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Preparation of FAU type zeolite membranes by electrophoretic deposition and their separation properties

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A novel method using electrophoretic deposition (EPD) is proposed for the preparation of dense FAU type zeolite membranes. The precursor membranes deposited through EPD were transformed into continuous bodies without interparticle pores by hydrothermal treatment in reaction mixtures with molar ratio $Na_2O:Al_2O_3:SiO_2:H_2O = 8:1:12:360$. It was found that the densification of the precursor membranes during the hydrothermal treatment was achieved *via* two reaction routes; one was crystal growth of FAU type zeolite seeds and the other was generation of FAU type zeolite particles in the interparticle pores from the reaction mixtures. The thus prepared FAU type zeolite self-supported membranes exhibited high performances with a selectivity of 20 in CO_2/N_2 gas separation.

Introduction

Zeolite membranes have gained much attention in many fields for their applications such as molecular sieve membranes, membrane reactors, sensors, and optical materials due to their potential advantage of well-defined pore structure with sub-nanometer size.[1–4] Some preparations of zeolite membranes with different structural types, which have been mainly carried out by *in situ* crystallization on a substrate, have been reported.[5–8] However, it is difficult to obtain zeolite membranes of complex shapes and/or high denseness over extended areas, owing to the influence of heterogeneous zeolite nucleation. Some researchers have recently performed the preparation of zeolite membranes using seed particles.[9–11] In the preparation of zeolite membranes, using seed particles is considered to be an effective means in terms of providing high reproducibility and control of membrane morphology. Although thin MFI membranes with sub-micrometer thicknesses were successfully obtained using nanometer sized seed particles,[12] this method yielded polycrystalline membranes with interparticle pores. Improving densification processes of the seed particle layer, *i.e.*, the precursor membrane, is necessary in this method since membranes without interparticle pores are required to utilize only the inherent pores of the zeolite structure.

Electrophoretic deposition (EPD) is a colloidal process for forming ceramic bodies from suspensions with ceramic particles. This process has advantages such as the uniformity of deposition even for complex and large forms, thickness control of the deposit and simplicity of operation. Thus EPD seems to be a favorable method to form zeolite seed layers, compared with other methods such as rubbing, dip coating and laser ablation. We have investigated the preparation of dense zeolite membranes using EPD.[13,14]

We describe here the preparation method for FAU type zeolite membranes using EPD followed by hydrothermal treatment. Furthermore, the microstructure and properties of the resulting FAU membranes are examined *via* permeation measurements of CO_2 and N_2. Recently, FAU type zeolite membranes prepared by a seeding method were reported to exhibit high CO_2/N_2 selectivities of 20–30 arising from the difference of sorptivities between CO_2 and N_2 in the intracrystalline pores.[11]

Experimental

Aqueous suspensions of FAU (NaY type) zeolite particles (particle size ~1 μm, Catalysts & Chemicals Industries Co., Ltd., Japan) were prepared at a concentration of $4\ g\ L^{-1}$. Stainless plates were used as the electrodes after cleaning and degreasing treatments. The distance between the electrodes was set at 1 cm and both electrodes had a specific surface area of $1\ cm^2$. Deposition was carried out under a dc electric field of 10 V with slow stirring in order to maintain the homogeneity of the suspension. The reaction mixtures used for densification processes of the precursor membranes were set to a molar ratio of $Na_2O:Al_2O_3:SiO_2:H_2O = 8:1:12:360$. The reaction mixtures were prepared by dissolving sodium hydroxide, sodium aluminate and colloidal silica into deionized water followed by vigorous stirring for 5 h. As-precursor membranes on the stainless plates were vertically immersed into the mixture in a Teflon-lined stainless steel autoclave. The autoclaves were then placed in an oven at 353 K for ~30 h. The resulting samples were washed thoroughly with deionized water and dried at 333 K overnight. After drying, the resulting membranes were peeled from the stainless plate to obtain the self-supported membranes.

The samples were characterized by powder X-ray diffraction (XRD), using a Shimadzu XD-3A diffractometer with Cu-Kα radiation. The morphologies of the resulting membranes were examined by scanning electron microscopy (SEM), using a JEOL JSM-6300 instrument.

Permeation measurements were performed with the Wicke-Kallenbach set up. The total pressures on the feed and permeate sides of the resulting membranes were held at atmospheric pressure, and the temperature was kept at 298 K. He was used as a sweep gas. The feed gases used single components of CO_2 or N_2 or a binary mixture of $CO_2:N_2 = 1:1$. The flow rates of all streams were controlled by mass flow controllers. The compositions of the permeate gas were analyzed by gas chromatography, using a Shimadzu GC-8AIT equipped with a thermal conductivity detector. Permeances were calculated from eqn. (1):

$$\text{Permeance} = \frac{\text{(mole of gas transferred per unit time)}}{\text{(membrane area)(partial pressure difference)}} \quad (1)$$

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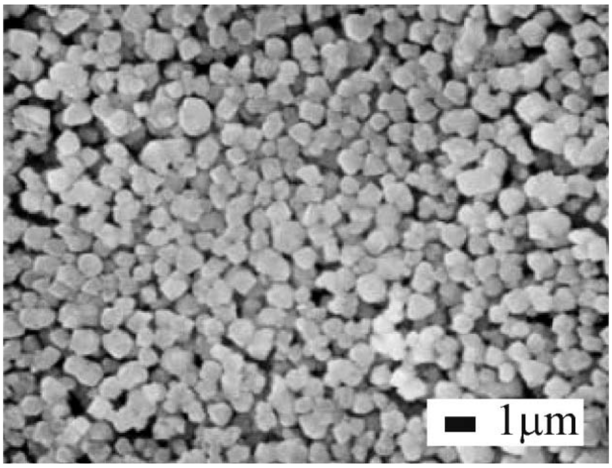

Fig. 1 Free surface of the FAU precursor membrane deposited on the anode at 10 V.

while the CO_2/N_2 selectivity is defined by eqn. (2):

$$CO_2/N_2\ \text{selectivity} = \frac{(\text{permeance of } CO_2)}{(\text{permeance of } N_2)} \qquad (2)$$

Results and discussion

Fig. 1 shows the free surface of a precursor membrane deposited on the anode at 10 V. The precursor membranes showed no large defects although individual particles were recognizable. In the EPD process, the resulting precursor membranes were relatively uniform over a wide area, and the membrane thickness was successfully controlled to ~60 μm.

The resulting membranes were hardened into self-supported membranes after hydrothermal treatment. Fig. 2 shows SEM photographs of fractured sections of a precursor membrane deposited at 10 V for 15 min and for membranes hydrothermally treated at 358 K for 5 and 15 h. Increased densification of the resulting membranes was observed with increasing treatment time. In the early stage of the densification reaction, as seen in Fig. 2(e), the crystal growth of seed particles and the formation of smaller particles in the interparticle pores were observed. The membrane treated for 15 h, as seen in Fig. 2(f), was too dense to distinguish the morphology of individual particles. These results revealed that during the densificaton mechanism of the precursor membranes the interparticle pores in the membranes were filled up through the growth and incorporation of two kinds of particles, the seed particles and particles generated in the interparticle pores. Since XRD analyses confirmed no extra phases during this process, as seen in Fig. 3, it was judged that the newly formed particles were FAU type zeolites from the reaction mixture soaked into interparticle pores.

Fig. 4 shows the permeances of N_2 and CO_2 and the CO_2/N_2 selectivities from the binary mixture as a function of hydrothermal reaction times for the resulting FAU membranes. The permeances of both N_2 and CO_2 vary with elongation of reaction time, *i.e.*, the progress of the densification reaction. The permeance of CO_2 became steady for membranes treated for a longer period than 17 h, whereas that of N_2 was continuously lowered. Significant CO_2/N_2 separation could thus be realized. Membranes treated for 30 h showed permeances of CO_2 and N_2 of 5.4×10^{-7} and 2.7×10^{-8} mol m^{-2} s^{-1} Pa^{-1}, respectively,

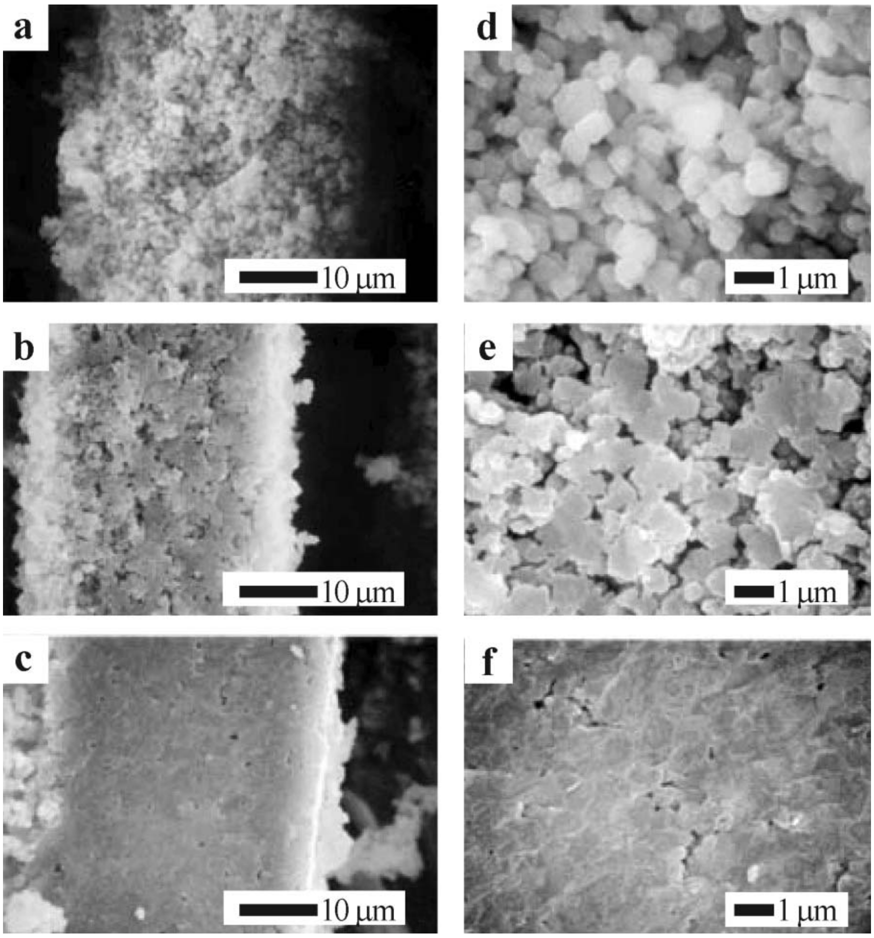

Fig. 2 Fractured sections of (a), (d) the precursor membrane deposited at 10 V for 15 min and the membranes hydrothermally treated at 353 K for (b), (e) 5 h and (c), (f) 15 h.

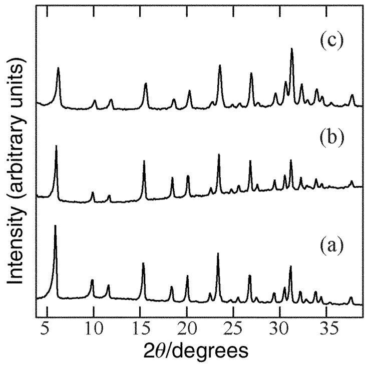

Fig. 3 XRD patterns of (a) FAU seed particles used, (b) the precursor membranes electrophoretically formed at 10 V for 15 min and (c) the membranes hydrothermally treated at 353 K for 15 h after EPD.

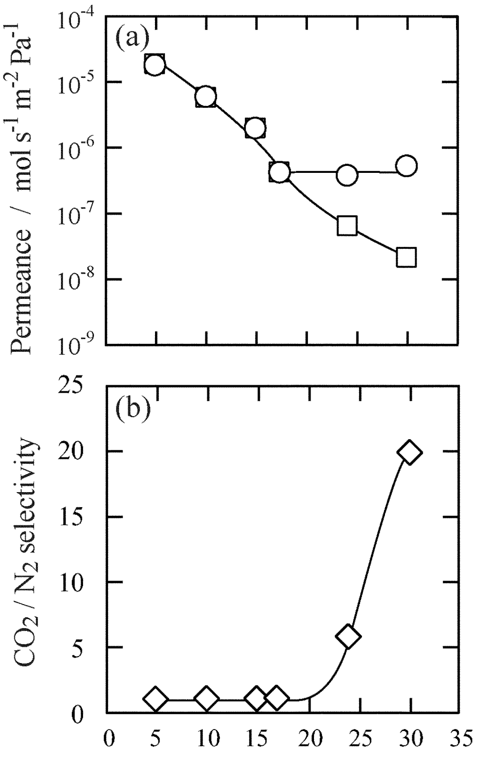

Fig. 4 Permeance changes found for membranes in the binary system as a function of hydrothermal reaction time; (a) permeances of CO_2 (○), N_2 (□) and (b) the CO_2/N_2 selectivities.

in the binary system. Consequently, the CO_2/N_2 selectivity was found to reach a value of 20. The drastic increase of CO_2/N_2 selectivities with the treatment time implied that the diffusion mechanism for the binary system changed from Knudsen diffusion to surface diffusion in the membranes densified by hydrothermal treatment; that is, the preferential gas permeation routes changed from the interparticle pores to the intracrystalline pores. On the other hand, the permeances of CO_2 and N_2 by the membranes treated for 30 h were estimated to be 4.26×10^{-7} and 7.05×10^{-8} mol m^{-2} s^{-1} Pa^{-1}, respectively, in the single component systems. This difference of N_2 permeance in single and binary systems seems to be due to the fact that CO_2 was adsorbed on permeation routes so as to prevent N_2 permeation. This result supports the above explanation for the change of diffusion mechanism caused by the densification process. The membranes hydrothermally treated for 30 h can, therefore, be regarded as dense membranes without interparticle pores.

Table 1 Permeance of the FAU type zeolite membranes

	Permeance/mol s^{-1} m^{-2} Pa^{-1}		CO_2/N_2 selectivity
	CO_2	N_2	
This study	5.4×10^{-7}	2.7×10^{-8}	20
Kusakabe *et al.*[11]	13×10^{-7}	4.4×10^{-8}	30
Hasegawa *et al.*[15]	8.6×10^{-7}	4.5×10^{-8}	19
Clet *et al.*[8]	3.4×10^{-7}	8.7×10^{-8}	4

Table 1 shows the results of separation measurements of a CO_2/N_2 mixture using the FAU membranes prepared here, compared with other reports. Kusakabe *et al.* and Hasegawa *et al.* prepared FAU membranes supported on porous Al_2O_3, using a rubbing method for seeding,[11,15] while Clet *et al.* prepared FAU membranes supported on a porous stainless disk coated with porous titania layers, using an *in situ* crystallization method.[8] It turns out that the CO_2/N_2 separation ability of the FAU self-supported membranes prepared using EPD approaches those of the membranes prepared by the rubbing method, as seen in Table 1.

Conclusions

A novel method using EPD together with hydrothermal treatment has been described here and FAU type zeolite self-supported dense and continuous membranes successfully fabricated. It was found that the FAU precursor membranes prepared by EPD were densified in the hydrothermal treatment *via* the crystal growth of the seed particles and newly formed particles in the interparticle pores. As-prepared FAU membranes showed high separation for CO_2/N_2, giving a CO_2/N_2 selectivity of 20, by a mechanism of surface diffusion.

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