the performance of silicalite membranes.[11] Moreover, we found that the ethanol selectivity is improved by coating the silicalite membrane with hydrophobic silicone rubber.[9]

In this study, we investigated the preparation of silicalite membranes by controlling the aging time and temperature of the hydrothermal synthesis gel. We estimated the ability of the silicone-rubber-coated silicalite membrane to separate butanol from 1 wt % butanol solution by PV.

Tubular silicalite membranes were prepared on a tubular porous stainless-steel support.[10] The seeding conditions for the silicalite crystals were 5 g L^{-1} propanol in an EPD bath and applied at 20 V for 5 min. The aging conditions for the hydrothermal synthesis gel were detail-controlled at 25 and 27 °C for 3 h 20 min and 3 h 40 min. Silicalite membranes were coated with two types of silicone rubber, as used in our previous study.[12] Batch PV experiments using the silicalite membranes were carried out at 45 °C.[12] The butanol to water composition of the feed solution was 1 to 99 wt %. Butanol concentrations in the feed and the permeate were determined on a gas chromatograph (GC 323, GL Sciences Inc., Japan) equipped with a TCD by direct aqueous injection at 190 °C onto a 3-m packed column consisting of 5% Thermon 1000 on Sunpak-A with 50/80 mesh (Shinwa Chemical Industries Ltd., Japan) at 170 °C. When the permeate had separated into two phases, the condensate was diluted with water generating a single phase before analysis. *Flux* and α were calculated by the following equations:[9]

$$\mathit{Flux}\ (\mathrm{kg\,m^{-2}\,h^{-1}}) = \text{permeate (kg)}/[\text{membrane area } (\mathrm{m^2}) \times \text{permeation time (h)}] \quad (1)$$

$$\alpha = [C_{\mathrm{BuOH}}/C_{\mathrm{H_2O}}]\ (\text{permeate})/[C_{\mathrm{BuOH}}/C_{\mathrm{H_2O}}]\ (\text{feed}) \quad (2)$$

where C_{BuOH} and $C_{\mathrm{H_2O}}$ are the weight of butanol and water, respectively.

The necessary energy was estimated from the mass balance of butanol and water, the evaporative latent heat, and the electrical power needed to run the membrane separation system. The evaporative latent heat of water and butanol was both 20 °C. In the wattmeter calculation of the electrical power of the chiller, which is needed to cool and condense the butanol gas, the

Table 1. Pervaporation performance of silicalite membrane

Membr. No	Hydrothermal synthesis gel		Silicone rubber coating	PV properties of BuOH at 45 °C					PV properties of EtOH at 30 °C[a]
	Aging temp/°C	Aging time		Feed concn /wt %	Permeation concn/wt %	Total flux /$g\,m^{-2}\,h^{-1}$	BuOH flux /$g\,m^{-2}\,h^{-1}$	α	
S-1	R.T.	3 h 20 min	None	1.05	50.3	23.9	12.0	96	75.4
			0.3% coated	1.09	54.7	13.3	7.3	110	78.9
S-2	R.T.	3 h 20 min	None	1.05	66.0	18.7	18.7	184	83.2
			0.3% coated	1.15	69.0	10.7	10.7	191	81.0
S-3	25	3 h 20 min	None	1.04	77.3	44.7	34.6	325	80.2
			0.3% coated	1.04	82.9	38.4	31.9	465	80.7
S-4	25	3 h 40 min	None	1.02	68.4	54.5	37.3	210	75.4
			0.3% coated	1.01	81.8	35.6	29.1	444	77.6
S-5	27	3 h 40 min	None	1.13	74.2	55.0	40.8	252	76.0
			0.3% coated	0.99	81.3	34.5	28.1	440	80.2

[a] Feed solution: 5 wt % of EtOH/water at 30 °C.

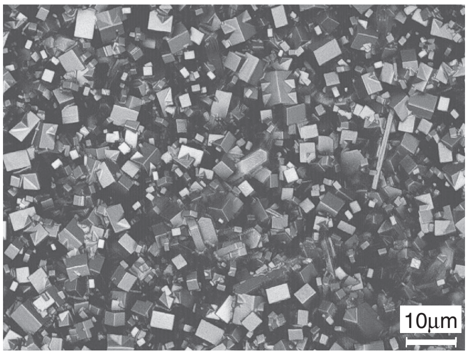

Figure 1. Surface photograph of silicone-rubber-coated silicalite membrane (Membr. No. S-3).

resulting coefficient of performance was assumed to be 2. The conversion efficiency from heat to electrical power was assumed to be 0.37 (This is commonly used in Japan.).

Figure 1 is a surface photograph of the silicone-rubber-coated silicalite membrane. Crystals of about 5 µm were observed. No differences were found between the structures of the membrane obtained and that of the membrane already reported.[10]

The preparation conditions and the PV performance of butanol and ethanol are shown in Table 1. A butanol concentration of over 80 wt % was not obtained with the silicalite membrane. When the aging temperature was not exactly controlled such as room temperature, the silicalite membrane did not give high butanol concentration, although high ethanol concentration is given (Membr. Nos. S-1 and S-2). Those membranes gave concentrated butanol solutions which were separated into two phases. On the other hand, the selectivity for butanol was improved although the total flux decreased, because the silicalite membrane was covered with the silicone rubber. The butanol solution can be concentrated to 81 wt % or more on silicone-rubber-coated silicalite membranes when the aging temperature is controlled exactly (Membr. Nos. S-3, S-4, and S-5). These conditions give separation factors of over 440. At this butanol concentration, the butanol solution does not separate into two layers. Obtaining the butanol solution as a single phase as a permeate is excellent for refining pure butanol fuel. This means the highly ethanol selective silicate membranes prepared by the reported method[10,12] do not always exhibit high selectivity for the butanol. This indicates that the previous method includes some factors to be controlled in order to prepare highly butanol permselective silicalite membrane. Here, we do not discuss the details of these factors in the absence of the fundamental data. However, by stabilizing aging temperature, a homogeneous hydrothermal synthesis gel solution may be prepared and a better membrane may form. Further investigations are currently under way.

Here we consider in detail the function of the butanol dehydration system that uses this separation membrane. With past butanol concentrate membranes, the butanol concentration obtained from a 1 wt % butanol solution is less than 80 wt %. In this case, the collected solution separates into two layers. The butanol concentration in the upper layer is about 80 wt %. The upper layer can be dehydrated to the next stage by processing using a dehydration membrane such as an A-type zeolite dehydration membrane, which has been reported on in recent years.[13] The lower layer contains butanol at 8 wt % that also needs to be collected. Figure 2A shows the butanol dehydration system in this case. The lower layer solution is separated by the silicone membrane and a permeate with an butanol concentration of 58 wt % is obtained. This solution also separates out into two layers. The solution of about 80 wt % in the upper layer is dehydrated by the dehydration membrane. The lower layer, again of 8 wt %, is fed back into the separation by the silicone membrane. The butanol concentration in the feed solution falls to 1 wt % by use of the silicone membrane and the butanol is fed back into the first process. Thus, when the butanol concentration is less than 80 wt % the separation process becomes complex.

On the other hand, an butanol solution concentrated to 80 wt % or more from a 1 wt % butanol solution can be produced by using the silicone-rubber-coated silicalite separation membrane that we developed. The dehydration membrane is used as the second stage. As a result, butanol at almost 100% is obtained. Figure 2B shows the butanol dehydration system used in this case.

Thus, the butanol concentrate system differs greatly according to the performance of the separation membrane. We

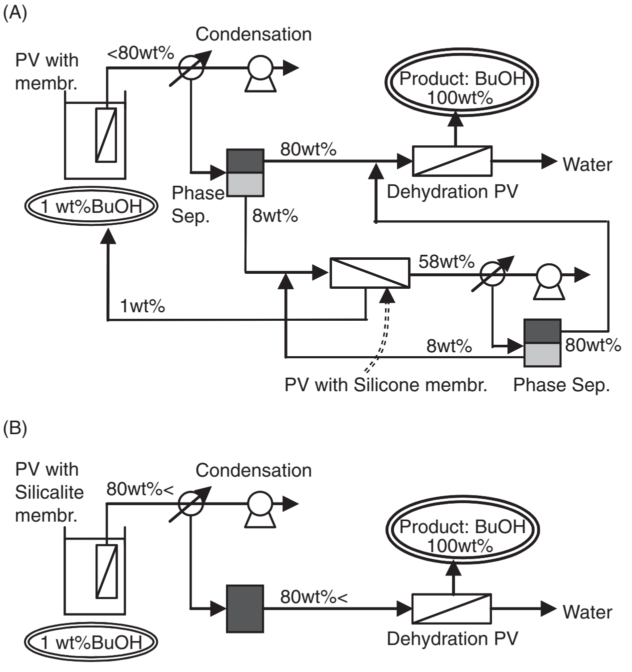

Figure 2. The butanol dehydration system depends on the performance of the separation membrane. (A) Use of a separation membrane that yields less than 80 wt % butanol from 1 wt % butanol solution, (B) use of a separation membrane that yields more than 80 wt % butanol from 1 wt % butanol solution.

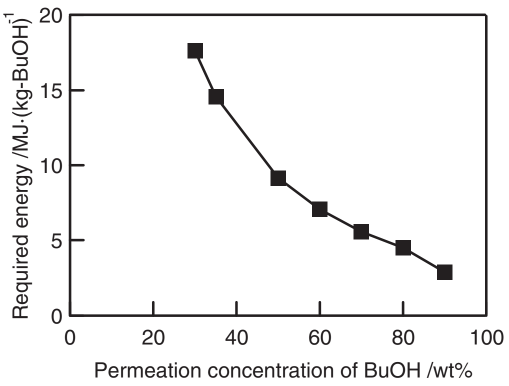

Figure 3. Energy required to produce butanol from 1 wt % butanol solution by membrane separation.

calculated the energy required by a system that used the PV method for the production of dehydrated butanol. The feed solution was 1 wt % butanol solution, and we assumed continuous extraction of the butanol. Figure 3 shows the result. The horizontal axis is the concentration of butanol solution obtained from 1 wt % butanol solution by PV. The vertical axis is the energy necessary for the entire system, including the dehydration and butanol concentration. The concentration of butanol from the 1 wt % butanol solution by PV uses a large percentage of the energy of the entire system. When the membrane separation performance rises, the amount of energy required becomes smaller. When the concentration of permeation exceeds 80 wt %, the system becomes simple. Consequently, the amount of energy needed becomes even smaller. When the concentration of permeation is 81.8 wt %, the energy needed for pure butanol production is 4.3 MJ kg^{-1}-butanol. This is about 13% of the energy provided by the butanol.

In conclusion, we developed a silicone-rubber-coated silicalite separation membrane that yields an butanol concentration of 80 wt % or more from a 1 wt % butanol solution. Preparation of the hydrothermal synthesis gel and silicone rubber coating was important. The butanol solution could be collected in a single phase, and the separation factor was over 440. The butanol concentration process in which the separation membrane was used was simplified greatly by the development of this separation membrane. The energy needed to refine the butanol from 1 wt % butanol solution was equal to 13% of the energy of the butanol.

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