

Synthesis of Highly Acid-Resistant ZSM-5 Zeolite Membranes for Membrane Separation of Biomass Ethanol

Xiansen Li, Hidetoshi Kita*, Kazuhiro Tanaka

Department of Advanced Materials Science and Engineering, Faculty of Engineering,
Yamaguchi University, Tokiwadai 2-16-1, Ube, Yamaguchi 755-8611
Tel. and Fax: 81-836-85-9661, E-mail: kita@yamaguchi-u.ac.jp

The effect of preparative conditions for aluminum-rich ZSM-5 membranes from SDA-free precursor gel upon the pervaporation (PV) separation properties was studied. The products synthesized were characterized by XRD, FE-SEM and ICP analyses. Under the optimized conditions, ZSM-5 membranes obtained were demonstrated to be fairly efficient for the dehydration of different organic aqueous solutions. Furthermore, long-term tests for acid stability showed that ZSM-5 membranes displayed a reasonably high acid resistance. Comparative study in terms of acid stability was carried out between MOR- and MFI-type zeolite membranes.

Key words: ZSM-5 zeolite membrane, pervaporation, acid stability, SDA-free synthesis

1. INTRODUCTION

The efficient production of bioethanol by yeast fermentation of renewable biomass for application as an alternative liquid fuel is becoming extremely important from a global environmental protection viewpoint. Because innovative alternatives to conventional distillation have not yet been established, nowadays, distillation is still widely used to refine low-concentration bioethanol. However, after distillation, the concentrated bioethanol from fermentation broths generally contains a given amount of volatile carboxylic acids. Some extra purification steps have to be required because absolutely anhydrous ethanol is desirable to be massively manufactured by this biotreatment route.

It has previously been demonstrated that zeolite A membranes have a very high selectivity for water over alcohols [1]. However, a major drawback of zeolite A membranes is their acid-sensitivity. One solution to this problem is the use of an acid-resistant zeolite, such as ZSM-5. Our findings here corroborate that hydrophilic and robust ZSM-5 membranes are almost inert to carboxylic acid attack. Due to the concern about production cost and post waste disposal, it is strongly desirable to prepare ZSM-5 zeolite membranes in the media involving very expensive tetrapropylammonium (TPA⁺) cations' quantity as low as possible or at the absence of TPA⁺ cations as structure-directing agent (SDA).

Although a few papers [2-6] have presented the template-free synthesis of ZSM-5 membranes, the results in the literature have almost exclusively concentrated on ZSM-5 membranes statically prepared in hydroxide media. More importantly, no data on the long-term acid stability of hydrophilic ZSM-5 membranes could be available.

Moreover, the pervaporation performance of the resultant ZSM-5 membranes was not high enough for the potential industrial applications. In this report, ZSM-5 membranes were hydrothermally prepared without SDA onto 10-cm-long tubular mullite supports by seeding method in order to develop highly acid-resistant zeolite membranes applicable for dehydration of acid-containing solution.

2. EXPERIMENTAL

ZSM-5 membranes were hydrothermally prepared onto 10-cm-long tubular mullite supports (12 mm o.d., 1.5 mm thickness and 1.3 μm average pore size). Before synthesis, the outer surface of mullite tube was simply rubbed with water slurry of ZSM-5 crystal seeds. Then the seeded support was dried at 80 °C for several hours. The synthetic recipe was altered based on the molar composition of SiO₂: (0.0125-0.067)Al₂O₃: (0.201-0.0375)Na₂O: NaF: 50H₂O. To examine the effect of alumina source, three types of alumina sources were used, such as AlCl₃·6H₂O, Al₂(SO₄)₃·14-18H₂O and Al(NO₃)₃·9H₂O, whereas precipitated silica (abbreviated as PS hereafter) alone was chosen as silica source to minimize the production cost. Herein, NaF and NaOH were utilized as the co-mineralizing agents. The hydrothermal crystallization was conducted at 180 °C with rotating at 37.5-50 rpm for 3 days. After hydrothermal reaction, the sample was recovered, washed with hot water and air dried at 100 °C overnight for further measurements.

XRD patterns of the membranes and powders were recorded on a Rigaku RINT 2200YS X-ray diffractometer. The bulk SiO₂/Al₂O₃ ratios of the concomitant pure-phase ZSM-5 powders of some representative zeolite membranes were determined by ICP-AES analysis (Perkin-Elmer Optima 4300DV

Spectrometer). The surface and cross-sectional morphologies of ZSM-5 membranes were observed using an FE-SEM microscopy (JEOL 6335F).

3. RESULTS AND DISCUSSION

Without TPA⁺ cations, the crystallization regime of MFI-type zeolites was restricted to a narrow window of gel Si/Al ratio, with the Si/Al ratio generally in the range of 20-90 [7]. In this work, an attempt was made to lower the Si/Al ratio of the starting gel down to as low as ca. 7.5, aiming to incorporate more amounts of aluminum species into zeolite framework. Fig. 1 showed the

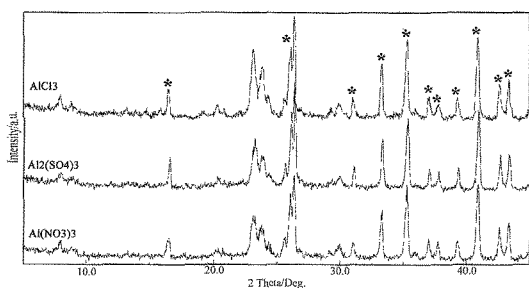


Fig. 1. XRD patterns of ZSM-5 membranes prepared with different Al sources.

(SiO₂: 0.067Al₂O₃; 0.201Na₂O; NaF: 50H₂O, 180 °C, 37.5 rpm, 3 d, PS; *: mullite phase)

XRD patterns of zeolite membranes prepared with different alumina sources. As revealed in Fig. 1, other than the peaks corresponding to MFI and mullite structures, other crystalline impurity phase could be identified from the XRD profiles of three composite membranes. Well-defined XRD profiles assigned to typical MFI structure suggested good crystallinities of the constituent crystals in the membrane layers. Therefore, in the absence of organic SDA, the unprecedentedly low gel Si/Al ratio adopted here was practicable for development of highly hydrophilic ZSM-5 membranes. By comparing the relative intensity of ZSM-5 peaks, it was concluded that ZSM-5 crystals in all of the membranes were aligned in a random orientation mode.

Fig. 2 showed an example of FE-SEM images of ZSM-5 membranes prepared. The surface image of ZSM-5 membranes revealed that numerous aggregated microrods of ca. 1 μm in length were grown on the mullite supports. Interestingly, the crystal morphologies shown in Fig. 2 were sharply distinct from hexagonal prism,

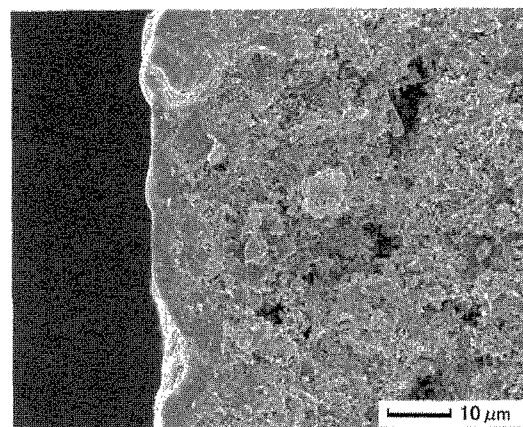
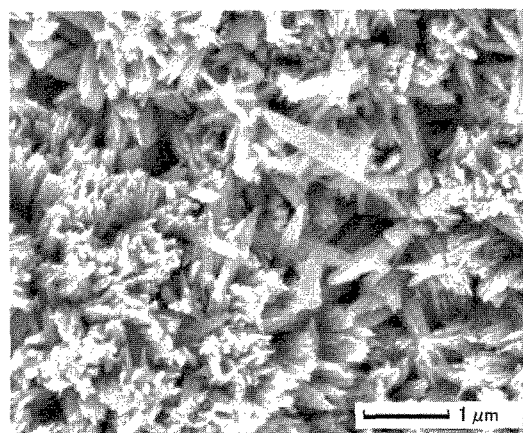


Fig.2 FE-SEM surface and cross-sectional photographs of Al₂(SO₄)₃-based ZSM-5 membranes. Same synthesis conditions as in Fig.1

characteristic of the shape of the crystals synthesized in TPA⁺-containing media. From the cross-sectional image in Fig. 2, there existed a compact top layer with a thickness of about 10 μm. Furthermore, the penetration of ZSM-5 crystals into the support made it difficult to discriminate the interface between mullite support and ZSM-5 top layer.

PV performances through ZSM-5 membranes prepared with different alumina sources were respectively summarized in Tables I. ZSM-5 membranes prepared with Al₂(SO₄)₃·14-18H₂O and Al(NO₃)₃·9H₂O as alumina sources were highly water-selective along with a large total permeation flux, whereas AlCl₃·6H₂O-derived

Table I. PV performance of ZSM-5 membranes prepared with different alumina sources for 10 mass% H₂O/EtOH mixture at 75 °C (Same synthetic conditions as in Fig. 1)

Alumina source	Si/Al of bulk powders [ICP analysis]	Permeate [mass%]	Flux [kg/(m ² ·h)]	α
AlCl ₃ ·6H ₂ O	8.46	77.69 H ₂ O	0.67	32
AlCl ₃ ·6H ₂ O	8.46	85.34 H ₂ O	0.70	52
Al ₂ (SO ₄) ₃ ·14-18H ₂ O	Amorphous/MFI	98.18 H ₂ O	1.48	540
Al ₂ (SO ₄) ₃ ·14-18H ₂ O	Amorphous/MFI	95.91 H ₂ O	1.30	240
Al(NO ₃) ₃ ·9H ₂ O	7.21	94.92 H ₂ O	0.93	190

membranes exhibited a moderate separation performance. Currently, the exact reason for this issue remained unclear. It is likely due to the fact that both sulfates and nitrates are ionically bound to the Al in contrast to AlCl_3 with more covalent than ionic Al-Cl linkages. The maximum selectivity reached 540 with accompanying flux as high as $1.48 \text{ kg}/(\text{m}^2\cdot\text{h})$ for separation of 90 mass% EtOH aqueous solution at 75°C . Moreover, a separation factor of 920 was achieved for $\text{H}_2\text{O}/\text{AcOH}$ mixture with 50 mass% water in the feed at 75°C . Meanwhile, rather high total flux of $3.64 \text{ kg}/(\text{m}^2\cdot\text{h})$ was measured (not shown). To our knowledge, ZSM-5 membranes with such high PV performance have not been previously reported to date. The unprecedentedly low Si/Al ratio of the starting gel (ca. 7.5) adopted here was expected to incorporate more amounts of aluminum into zeolitic framework, thereby strengthening the hydrophilicity of ZSM-5 membranes. From ICP results shown in table I, it is clear that the bulk alumina content of the accompanying powders is in close proximity to that in the feedstock mixture. On the other hand, in addition to the mineralizing effect, it is thought that fluoride ions may play another roles such as charge balance and acting as SDA.

PV performances through ZSM-5 membranes prepared with different gel Si/Al ratios were indicated in table II. With increasing the gel

Table II. PV performance of ZSM-5 membranes prepared at different gel Si/Al ratios for 10 mass% $\text{H}_2\text{O}/\text{EtOH}$ mixture at 75°C

Gel Si/Al	Permeate [mass% H_2O]	Flux [$\text{kg}/(\text{m}^2\cdot\text{h})$]	α
7.5	94.94	0.67	180
12.5	71.15	0.30	23
20	34.72	0.22	5
40	21.15	0.12	3

Si/Al ratio from 7.5 to 12.5, separation factor (α) for 10 mass% $\text{H}_2\text{O}/\text{EtOH}$ mixture declined correspondingly. This is responsible for a reduction in hydrophilicity of ZSM-5 zeolites as silicon content increases in the zeolitic framework. In particular, the total permeation flux exhibited a remarkable drop with increasing gel Si/Al ratio. In more siliceous synthesis media, the ZSM-5 membranes with poor separation performances resulted, suggesting an important contribution of the starting gel Si/Al ratio to the membranes' separation behaviors. Presently, the premise that the gel Si/Al ratio of 7.5 constitutes a lower bound value seems to be true. In a synthesis batch at Si/Al ratio of 5.5, an attempt to prepare high-quality ZSM-5 membranes failed. Figure 3 shows XRD patterns of ZSM-5 membranes prepared with different gel Si/Al ratios. The intensities of h0h peaks (e.g., 101 peak at $2\theta=7.95^\circ$ position and 303 at 23.99°) was gradually becoming dominant with increasing gel Si/Al ratio. At the starting gel Si/Al ratio of 40, h0h was relatively the strongest peaks in the

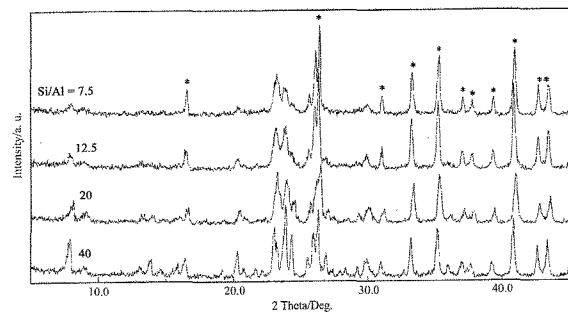


Fig. 3. XRD patterns of ZSM-5 membranes prepared with different gel Si/Al ratios. (SiO_2 : $x\text{Al}_2\text{O}_3$: $0.201\text{Na}_2\text{O}$: NaF : $50\text{H}_2\text{O}$, 180°C , 37.5 rpm, 3 d, $\text{Al}_2(\text{SO}_4)_3\cdot 14-18\text{H}_2\text{O}$, PS; *: mullite phase)

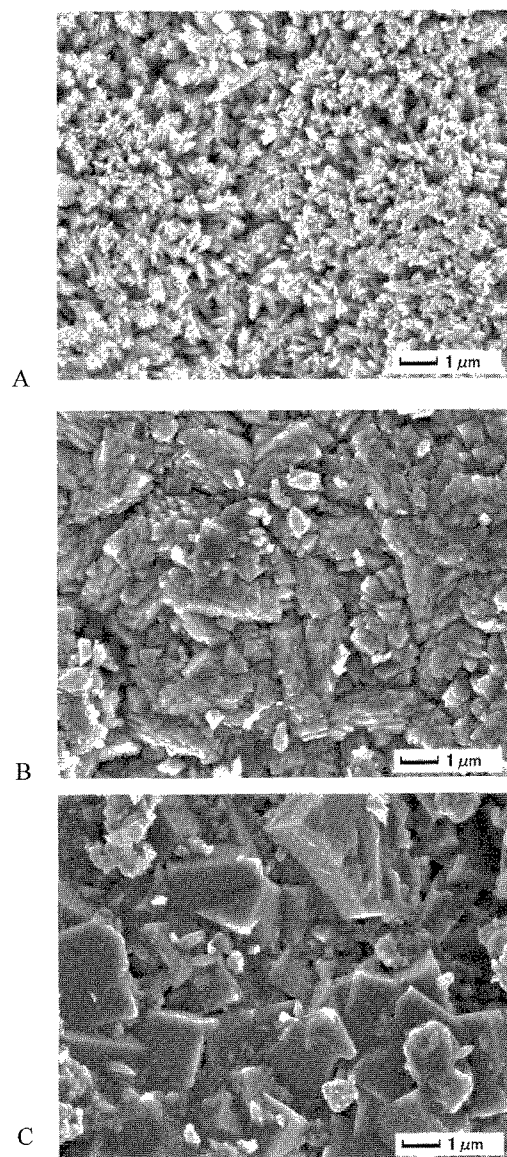


Fig. 4 FE-SEM surface images of ZSM-5 membranes prepared with the starting gel Si/Al ratios of 12.5(A), 20(B) and 40(C). The same synthetic conditions as in Fig.3

the pattern of Fig. 3, indicating that [h0h] were now the dominant grain orientations. That is, at high silica concentration crystal growth behavior in SDA-free media resembles that observed commonly in TPA⁺-containing ones. Figure 4 shows FE-SEM surface images of ZSM-5 zeolite membranes prepared with the starting gel Si/Al ratios of 12.5, 20 and 40. Sharp crystal morphology change from aggregated needles to monodispersed hexagonal prisms was observed with Si/Al ratio. Acid-proof results for MOR and MFI membranes were given in Table III. The

Table III. Acid stability of MOR and ZSM-5 membranes after immersion in 90 wt. % AcOH aqueous solution for certain periods of time

Phase type	Immersion period	Perm. [mass% H ₂ O]	Flux [kg/(m ² ·h)]	α
MOR	21.5 h	99.75	0.13	355
	50 d	98.08	0.059	460
	77 d	97.99	0.06	440
	415 d	97.91	0.067	400
MFI	14 h	99.47	0.60	167
	32 d	99.09	0.50	980
	98 d	99.02	0.45	890
	327 d	99.00	0.42	720

synthetic details and PV performances of MOR membranes were described on elsewhere [8]. ZSM-5 membranes displayed a reasonably high acid resistance and were almost capable of withstanding long-term harsh treatment with ca. 90 wt. % concentrated AcOH solution under ambient condition. After exposure to 90 mass% AcOH solution for 327 consecutive days, a representative ZSM-5 membrane only showed reductions by 30 % in total permeation flux and by 0.5 % in water permeate concentration. In contrast, at the immersion time of 415 days, the corresponding attenuation percentages for a typical fluoride-based MOR membrane prepared at the same gel Si/Al ratio as ZSM-5 membrane were 48 % and 1.8 %. In conclusion, acid stability of ZSM-5 membranes was superior to that of MOR membranes in concomitance with the former being much more productive than the latter (0.42 vs. 0.067 kg/m²·h). At present, it remains a great challenge for concentration of aqueous AcOH solutions from 90 to above 95 mass% due to acid instability and low productivity of the available membranes. At the AcOH concentration of 90 mass%, the total permeation fluxes reported in the literature through zeolite membrane [9] at 80 °C

and inorganic-organic hybrid membrane [10] at 30 °C were as low as < 0.1 kg/(m²·h), because of the strong association effect between AcOH and H₂O molecules. Consequently, our findings showed that ZSM-5 membranes were fairly suitable for dewatering concentrated AcOH solutions by PV.

4. CONCLUSIONS

Highly hydrophilic ZSM-5 membranes with promising potential for practical applications were successfully prepared in template-free and fluoride-containing media. These membranes were found to have been reasonably chemically stable in relatively low pH circumstances for a sufficiently long time. Therefore, they were well applicable for the dehydration of acidic mixtures such as biomass ethanol and aqueous AcOH. Finally, comparative study showed that higher acid stability and larger productivity was achieved for ZSM-5 membranes against MOR ones.

The present work was partly supported by MAFF project of Bioenergy Conversion and VBL project at Yamaguchi University in Japan.

References

- [1] H. Kita, K. Horii, Y. Tanaka, K. Okamoto, *J. Mater. Sci. Lett.*, 14, 206 (1995).
- [2] J. Hedlund, M. Noack, P. Kölsch, D. Creaser, J. Caro, J. Sterte, *J. Membr. Sci.*, 159, 263 (1999).
- [3] M. Noack, P. Kölsch, J. Caro, M. Schneider, P. Toussaint, I. Sieber, *Micropor. Mesopor. Mater.*, 35-36, 253 (2000).
- [4] R. Lai, G. R. Gavalas, *Micropor. Mesopor. Mater.*, 38, 239 (2000).
- [5] M. Lassinantti, F. Jareman, J. Hedlund, D. Creaser, J. Sterte, *Catal. Today*, 67, 109 (2001).
- [6] G. Li, E. Kikuchi, M. Matsukata, *Micropor. Mesopor. Mater.*, 60, 225 (2003).
- [7] R. Szostak, *Molecular Sieves: Principles of Synthesis and Identifications*, Van Nostrand Reinhold, New York, (1989).
- [8] X. Li, K. Takei, H. Kita, K. Okamoto, K. Itabashi, *Proceedings for the 10th APCChE (Asian Pacific Confederation of Chemical Engineering) Congress*, CD-ROM, 1P-12-003, 2004, Japan.
- [9] G. Li, E. Kikuchi, M. Matsukata, *J. Membr. Sci.*, 218, 185 (2003).
- [10] M. Y. Kariduraganavar, S. S. Kulkarni, A. A. Kittur, *J. Membr. Sci.*, 246, 83 (2005).

(Received January 15, 2006; Accepted March 30, 2006)