

Electronic Supplementary information

Self-defect-healing of silicalite-1 membrane in alkaline aqueous solution with surfactant

*Motomu Sakai,^{*a} Hayata Hori^b and Masahiko Matsukata^c*

^aResearch Organization for Nano & Life Innovation, Waseda University, 513 Wasedatsurumaki-cho, Shinjuku-ku, Tokyo 162-0041, Japan.

^bDepartment of Applied Chemistry, Waseda University. 513 Wasedatsurumaki-cho, Shinjuku-ku, Tokyo 162-0041, Japan.

^cAdvanced Research Institute for Science and Engineering, Waseda University, 513 Wasedatsurumaki-cho, Shinjuku-ku, Tokyo 162-0041, Japan.

*saka.moto@aoni.waseda.jp

Experimental Procedures

Preparation procedure of Na-*BEA, Na-ZSM-5 and Na-MOR membranes

Three types of membranes were synthesized by secondary-growth method without using organic structure-directing agent. Each seed crystal was loaded on an outer surface of tubular α -alumina support by a dip-coating technique. Hydrothermal treatments were carried out for each seeded support under given conditions. For Na-*BEA membrane, hydrothermal treatment was taken place at 393 K for 7 days with a synthesis solution having the composition of $100\text{SiO}_2:1\text{Al}_2\text{O}_3:30\text{Na}_2\text{O}:2000\text{H}_2\text{O}$. Na-ZSM-5 membrane was synthesized at 453 K for 12 h with a synthesis solution having the composition of $240\text{SiO}_2:1\text{Al}_2\text{O}_3:53\text{Na}_2\text{O}:8000\text{H}_2\text{O}$. For Na-MOR membrane, hydrothermal treatment was carried out at 453 K for 6 h with a synthesis solution having the composition of $240\text{SiO}_2:1\text{Al}_2\text{O}_3:67\text{Na}_2\text{O}:6400\text{H}_2\text{O}$. After hydrothermal synthesis, grown membranes were washed with boiling water for several hours. After drying for washed membranes at 373 K overnight, Na-*BEA, Na-ZSM-5 and Na-MOR membranes were finally obtained.

Details of preparation procedures were shown in elsewhere.^{1,2}

Results and Discussion

Reproducibility of alkaline-treatment with surfactant for silicalite-1 membrane

Separation test was performed to four silicalite-1 membranes to confirm a reproducibility of the alkaline-treatment with surfactant. Preparation and alkaline-treatment procedures for the four membranes were exactly the same. Table ES1 lists the membrane performances before and after alkaline-treatment. Separation factors through all membranes increased and serious decrease in permeance hardly occurred.

Alkaline-treatment with surfactant for Na-*BEA, Na-ZSM-5 and Na-MOR-type zeolite membranes

Alkaline-treatment was carried out for Na-*BEA, Na-ZSM-5 and Na-MOR-type zeolite membranes. Separation performance for Methanol/ CO_2 (10/90 kPa) mixture through Na-ZSM-5 membrane was evaluated at 473 K. Separation performance for an equimolar mixture of H_2O /isopropyl alcohol through Na-*BEA and Na-MOR membranes at 373 K were evaluated. Table ES2 shows relative permeances and relative separation factors of these membranes. All relative separation factors through Na-*BEA, Na-ZSM-5 and Na-MOR membranes increased by the post-treatment, suggesting that the novel defect-healing technique was effective for not only silicalite-1 but also other types of zeolite membranes.

Morphological change by the alkaline treatment by using NaOH and CTAB

Fig. ES3 shows the enlarged view of FE-SEM images of silicalite-1 membrane treated by NaOH and CTAB for (a), (b), (c) and (d) 15 min and (e), (f), (g) and (h) 70 min. Fig. ES3 (a), (c), (e) and (g) are the same images as Fig.2(c), (d), (e) and (f) in the manuscript, respectively. Fig. ES3 (b), (d), (f) and (h) are other views of Fig.2(c), (d), (e) and (f) in respectively. The partial dissolution of seed crystal was able to be observed in Fig. ES3 (c) and (d) indicated by blue arrowheads. Seed crystals pointed by blue arrows became hollow structure by the alkaline-treatment. We consider that silica leached from the seed crystal may contribute to heal defects in silicalite-1 membrane. After 70-min treatment, cracks

were clearly visible on the surface of silicalite-1 membrane as shown in Fig. ES3 (e) and (f) indicated by red arrowheads.

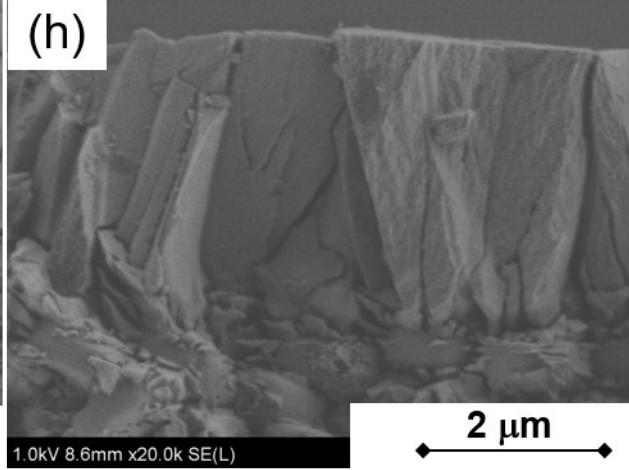
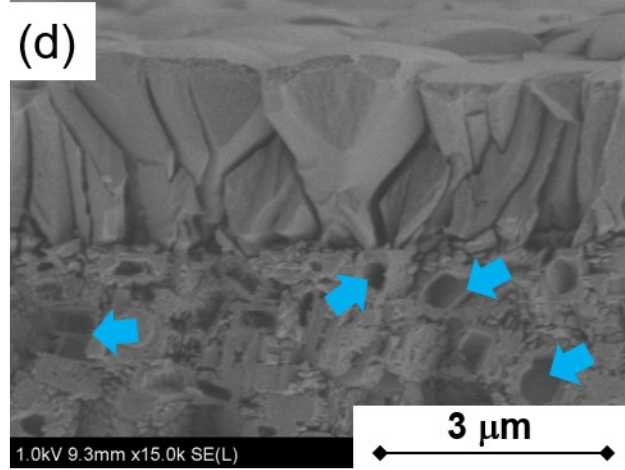
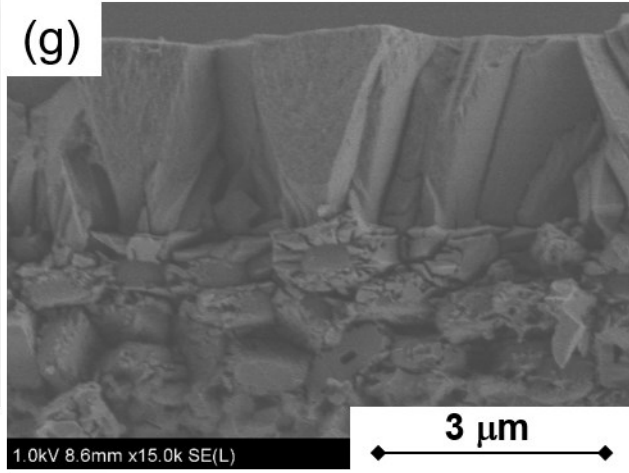
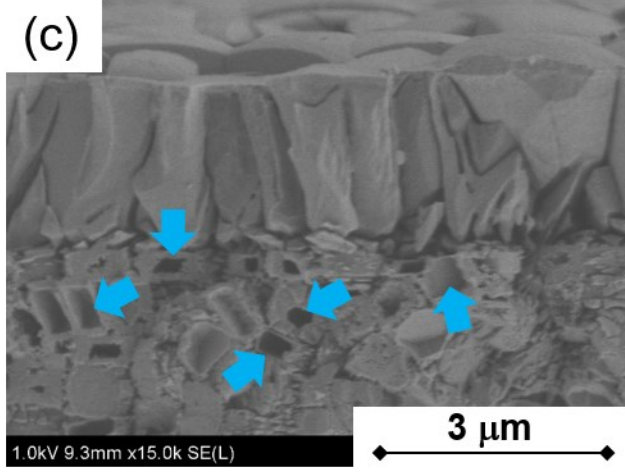
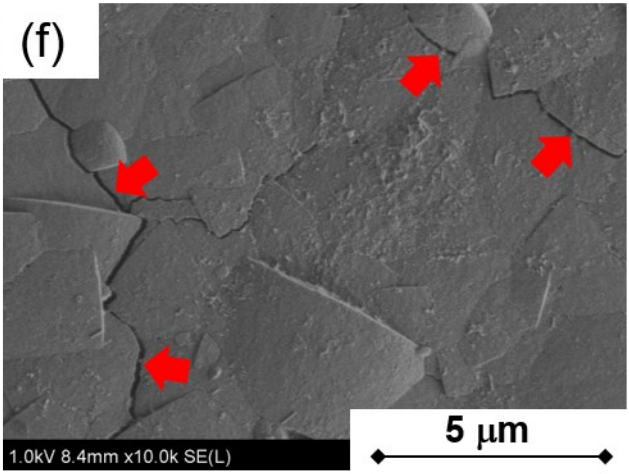
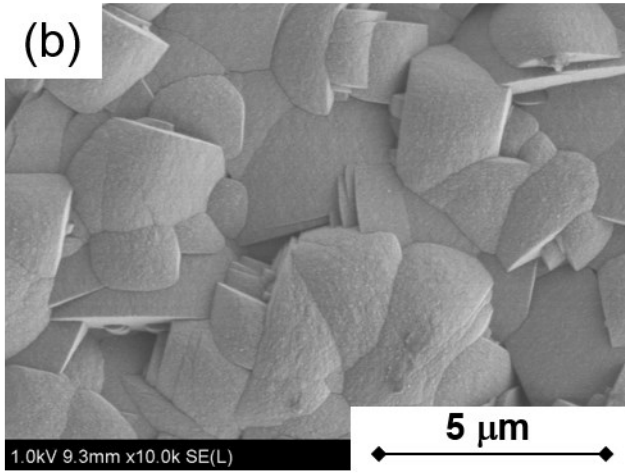
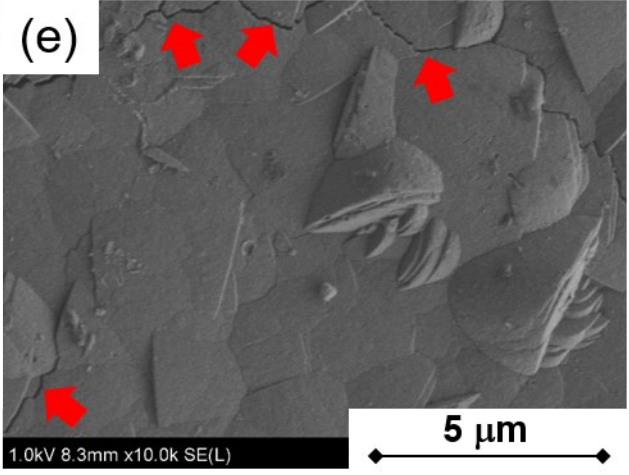
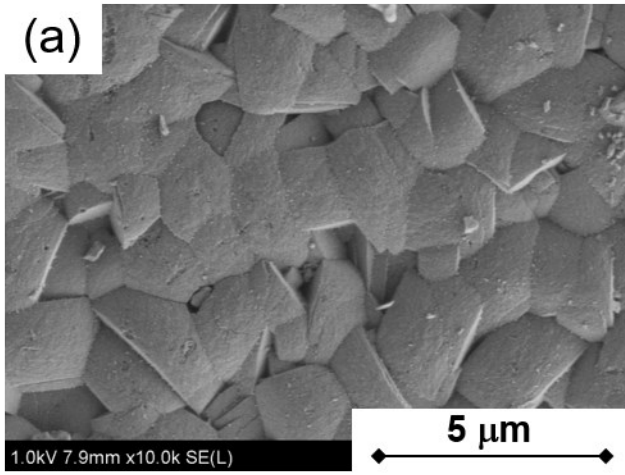
Table ES1. Permeation and separation property at 573 K in each alkali-treated membrane

Membrane	Permeance / $\times 10^{-8} \text{ mol m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$				Separation factor / -	
	Parent		After treatment (15 min)		Parent	After treatment (15 min)
	<i>n</i> -Hex	2,3-DMB	<i>n</i> -Hex	2,3-DMB		
1	6.60	0.0740	6.44	0.0205	89.2	314
2	5.69	0.0789	5.04	0.0216	72.1	233
3	5.49	0.119	5.32	0.0162	46.1	328
4	6.19	0.243	5.47	0.109	25.5	50.2

Table ES2. Relative permeances and separation factors of Na-*BEA, Na-MOR and Na-ZSM-5 membrane.

Membrane	System	Relative permeance / %	Relative separation factor / %
Na-*BEA	H ₂ O/isopropyl alcohol = 45/55 kPa at 383 K	93.2	442
Na-MOR	H ₂ O/isopropyl alcohol = 45/55 kPa at 383 K	80.6	211
Na-ZSM-5	MeOH/CO ₂ = 10/90 kPa at 473 K	104	127

Figure ES3. FE-SEM images silicalite-1 membrane treated by NaOH and CTAB for (a), (b), (c) and (d) 15 min and (e), (f), (g) and (h) 70 min. (a), (b) (e) and (f) are membrane surface. (c), (d), (g) and (h) are cross-section of membrane.



References

- [1] M. Sakai, N. Fujimaki, G. Kobayashi, N. Yasuda, Y. Oshima, M. Seshimo and M. Matsukata, *Microporous Mesoporous Mater.*, 2019, **284**, 360.
- [2] G. Li, E. Kikuchi and M. Matsukata, *Microporous Mesoporous Mater.*, 2003, **62**, 211.