ACID CONCENTRATION THROUGH ULTRAHIGH FLUX MEMBRANES

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ABSTRACT

Dehydration of water from acetic acid is important because acetic acid is a major intermediate chemical. Distillation of acetic acid solution consumes a large amount of energy due to low relative volatility of water and acetic acid. Condensation of acetic acid through a membrane at the top of distillation tower must be effective. Membranes with acid resistance, water resistance and heat resistance are required. However, no membranes have been reported for selective permeation of acetic acid. We have focused on zeolite as membrane material. Zeolite is a porous aluminosilicate crystal with high chemical stability and mechanical strength. MFI zeolite is a hydrophobic zeolite. The unit-cell of MFI structure consists with 96 T-atoms. MFI membranes show hydrophobic permselectivity in the case of all the T-atoms consisted with Si. Zeolite membranes have been prepared mainly on alumina substrates. In order to avoid the dissolution of Al from the substrates, we have been developing the MFI membranes prepared on novel silica substrates. MFI membranes were crystalized at 180 °C for 16 h in an autoclave by using a hydrothermal synthesis method. The composition of the parent gel was SiO_2: TPABr: Na_2O: Al_2O_3: H_2O = 1: 0.22: 0.017~0.067: 0~0.067: 200. Vapor permeation tests from the 31 wt% acetic acid aqueous solution were carried out at 60 °C. The parent gel compositions of Al and Na were important. The thickness of the MFI layer increased with increasing the Na ratios in the parent gel. Acetic acid permeance was 3.6×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with the separation factor of 8.4 were obtained through the membrane prepared from1.3 Al atoms in the MFI unit-cell. Acetic acid permselective membranes were successfully obtained on the porous silica substrates.

1. INTRODUCTION

Acetic acid has been used as an intermediate chemical of various important chemicals such as telephthalic acid. More than 3 million tons of water should be removed from acetic acid solution for a year in Japan. This is one of the largest dehydration demand in the Japanese petro-chemical industries. Distillation is one of the efficient separation method by using the different of liquid–vapor equilibrium. However, the relative volatility of water and acetic acid is low. Thus, a large amount of energy is consumed at the distillation of acetic acid condensation. Membrane separation is one of the energy saving separation methods. Heat demand at the distillation tower can be reduced dramatically by combination of distillation and membrane. The membranes require high acid resistance, water resistance and heat resistance.

Membranes can be classified in 2 types as inorganic membranes and polymer membranes. Polymer membranes have been developed for the industrial application (e.g. seawater desalination etc). On the other hand, inorganic membranes have been developing by using zeolite, metal, titania, zirconia, carbon or silica as membrane materials.

Zeolite is an aluminosilicate crystal with porous structures. Catalytic, ion exchange and adsorption properties are based on pores and Al in the structures. Zeolite crystal consist with a unit-cell. Amounts of Al atoms in the unit-cell are key factor for hydrophilic-hydrophobic properties of the zeolites. High silica zeolites such as MFI zeolite show hydrophobic properties. MFI zeolite has 0.55nm pores and has been studied widely all over the world. On the other hand, low silica zeolites such as LTA zeolite or MOR zeolite show hydrophilic properties.

Dehydration is a very important separation process. Various hydrophilic zeolite membranes have been studied in order to apply at the dehydration separation. Total permeation flux through the MOR zeolite membrane was 0.44 kg m^{-2} h^{-1} and high separation factor of 2300 by the pervaporation (PV) of a 90 wt% acetic acid aqueous solution at 75 °C (Zhu et al., 2014). MOR zeolite membrane showed the higher permeation flux of 10.9 kg m^{-2} h^{-1} with the separation factor of 500 at 130 °C for the PV of a 50wt% acetic acid aqueous solution (Sato et al., 2011). CHA zeolite membrane showed water permselectivity. The permeation flux was ca. 8 kg m^{-2} h^{-1} and separation factor with ca. 2500 by the PV of a 50 wt% acetic acid aqueous solution at 75 °C (Yamanaka et al., 2012). Low silica MFI zeolite membrane showed also hydrophilic properties. The permeation flux was 0.785 kg m^{-2} h^{-1} and separation factor of 381 by the PV of a 50wt% acetic acid aqueous solution at 343K (Li et al., 2003). Wang et al. (2014) developed an Sn doped MFI zeolite membranes. The permeation flux was 0.84 kg m^{-2} h^{-1} and separation factor of above 1×10^{10} by the PV of 98wt% acetic acid aqueous solution.

MFI zeolite shows hydrophobic properties under low Al in the structure. However, MFI membranes have been prepared mainly on alumina substrates. It is not easy to control Al amounts in the structures by the Al dissolution from the alumina substrates during the synthesis procedures (Caro et al., 2000). We have been developing the MFI membranes on novel porous silica substrates (Sugiyama et al., 2015). The gas permselectivity through the MFI membranes on the silica substrates were excellent.

In this study, the MFI zeolite membranes prepared on the silica substrates were applied for condensation of acetic acid in the vapor phase. Effects of Na and Al in the parent gel for the synthesis were investigated.

2. EXPERIMENT

2.1 Membrane preparation

MFI seed crystals were synthesized based on the previous study (Zhou et al., 2010). The composition of the parent gel was SiO_2: TPABr: Na_2O: H_2O = 1: 0.25: 0.15: 40. Colloidal silica (Nissan Chemical Industries, Limited) was used as silica source. Tetrapropylammoniumbromide (Wako Pure Chemical Industries, Ltd.) was used as template. Crystallization was carried out in an autoclave at 130 °C for 20 h. The seed crystals were dispersed at 8 g L^{-1} in an HCl aqueous solution controlled for pH 2.

The tubular silica substrates (Sumitomo Electric Industries: outer diameter: ϕ 10 mm, thickness: 1.3 mm, length: 30 mm, pore size: 500 nm) were washed with deionized water and dried at 180 °C for 20 min. The silica substrates were immersed in the seed slurry for 30 s. The seed coated silica substrates were dried at 180 °C for 20 min.

MFI zeolite layers were synthesized based on the previous study prepared on the alumina substrates (Zhou et al., 2010). The composition of the parent gel was SiO_2: TPABr: Na_2O: Al_2O_3: H_2O =1: 0.22: 0.017~0.067: 0~0.067: 200. The parent gel was stirred for 60 min at room temperature. The silica substrates with seed crystals were soaked into the parent gel in an autoclave. The crystallization was carried out at 180 °C for 16 h. After the crystallization, the obtained MFI membranes were calcined at 500 °C for 15 h to remove tetrapropylammonium ion in the MFI structure.

2.2 Characterization

Gas permeances through the membranes were evaluated by a bubble film flow method with H_2, N_2, SF_6 at room temperature. Surface and cross-sectional observations for the membranes were carried out by using a scanning electron microscope (SEM : KEYENCE, VE-8800). Crystallinity of the zeolite membrane was measured by an X-ray diffraction (XRD : Rigaku, RINT-TTR Ⅲ).

2.3 Vapor permeation test

The schematic diagram for the vapor permeation apparatus is shown in Fig. 1. Both ends of the membrane were sealed by o-ring in the metal membrane module. The effective membrane area was 6.3 cm^2. Ar was used as sweep gas at 55 ml min^{-1} in the inner side of the membrane. Acetic acid solution was purred into the metal bottle and N_2 bubbling was carried out at 200 ml min^{-1}. Flow rates of Ar and N_2 were controlled through the mass flow controllers (MFC: HORIBA STEC, SEC-E40). The bubbler bottle was kept at 50 °C and the stainless steel tubes between the bubbler bottle and the metal membrane module were kept at 130°C by using the ribbon heaters. Membrane temperature was kept at 60 °C. Concentration of the feed vapor and the permeate vapor was analyzed by a gas chromatography (SHIMADZU, GC-8A).

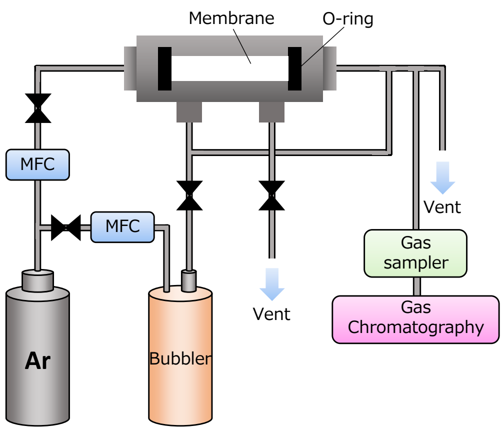

Fig. 1 Schematic diagram of the vapor permeation apparatus

2.4 Analysis for vapor permeation test

Vapor pressure of acetic acid was calculated by assuming the Antoine equation. Acetic acid concentration from the 31wt% acetic acid aqueous solution was about 10% at 50 °C. Permeances and the separation factors were calculated by using the following equations.

Permeance

$$= \frac{\frac{Sweep\ gas\ flow\ rate \times Partical\ pressure}{Volume\ per\ mol}}{membrane\ area}$$

$$= mol\, m^{-2} s^{-1} Pa^{-1}$$

$$\alpha_{\text{Acetic acid/Water}} = \left(\frac{y_{Acetic\ acid}}{y_{Water}}\right) / \left(\frac{x_{Acetic\ acid}}{x_{Water}}\right)$$

3. RESULTS AND DISCUSSION

3.1 Effects of Na_2O/SiO_2 ratio

Fig. 2 shows the cross-sectional views of the SEM images of the membranes prepared by changing the Na_2O/SiO_2 ratios of the parent gels. The thickness from the parent gel of Na_2O/SiO_2=0.017 was 7.9 μm. The membrane thicknesses increased with increasing Na_2O/SiO_2 ratios. Fig. 3 shows the single gas permeances at room temperature as a function of the Na_2O/SiO_2 ratios of the parent gels. The H_2 permeance through the membrane prepared by the parent gel of Na_2O/SiO_2=0.017 was 8.4×10^{-6} mol m^{-2} s^{-1} Pa^{-1}. All membranes showed high N_2/SF_6 selectivities over 60. The gas permeances of H_2 and N_2 decreased with increasing Na_2O/SiO_2 ratios. The gas permeances must depend on the membrane thicknesses. All membranes were crystalized from the same amount of Al contents (0.96 Al/unit-cell) in the parent gel. The amounts of Na in the parent gel were controlled by changing the amounts of NaOH. The gas permeances decreased by increasing Na_2O/SiO_2 ratio. Blocking gas permeation was thought to have been caused by containing Al atoms in unit-cell. Thus, high Na_2O/SiO_2 ratio show high Al concentration in the parent gel. Therefore Al atoms in MFI structure was thought depended on Na_2O/SiO_2 ratio.

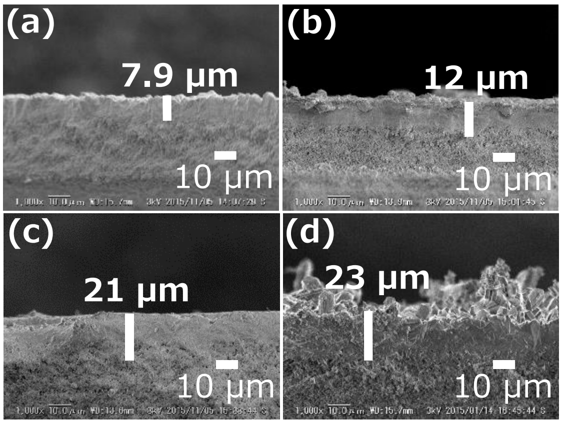

Fig. 2 SEM images of the cross-sectional views for the MFI zeolite membranes on silica substrates prepared from the parent gel with a molar ratio of
(a) Na_2O/SiO_2=0.017, (b) Na_2O/SiO_2=0.023,
(c) Na_2O/SiO_2=0.028, (d) Na_2O/SiO_2=0.034

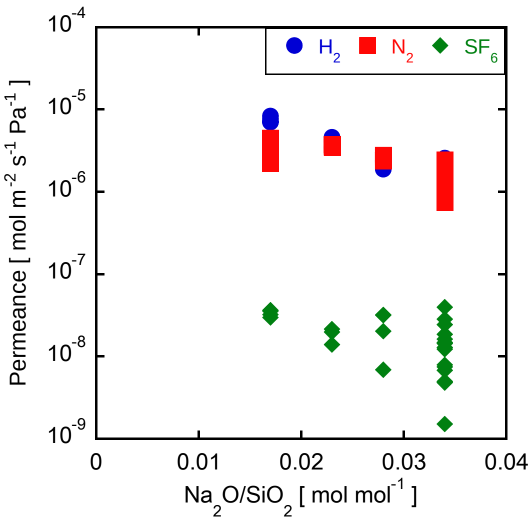

Fig. 3 Permeation performances through the MFI membranes by changing the Na_2O/SiO_2 molar ratios of the parent gel

3.2 Separation of Acetic acid/Water Vapor

Vapor permeation tests from the 31 wt% acetic acid aqueous solution at 60 °C were carried out by using the membranes prepared from the parent gel by changing the Na_2O/SiO_2 ratios between 0.017 and 0.034. Fig. 4 shows the Na_2O/SiO_2 ratio dependence of the acetic acid and the water permeances. All membranes showed the high acetic acid permeances over 3.7×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, and the acetic acid permeances showed the low dependence on the Na_2O/SiO_2 ratios. This trend was different from the single gas permeances shown in Fig. 2. The maximum separation factor over water was found by the membrane prepared from the parent gel of Na_2O/SiO_2=0.028. The acetic acid permeance was 3.6×10^{-7} mol m^{-2} s^{-1} Pa^{-1} and acetic acid/water separation factor was 8.4. These phenomena can be explained as follows. Permeation properties of zeolite membranes depend on the types of the cations or the amount of the cations in the zeolite structure. When Na_2O/SiO_2 ratio is under 0.028 in the parent gel, amounts of Al atoms in membranes were increased with increasing the Na_2O/SiO_2 ratios. Al atom in the MFI structure relates to the adsorption amounts of water in the MFI structure. The adsorbed water in the MFI structure is not easy to diffuse. Thus, water permeances decreased with increasing the Na_2O/SiO_2 ratios. When Na_2O/SiO_2 ratio is over 0.028 in the parent gel, the compactness of the membranes were not enough as shown in Fig.2. SF_6 permeance through the membrane prepared from the parent gel of Na_2O/SiO_2 ratio of 0.034 was slightly higher than that prepared from the parent gel of Na_2O/SiO_2 ratio of 0.028.

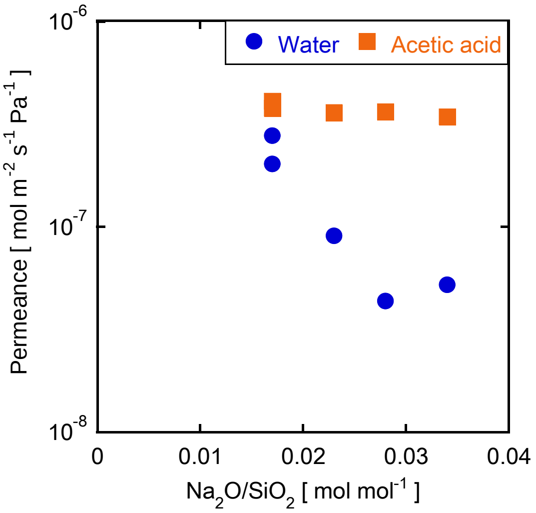

Fig. 4 Permeation performances of acetic acid/water through MFI membranes from the parent gels of the Na_2O/SiO_2 ratios

4. CONCLUSION

MFI zeolite membranes with acetic acid permselectivities were successfully synthesized on the porous silica substrates by using a hydrothermal synthesis method. Parent gel with a molar ratio of SiO_2: TPABr: Na_2O: Al_2O_3: H_2O = 1: 0.22: 0.017~0.067: 0~0.067: 200 was used for the crystallization. Permeance decreased by increasing the Na_2O/SiO_2 ratios in the parent gels for gas permeation of H_2 and N_2. Acetic acid permeance was 3.6×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with acetic acid/water separation factor was 8.4 through the membrane prepared from the parent gel of Na_2O/SiO_2=0.028. Amounts of Al atoms in MFI membranes were important parameters.

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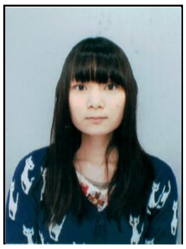

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