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Fast Preparation of High-performance Zeolite T Membranes in Fluoride Media

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A high-quality zeolite T membrane was prepared in only 6 h using a fluoride-mediated gel with NaF/SiO_2 ratio of 0.5 on mullite tubes seeded with nanosized zeolite T. The ^{19}F MAS NMR evidence shows that fluorine anion presents in channels as counter ion of cations. Zeolite T membranes synthesized in fluoride media displayed the high flux values of 4.43 and 3.64 $kg\,m^{-2}\,h^{-1}$ with high separation factors of 8200 and 2900 toward 10 wt % water/isopropanol and 10 wt % water/ethanol mixtures at 348 K, respectively.

Zeolite membranes are considered to be promising candidates for application to separation, catalysis, and sensors. Zeolite NaA membranes with excellent pervaporation (PV) performance have been successfully applied for dehydration of some organic solvents on a large scale.[1] However, zeolite NaA membranes are unstable in solution containing even a trace of acid, as well as zeolite FAU membranes because of strong dealumination.[2,3] Zeolite T membranes with Si/Al ratio of 3–4 in framework have good PV performance and are more stable in acid solutions than zeolite LTA and FAU membranes.[4–6] Only a few studies on the preparation of zeolite T membranes have been so far reported. Cui et al.[4] synthesized randomly oriented zeolite T membranes on seeded mullite supports using 2–4 µm zeolite T crystals for a long synthesis time of 30 h. Zhou et al.[5] reported the preparation of *a* and *b*-oriented zeolite T membrane due to the induction effect of an *a* and *b*-oriented zeolite T seed layer with particle size of about 8 µm. It has also been reported that seed size had a great effect on the growth of zeolite membranes and that nanosized seed layer normally improved the formation of zeolite membrane with few defects.[7,8]

It is well known that the addition of fluoride into the starting gel favors the crystallization of high-silica zeolites as a mineralizing agent and/or a structure-directing agent. Oriented zeolite MFI[9] and β[10] membranes were prepared in fluoride media on seeded alumina support and stainless steel mesh, respectively. Tavolaro et al.[11] reported the in situ hydrothermal synthesis of a vanadium-containing silicalite-1 film from a fluoride-containing mixture. Few studies, however, reported the preparation and especially the role and location of F^- ion in view of low-silica zeolite using fluoride-mediated gels. In the present study, we first prepared zeolite T membranes using NaF-containing gels on seed tubes with nanosized zeolite T seeds. The addition of fluoride played a surprisingly positive effect on both crystallization rate and separation performance of the membrane. The role and location of F^- ion were also clarified briefly.

Zeolite T membranes were prepared on 10-cm-length porous mullite tubes with average pore size of 1 µm and porosity of 43% (Nikkato Corp.). A fluoride-containing gel was obtained by mixing colloidal silica (SM-30, 30 wt % in water, Aldrich), $Al(OH)_3$ (Wako), NaOH (96 wt %, Aldrich), NaF (99 wt %, Aldrich) and deionized water under vigorous stirring for 1 h and aging for 24 h at room temperature. The molar composition of resultant solution was $1SiO_2{:}0.05Al_2O_3{:}0.26Na_2O{:}0.09K_2O{:}(0–1)NaF{:}35H_2O$. The tubes were polished with SiC sandpaper, washed, and dried. Before hydrothermal synthesis, the tubes were rub-coated with a water slurry of nanosized zeolite T powder. The spherical seeds of 80–200 nm in diameter were prepared with TMAOH as template under relatively low synthesis temperature of 358 K. The detailed preparation procedure of nanosized seeds and seeded support are described in Supporting Information.[15] The seeded tubes were then vertically placed in an autoclave holding 300 mL of synthesis gel. The crystallization was carried out at 423 K for a certain period (Table 1). After the synthesis, samples were washed carefully with hot deionized water and dried at 373 K for 6 h. For the study of the location of F^- ion in the crystal, zeolite T powder was in situ prepared with a fluoride-containing gel with a composition of $1SiO_2{:}0.05Al_2O_3{:}0.26Na_2O{:}0.09K_2O{:}0.5NaF{:}35H_2O$ at 423 K for 3 d.

Zeolite membranes were verified by X-ray diffraction (XRD) (Advance D8, Bruker) with Cu Kα radiation. The morphology and thickness of the membranes were characterized by field emission scanning electron microscopy (FE-SEM) (Quanta 200F, FEI). ^{19}F MAS NMR spectra were recorded using a spectrometer (Advance III 400 WB, Bruker) at 376.4 MHz. The spectra were accumulated with 4 µs pulses, 20 s recycle delay, and 1024 scans. $CFCl_3$ was used as chemical shift reference. PV performance test toward 10 wt % water/alcohols mixtures was carried out at 348 K using a PV experimental apparatus described elsewhere.[12]

Table 1. PV performance of zeolite T membranes prepared with different NaF/SiO_2 ratio

Membr. No.	NaF/SiO_2 ratio	Time/h	PV performance[a]	
			$Q/kg\,m^{-2}\,h^{-1}$	$\alpha_{A/B}$
T-1	0	16	2.80	2000
T-2	0.1	10	4.30	1850
T-3	0.3	6	4.10	1950
T-4	0.5	6	4.43	8200
T-5	0.5	10	2.90	600
T-6	0.8	4	4.45	2560
T-7	1.0	4	4.80	3700

[a]PV: 10 wt % water/isopropanol mixture at 348 K.

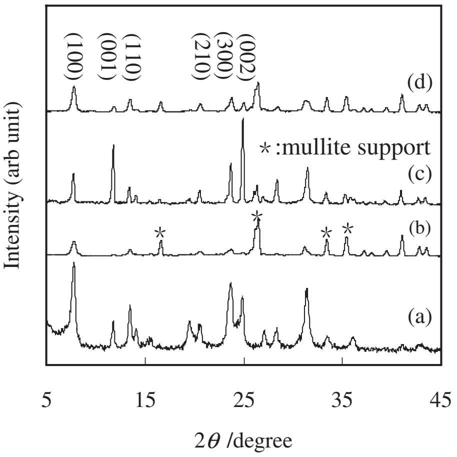

Figure 1. XRD patterns for (a) nanosized seeds, (b) seeded mullite support, (c) membrane T-1, and (d) membrane T-4.

Figure 1 shows the XRD patterns of seeds, seeded support, and zeolite T membranes T-1 and T-4. The synthesis conditions are also shown in Table 1. It was seen that both as-synthesized membranes had the zeolite T structure. And the membrane T-1 prepared from fluoride-free gels showed a stronger orientation along *c* axis than membrane T-4.

Figure 2 shows surface and cross-sectional FE-SEM images of zeolite T membranes prepared in fluoride-containing and fluoride-free media. The FE-SEM surface image (Figure 2a) revealed that zeolite T layer (T-1) prepared from fluoride-free gel at 423 K for 16 h had column-like crystals of 0.1–0.5 µm in diameter. The cross-sectional image (Figure 2b) showed the column-like crystal top layer with thickness of about 6 µm vertically grown upon seeded mullite outsurface. Zeolite T membrane T-4 prepared from fluoride-derived gel for only 6 h of hydrothermal treatment at 423 K consists of agglomerative needle-like particles judged from its surface FE-SEM image (Figure 2c). The FE-SEM cross-sectional image of zeolite T membrane (Figure 2d) showed that the membrane T-4 has a thinner top zeolite T layer with about 3 µm in thickness upon an about 5 µm seed layer. Figures 2e and 2f showed membrane T-5 obtained from fluoride-containing gel for a prolonged synthesis time of 10 h had a thick oriented top layer similar to membrane T-1, but its surface is rough compared with membrane T-1 and T-4.

Figure 3 shows the ^{19}F MAS NMR spectra of zeolite T powder by in situ hydrothermal synthesis from fluoride-containing gel. It was found that only one peak was observed at ca. -122.72 ppm in its MAS NMR spectrum. Lu et al.[13] reported that a high-silica mordenite from the starting gel with NaF showed only one peak at ca. -72 ppm in the spectrum, which was assigned to the presence of NaF as inclusions between the domains due to the spectrum corresponding with that of pure NaF. In our system, the peak at ca. -122.72 ppm is presumably due to the presence of the F^- counter ion of cations such as Na^+ and H^+ in the channels[14] because of the low-silica zeolite T permitting a relatively high density of cations in channel and cage. Fluoride as a mineralizing agent is known to easily bond with Si as SiF_6^{2-}, and SiF_6^{2-} undergoes hydrolysis as follows:[14]

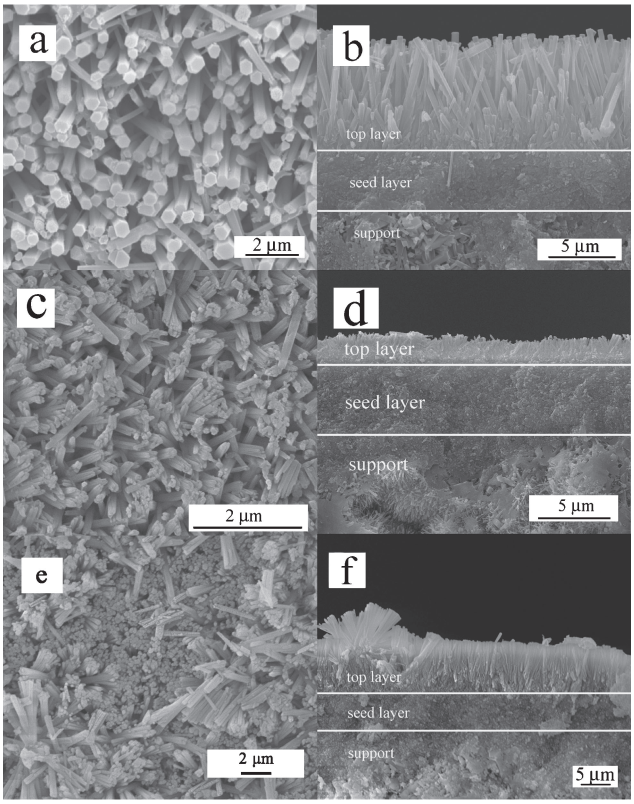

Figure 2. FE-SEM surface and cross-sectional photographs of (a) and (b) membrane T-1, (c) and (d) membrane T-4, and (e) and (f) membrane T-5.

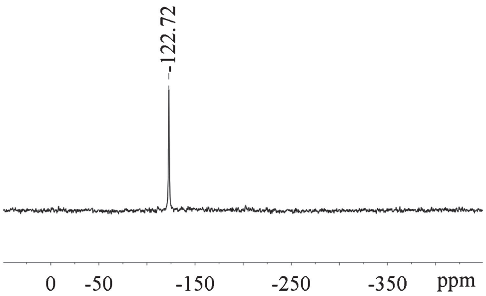

Figure 3. ^{19}F MAS NMR spectra of zeolite T powder by in situ hydrothermal synthesis.

$$SiF_6^{2-} + H_2O \rightleftharpoons Si(OH)_4 + 6F^- + 4H^+ \ (K_d \approx 10^{-30}) \quad (1)$$

The reaction is strongly shifted to the right when pH becomes higher than 7. In our system, fluoride as free F^- ion exists in the gels with strong alkalinity. During the nucleation, F^- ion probably presents among the silicate and aluminate hydrates and then enters the "center" of nuclei as counter ion when the hydrates are condensed. Finally, F^- ion exists in the channels (pores) of crystals when the nucleation and crystal growth further continues.

Table 1 shows PV performance of zeolite T membranes as a function of NaF/SiO_2 ratio. The synthesis time decreased with the increase of added amount of NaF. Zeolite T membranes from NaF-mediated gel under optimized synthesis time showed

Table 2. PV performance of zeolite T membranes toward 10 wt % water/organics mixtures at 348 K

Support	Water/Organics	PV performance		Ref
		Q/kg m^{-2} h^{-1}	$\alpha_{A/B}$	
Mullite	Water/isopropanol	4.43	8200	This work
	Water/ethanol	3.64	2900	
Mullite	Water/isopropanol	2.20	8900	4
	Water/ethanol	1.10	900	
α-Al_2O_3	Water/isopropanol	2.15	10000	5
	Water/ethanol	1.77	1116	
Mullite	Water/isopropanol	1.77	10000	6
	Water/ethanol	1.25	2200	

normally a higher flux than that prepared using fluoride-free gel. Membrane T-4 prepared with NaF/SiO_2 ratio of 0.5 had the high flux of 4.43 kg m^{-2} h^{-1} and high separation factor of 8200 toward a 10 wt % water/IPA mixture at 348 K. Membrane T-5 prepared for a prolonged synthesis time of 10 h showed similar layer thickness to membrane T-1 from their FE-SEM images (Figure 2); however, it had the low separation factor of 600 because defects are easily formed by crystal overgrowth. The high PV performance of zeolite T membrane prepared in fluoride media under optimized synthesis time is probably ascribed to the effect of fluoride. The mineralizing of fluoride supplies higher concentration of silicate and aluminate, which accelerates preferentially the nucleation and crystal growth, occurred upon the seeded support. The more nuclei produce more crystals with out-of-plane growth and form a needle-like array vertical with respect to support surface. As a result, a thin and compact top layer could be formed in a short time, as shown in Figures 2c and 2d.

Table 2 shows PV performance of water/organics through zeolite T membranes. Zeolite T membranes prepared from a concentrated gel with H_2O/SiO_2 ratio of 16 had a good water-selectivity toward water/organic mixtures.[4] Zhou et al.[5] announced a microwave-assisted hydrothermal technique for the synthesis of zeolite T membrane using the gel composition similar to the former and obtained a good-quality membrane for a short time of 9 h. In our previous investigation,[6] we prepared zeolite T membranes with good PV performance using a diluted gel with H_2O/SiO_2 ratio of 25 for 40 h of hydrothermal treatment at 423 K. In this work, we introduced NaF to the more diluted synthesis gel with H_2O/SiO_2 ratio of 35 and achieved high-performance zeolite T membranes by secondary growth with nanosized seeds for only 6 h. This membrane shows the highest flux of 3.64 kg m^{-2} h^{-1} together with the highest separation factor of 2900 toward a 10 wt % water/ethanol mixture at 348 K in contrast with these membranes reported in the literature.[4–6]

In conclusion, we have shown a novel and fast synthesis method of high-performance zeolite T membranes in fluoride media. The crystallization rate and formation quality of zeolite T membranes were greatly improved by fluoride species. The membrane prepared with NaF/SiO_2 ratio of 0.5 had the highest ethanol/water flux of 3.64 kg m^{-2} h^{-1} together with the highest separation factor of 2900 for a 10 wt % water/ethanol mixture at 348 K to date.

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