NEW MEMBRANE SHAPE CERAMIC ADSORBENTS FOR WATER PURIFICATION

Mikihiro Nomura, Ayumi Ikeda, Yuki Hayashi

Shotaro Tanaka, Yo Matsuo, Toyomitsu Itai

Department of Applied Chemistry, Shibaura Institute of Technology

Takagi Co. Ltd.

Lscathy@shibaura-it.ac.jp

ABSTRACT

A novel zeolitic membrane shape adsorbent for water purification was successfully prepared by using a dry gel conversion method. The parent gel composition was SiO_2: Na_2O: TPABr (Tetrapropyl Ammonium Bromide) = 1.0: 0.041: 0.12. The dried gel was put in the ϕ 13 mm stainless case, and the gel was pressed at 7.0 t. The pore size of the membrane was controlled by adding carbon fibers of ϕ7 μm to the dried gel. Crystallization was employed at 180 °C for 10 days in the 100 ml autoclave with 2.5 ml of water. The carbon fibers were calcined at 500 °C after the crystallization to be pores of the membrane. The MFI structure was confirmed by the XRD measurement after the calcination. The surface properties of the carbon fibers were important to obtain the MFI zeolite membrane. Hydrophobic carbon fibers were preferred. The permeation tests of pure water or kaolinite slurry performed at room temperature. The water flux was 8100 kg m^{-2} h^{-1} at the pressure difference of 5.9 kPa. The flux improved more than twice by adding the carbon fibers. The rejection of the kaolinite was about 40%. Smectite was the candidate for the additive to improve the mechanical strength of the membrane tablets.

1. INTRODUCTION

Water purification using a membrane is important because of a demand for pure water (Nakao, 2003). A personal water purifying device is usually a combination of a microfiltration and an adsorbent. Bacteria in water can be removed by the microfiltration, and organic molecules can be removed by the adsorbent under low pressure difference by using this type of the membrane system. We have been developing a new type of a ceramic zeolite membrane that the size of the non-zeolitic pathways is controlled at around μm order by adding polymeric template (Nomura & Uchida, 2009). Zeolite is a porous ceramic crystal with an adsorption property. Fig. 1 shows the schematic diagram of a membrane preparation and a characterization method. First, zeolite layer is crystallized with a template (cf. polyethylene glycol or carbon fiber) for the non-zeolitic pores. Crystallization was carried out by using a dry gel conversion method (Matsukata, et al., 1999). The parent gel is dried and the dried gel is converted into a zeolitic structure under high temperature water vapor for the dry gel conversion method. Next, the as-made membrane is calcined to remove the template in the non-zeolitic pores. We can combine the filtration function and the adsorption function in one device. However, the procedures to prepare the dried gel were not clear. In this study, the preparation procedures to obtain MFI zeolite membranes were investigated.

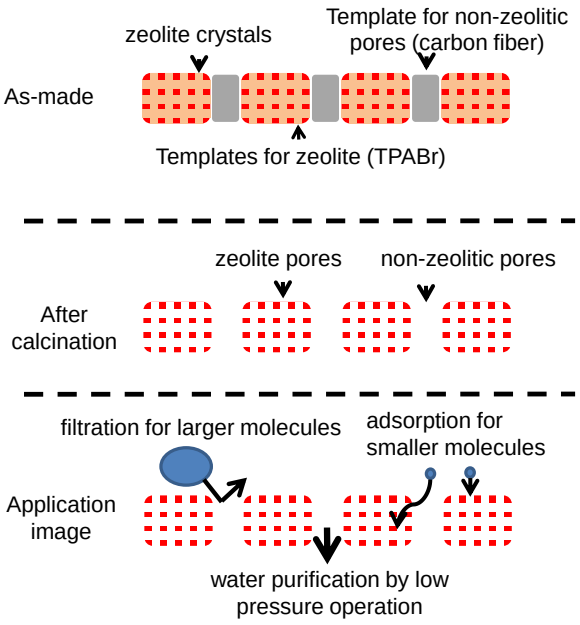

Fig. 1 Preparation image for a novel zeolite membrane for water purification.

2. EXPERIMENT

2.1 Experimental Apparatus

MFI zeolite membranes were crystallized by using a dry gel conversion (DGC) method. The weight ratio of the parent gel was SiO_2: Na_2O: TPABr (Tetrapropyl Ammonium Bromide) = 1.0: 0.041: 0.12. These chemicals were dissolved in pure water. After stirring at 80 °C for 4 h, the gel was dried on a hot plate. MFI seed crystals were added to the parent gel. There were 2 kinds of the seed crystals. One was the as-made MFI seed crystals with a size of ca. 3 μm and the other was ultra-milled crystals with a size of ca. 0.1 μm. Carbon fibers (ϕ: 7 μm, Toho Tenax Co.) were employed for templates of the non-zeolitic pores. Smectite or kaolin was used as an additive to improve the mechanical strength of the membranes. The parent gel (0.40 g), seed crystals (0.02 g), carbon fibers (0.02 g) and the additives (0.10 g) were mixed, and the mixture was put into the stainless steel case (ϕ: 13 mm) under 7.0 t of the pressure. The pressed tablet was placed in a 100 ml autoclave with 2.5 ml of pure water. Crystallization was carried out at 180 °C for 10 days. The crystallized tablets were calcined at 600 °C for 2 h to remove the carbon fibers and TPABr. Characterization of the tablets was carried out by using an X-ray diffraction (XRD: RINT-TTR III, Rigaku Co.) and a scanning electron microscopy (SEM: VE-8800, Keyence Co.).

3. RESULTS AND DISCUSSIONS

3.1 Effects of carbon fibers

Fig.2 shows SEM images of the carbon fibers and the surface of the membrane with carbon fibers. The surface morphology of the carbon fibers was transcripted on the MFI membrane. This shows that the affinity between the carbon fibers and the membrane is very well. Surface property of the carbon fibers is hydrophobic. MFI zeolite grows from the hydrophobic surface.

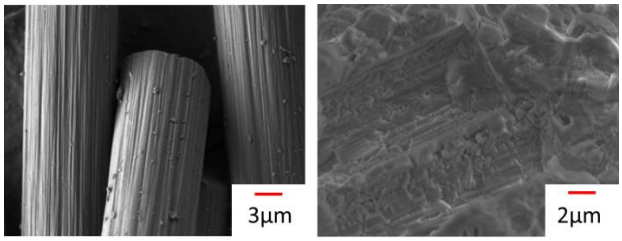

Fig.2 SEM images of the carbon fibers (left) and the surface of the membrane with carbon fibers (right).

Fig. 3 shows the pure water permeation plotted against the feed water pressures through the membranes with or without carbon fiber addition. The dotted line shows the requirement for the commercial water purifier. The solid line shows the former result for the MFI membrane crystallized on the α-alumina substrate (Nomura & Uchida, 2009). All the water fluxes were proportional to the feed pressures showing that the experimental procedures were adequate. Water fluxes increased by the carbon fiber addition. The non-zeolitic pores created by the addition of the carbon fiber was effective to improve the water flux. The water flux through the membrane tablet with carbon fiber is over the requirement for the commercial water purifier. The rejection of the kaolinite was about 40%.

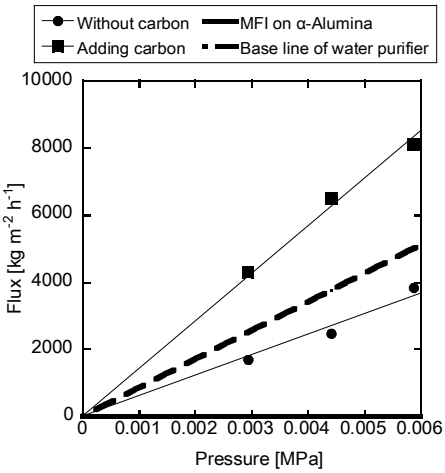

Fig.3 Pure water permeation through the membranes.

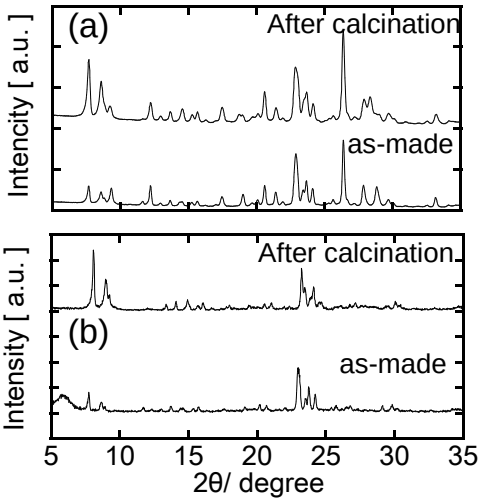

Fig.4 XRD patterns of the membranes
(a) with kaolin (b) with smectite

3.2 Effects of additives

Fig.4 shows the XRD patterns of the membranes with kaolin or with smectite. The mechanical strengths for the tablets were improved by adding the additives. There are sharp peaks at 8 ° and 23 ° found from all the samples. These peaks show the MFI zeolite structure. MFI zeolite was successfully obtained by using the DGC method. There was a unique broad peak at 5 ° found from the as-made tables with smectite addition. This peak indicates the smectite structure. Thus, smectite structure was remained after the DGC method while the parent gel was converted to the MFI structures. However, the broad peak at 5 ° was not found from the XRD pattern for the calcined tablet. The smectite structure was broken by the calcination. This can be explained by the removal of water in the smectite structure by the 500 °C calcination procedure. The mechanical strength of the calcined tablet

was enough. Smectite might work as connection between the MFI zeolite crystals. Smectite can be a candidate of the additive to form MFI zeolite membrane tablets.

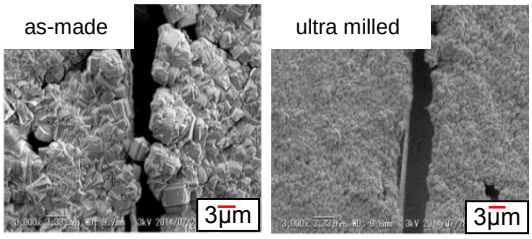

Fig.5 SEM images of the membranes prepared by using the as-made seed crystals (left) and by using ultra-milled seed crystals (right).

3.3 Effects of seed crystals

Fig. 5 shows the SEM images for the surface views of the MFI membrane tablets with the different seed crystals. Both membrane tablets were confirmed as the MFI structure by the XRD measurements. The MFI membrane tablets were polycrystalline structures. The black lines in the SEM images are the trace of the calcined carbon fibers. The MFI crystal sizes were different by the different of the seed crystals. Smaller MFI crystals were found from the ultra-milled seed crystals. The number of the seed crystals relate to the numbers of the nuclei in the parent gel. The total amounts of the silica source was fixed. Thus, the MFI crystal size from the ultra-milled membrane tablet was smaller due to large number of the nuclei. Surface area for the smaller crystals should be larger. The membrane tablets from the ultra-milled seed crystals must be better adsorbents by the larger surface area of the crystals.

4. CONCLUSION

A zeolitic membrane tablet for water purification was successfully prepared by using a dry gel conversion method. The surface properties of the carbon fibers were important to obtain the MFI zeolite structure. Hydrophobic carbon fibers were preferred. The permeation tests of pure water or kaolinite slurry performed at room temperature. The water flux was 8100 kg m^{-2} h^{-1} at the pressure difference of 5.9 kPa. The flux improved more than twice by adding the carbon fibers. The rejection of the kaolinite was about 40%. Smectite was the candidate for the additive to improve the mechanical strength of the membrane tablets.

REFERENCES

Matsukata, M., Ogura, M., Osaki, T., Rao, P.R.H.P., Nomura, M., and Kikuchi, E., Conversion of dry gel to microporous crystals in gas phase, *Topics in Catal.*, vol. 9, pp. 77-92, 1999.

Nakao, S., Development of system making efficient use of water resources based on membrane technologies, *Membrane*, vol. 28, pp. 215-220, 2003.

Nomura, M., and Uchida, H., Control of an intercrystalline pathway of a zeolite membrane for water purification, *Kagakukogaku Ronbunshu*, vol. 35, pp. 122-126, 2009.

Mikihiro Nomura received the B.E. (1990) and the M.E. (1992) degrees Chemical Engineering from the University of Tokyo. He received the D.E. (1998) degrees Chemical System Engineering from the University of Tokyo. He is a Professor, Department of Applied Chemistry, Shibaura Institute of Technology. His Current interest is membrane separation.

Ayumi Ikeda received the B.E. (2012) and the M.E. (2014) degrees in Applied Chemistry from Shibaura Institute of Technology.

She is a doctor course student, Department of Regional Environment Systems, Shibaura Institute of Technology.

Yuki Hayashi is a bachelor course student, Department of Applied Chemistry, Shibaura Institute of Technology.