ETHANOL PERMEATION FROM SAKE THROUGH CERAMIC MEMBRANES

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ABSTRACT

Japanese "Sake" is Japan's national liquor that is brewed from rice grains. Ethanol concentration of Sake is usually 15 wt%. Recently, Japanese people prefer light liquor with lower ethanol concentration. Ethanol concentration of Sake should be diluted keeping its unique smell and taste. Thus, ethanol separation procedures must be conducted under room temperature to keep their smell and taste. Membrane separation is one of the separation method without heating. We have been developing inorganic membranes such as silicalite membranes to separate ethanol from water. In this study, effects of impurities of Sake on ethanol permeation through the inorganic membranes were investigated. Ethanol permselective silicalite membrane having high ethanol flux was prepared by using the ultra-milling silicalite seed crystals. Silicalite membranes were synthesized by the secondary growth method. The ultra-milling seed crystals were prepared by the planetary ball mill. Seed crystals were coated on a substrate, the silicalite layer was grown by a hydrothermal synthesis method. EtOH permeance increased to 1.6 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1} from 1.4 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1} by using the ultra-milled crystals. However, separation factor of ethanol was 18 through the membrane prepared by using the ultra-milled crystals, while that prepared by using the as-made silicalite crystals was 25.

1. INTRODUCTION

Japanese "Sake" is Japan's national liquor that is brewed from rice grains. There are many kinds of Sake that are the special products of the districts due to the difference of the climates. Ethanol concentration of Sake is usually 15 wt%. Recently, Japanese people prefer light liquor with lower ethanol concentration. Ethanol concentration of Sake should be diluted keeping its unique smell and taste. Thus, ethanol separation procedures must be conducted under room temperature to keep their smell and taste. Membrane separation is effective separation method that can be operated under room temperature. If ethanol is selectively extracted thorough a membrane without permeating the organic components for the smell and teste, low ethanol concentration Sake can be produced. We have been developing inorganic membranes such as silicalite zeolite membranes to separate ethanol from water (Nomura, et al., 1998 and 2002). Zeolites are aluminosilicate crystals. Ratios of Si/Al of the crystal structures are important properties for the adsorption. Higher Si/Al ratio shows hydrophobic properties. Silicalite zeolite contains no Al in the structure (Si/Al $=\infty$) with ethanol selective adsorption property. Thus, silicalite zeolite membranes have been investigated as ethanol permselective membranes. However, there are no reports for the ethanol permeation from Sake. In this study, effects of impurities of Sake on ethanol permeation through the silicalite zeolite membranes were investigated.

2. EXPERIMENTAL

2.1 Preparation of silicalite zeolite membranes

Silicalite zeolite membranes were crystallized by using the following procedures based on the former report (Zhou et al., 2010). The molar ratio of the synthesis gel for the seed crystal was $1SiO_2$: 0.25TPABr (Tetrapropyl Ammonium Bromide, Wako Pure Chem. Ind., Ltd.): $0.15Na_2O$: $45H_2O$. NaOH (KANTO KAGAKU) and Tetramethylorthosilicate (Shin-Etsu Chemical Co., Ltd.) were used as chemicals. The parent gel was stirred at room temperature for 1 h. This gel was placed in an autoclave to crystallize at 130 °C for 20 h. The obtained seed crystals were dip coated on an α-alumina substrate. The molar ratio of the synthesis gel for the membrane preparation was $1SiO_2$: 0.3TPABr: $0.05Na_2O$: $800H_2O$. The coated substrate was placed vertically in an autoclave. Crystallization was carried out at 180 °C for 16 h. After the crystallization, the membranes were calcined at

500 °C to remove TPABr in the silicalite structure.

2.2 Characterization

The permeation properties of the obtained membranes were measured by single gas permeation tests and EtOH (ethanol) /water PV (pervaporation). Gas permeances of H_2, N_2 and SF_6 were evaluated by a bubble film flow method at room temperature. EtOH/water PV was employed with 10 wt% of EtOH aqueous solution at room temperature. In order to inestigate the effects of compositions for Sake, lactic acid, malic acid or succinic acid was added to the EtOH aqueous solution. Surface morphology was observed by using a scanning electron microscopy (SEM: KEYENCE, VE-8800). Crystallinity of zeolite was measured by an X-ray diffraction (XRD: Rigaku, RINT-TTR Ⅲ).

3. RESULTS AND DISCUSSIONS

3.1 Effects of acids on permeation properties

Sake PV test was conducted through the silicalite zeolite membranes. However, ethanol permeance decreased by the permeation test. Thus, the acid component in Sake was added to the EtOH aqueous solution for the PV tests.

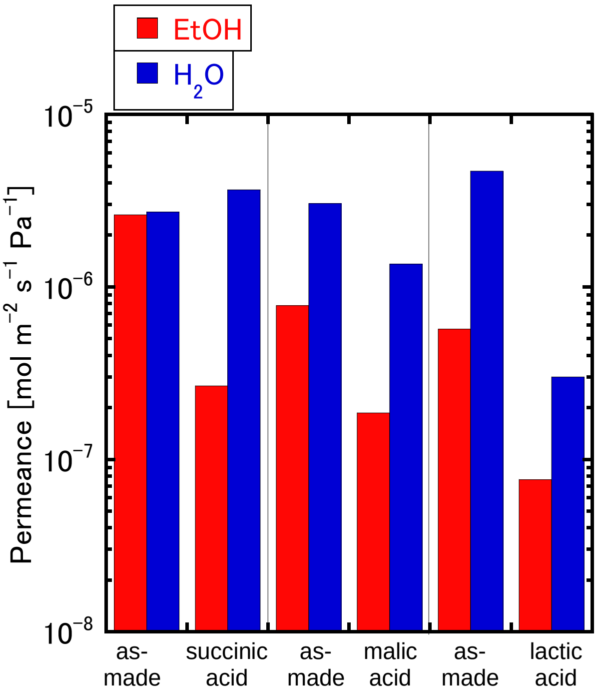

Fig. 1 EtOH/water PV tests with or without an acid.

Fig. 1 shows the Effects of the acid addition on the permeation properties of the PV tests. 3 kinds of acids (succinic acid, malic acid or lactic acid) were used for the PV tests. EtOH permeances decreased by the addition of the acid, while water permeances were slightly changed. Especially for the succinic acid, ethanol permeance decreased by 90 %. As a results, EtOH selectivity decreased by the addition of succinic acid. EtOH selectivity also decreased by the malic acid addition. On the other hand, EtOH selectivity increased by the lactic acid addition. Thus, succinic acid and malic acid must be the keys to decrease EtOH permselectivity.

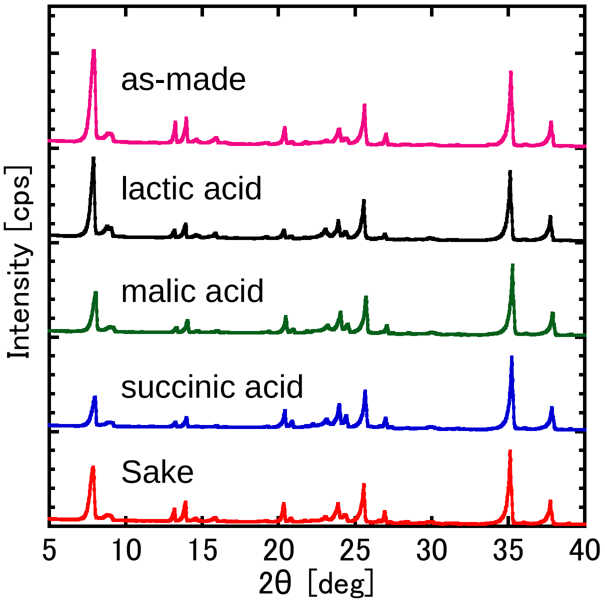

Fig. 2 XRD measurements after the PV tests with acids.

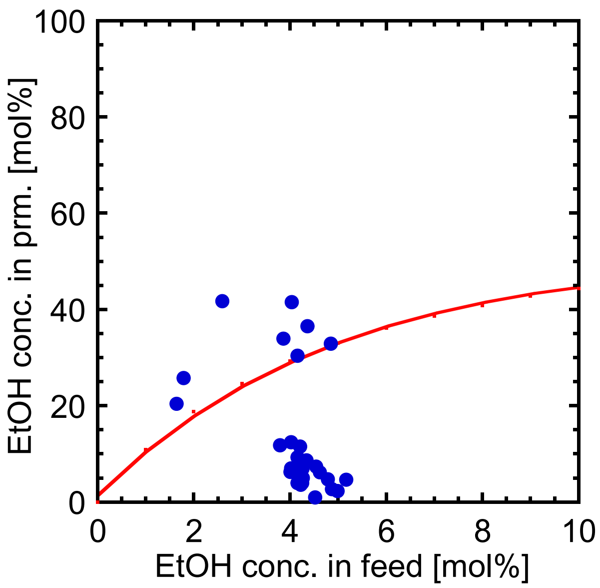

Fig. 3 Summery of the selectivities through the silicalite membranes

3.2 Membrane stability and selectivity

Zeolite can be broken by acids. Thus, XRD measurements were carried out after the PV tests. Fig. 2 shows XRD measurements after the PV tests with acids or PV test of Sake. The peaks at 8 ° and 23 ° show the MFI (silicalite) structure. The peak at 35 ° shows the γ-alumina substrate under the silicalite separation layer. However, XRD patterns were not changed by the acid and Sake showing that silicalite structure is stable under the acid conditions in Sake. The change for the permeation properties must be adsorption of the acid in the pores of silicalite.

Fig. 3 shows the summery of the selectivities through the silicalite membranes. The horizontal axis shows the feed EtOH concentration, and the vertical axis shows the permeate EtOH concentration. Feed liquid is vaporized through the membrane into permeate vapor for a PV separation method. If there is no permselectivity through the membrane, the permeate concentration should be the same to the liquid-vapor equilibrium. The solid line in Fig. 3 shows the liquid-vapor equilibrium for EtOH/water system. There are 7 membranes shown in the figure over the solid line. EtOH permselective silicalite membranes were successfully obtained by using the synthesis method. EtOH permeance increased to 1.6 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1} from 1.4 x 10^{-6} mol m^{-2} s^{-1} Pa^{-1} by using the ultra-milled crystals.

CONCLUSION

EtOH permeselective silicalite zeolite membranes were successfully obtained by using a hydrothermal synthesis method. EtOH permeance decreased by the Sake PV test. This decrease can be explained succinic aicd and malic acid adsorption to the silicalite structure.

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