

Organotemplate-free synthesis of ZSM-5 membrane for pervaporation dehydration of isopropanol

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Abstract. ZSM-5 membrane was prepared on tubular macroporous α -alumina support using a different synthesis route. The effects of organic template agent and Si/Al ratio of the synthesis gel on morphology, structure, and separation performance of the ZSM-5 membrane used for dehydration of isopropanol were investigated. High water perm-selectivity ZSM-5 membrane with a thickness of about 3.0 μm and a low Si/Al ratio of 10.1 was successfully prepared from organotemplate-free synthesis gel with a molar composition of $\text{SiO}_2 : 0.050\text{Al}_2\text{O}_3 : 0.21\text{Na}_2\text{O} : \text{NaF} : 51.6\text{H}_2\text{O}$ at 175 °C for 24 h. The ZSM-5 membrane exhibited high pervaporation performance with a flux of 3.92 $\text{kg}/(\text{m}^2\cdot\text{h})$ and corresponding separation factor of higher than 10,000 for dehydration of 90 wt.% isopropanol/water mixture at 75°C.

Keywords: Zeolite membrane; dehydration of isopropanol; pervaporation; organotemplate-free synthesis gel; hydrothermal synthesis

1. Introduction

Isopropanol is an important chemical raw material in industrial applications. It is widely used in solvents, chemical intermediates, pharmaceuticals, electronics, daily chemicals, and other applications (Kittur *et al.* 2005, Qiao *et al.* 2005, Bhat and Aminabhavi 2006, Zhang *et al.* 2007). Generally, dehydration of isopropanol is an essential process in the production of isopropanol (Pulyalina *et al.* 2013). Conventional separation techniques for dehydration of isopropanol, such as azeotropic distillation and extractive distillation, have heavy energy consumption and low efficiency. With increasing environmental pollution, energy consumption, and cost, a new and practical technique—namely, membrane separation—has emerged as an indispensable replacement for and/or supplement to the conventional energy-intensive operation used for the separation and purification of organics. This is especially true for the separation of azeotropic, isomeric, and thermosensitive liquid mixtures (Feng and Huang 1997, Lipnizki *et al.* 1999, Chen *et al.* 2013, Diban *et al.* 2013).

In the past two decades, zeolite membranes have been intensively studied. They possess considerable application potential for separation and purification of organics due to their uniform and regular pore size, ordered structure, good thermal/hydrothermal stability, and chemical resistance (Lin *et al.* 2002, Caro and Noack 2008). To date, many attempts

have been made to develop various zeolite membranes, including NaA (Xu *et al.* 2000, Morigami *et al.* 2001, Okamoto *et al.* 2001), NaY (Sato *et al.* 2008, Algieri *et al.* 2009, Premakshi *et al.* 2015), T-type (Cui *et al.* 2004), Mordenite (Lin *et al.* 2000, Li *et al.* 2003, Li *et al.* 2016), ZSM-5 (Gao *et al.* 2013, Yang *et al.* 2014, Li *et al.* 2015, Li *et al.* 2016), and Silicalite-1 (Bakker *et al.* 1996, Chen *et al.* 2007, Choi *et al.* 2009) membranes for the separation and purification of organics.

Among the various types of zeolite membranes, the ZSM-5 membrane, which has a unique channel structure, good shape selectivity, and high thermal and acid stability, has attracted extensive attention for the separation and purification of organics. Notably, the ZSM-5 membrane possesses a wide and adjustable Si/Al ratio range, from 3 to infinity, which can regulate the hydrophilicity of the membrane layer. The pore sizes (5.3 Å \times 5.6 Å and 5.1 Å \times 5.5 Å) of this membrane are close to the kinetic diameter of many organic molecules (e.g., the kinetic diameter of isopropanol is 4.7 Å) used in industrial applications (Chen *et al.* 2014). These characteristics make the ZSM-5 membrane a potential candidate for the dehydration of isopropanol.

It is well known that ZSM-5 zeolite membranes are often prepared using tetrapropylammonium hydroxide or tetrapropylammonium bromide as organic template agents (Noack *et al.* 2005, Korelskiy *et al.* 2013). However, after hydrothermal crystallization is complete, the organic template agent is retained in the pore structure of the membrane layer to block the pores. Therefore, it is usually necessary to use high-temperature calcination to remove the organic template agent from the pore structure. However, cracks and other defects tend to appear in the original

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continuous dense membrane caused by the removal of the organic template agent via the high-temperature calcination procedure because of the different extents of thermal expansion between the support and the membrane and/or the changes in lattice parameters of the crystals. This results in the deterioration of the separation performance of the ZSM-5 membrane.

In contrast, the preparation of ZSM-5 zeolite membranes using an organotemplate-free route can effectively avoid the cracks and other defects from appearing during the subsequent high-temperature calcination procedure. Since the successful development of a continuous thin ZSM-5 film on quartz substrate by Mintova *et al.* (1998), organotemplate-free synthesis of the ZSM-5 membrane has attracted considerable attention (Noack *et al.* 2000, Li *et al.* 2003, Tang *et al.* 2009, Zhu *et al.* 2012, Gao *et al.* 2013). Therefore, this study investigates the preparation of a hydrophilic ZSM-5 membrane without an organotemplate. Moreover, to increase potential practical applications, it is important to understand which synthesis route is more conducive to isopropanol dehydration by the ZSM-5 membrane. Thus, the effects of the organic template agent and Si/Al ratio of the synthesis gel on membrane morphology, structure, and separation performance of the ZSM-5 membrane used for dehydration of isopropanol were systematically investigated in this work.

2. Experiment

2.1 Preparation of ZSM-5 membrane

ZSM-5 membrane was prepared on a tubular macroporous α -alumina support (length = 50 mm, outer diameter = 12 mm, inner diameter = 8 mm, average pore diameter = 2–3 μm , Foshan Ceramics Research Institute) using hydrothermal secondary growth. An effective seeding method, namely variable temperature dip coating, was applied to deposit a uniform and thin ZSM-5 seed layer on the outer surface of the tubular macroporous α -alumina support. Commercially available ZSM-5 crystalline powders (Si/Al ratio = 15, average diameter = $\sim 1.5 \mu\text{m}$, Shanghai Zhuoyue Chemical Co., Ltd) were used as large seeds. Crushed submicrometer ZSM-5 crystalline powders obtained through the ball-milling method were used as small seeds. These seeds were mixed with an appropriate amount of deionized water to form 3.0 wt.% and 0.2 wt.% suspensions, termed as large and small seed suspensions, respectively. The typical seeding process was as follows. For the intermediate seeded support, the tubular support, with both ends sealed, was preheated at 175 $^{\circ}\text{C}$ for ~ 30 min, dipped into the 3.0 wt.% large seed suspension for 25 s, and dried at 80 $^{\circ}\text{C}$ for 3 h. Then, the outer surface of the seeded support was gently wiped to remove loose and superfluous crystals using clean cotton wool. To obtain the final seeded support, the intermediate seeded support was preheated at 80 $^{\circ}\text{C}$ for above 2 h, dipped into the 0.2 wt.% small seed suspension for 20 s, and dried at 80 $^{\circ}\text{C}$ for 2 h. It was then calcined at 550 $^{\circ}\text{C}$ for 6 h to significantly improve adhesion of the ZSM-5 seed crystals to the α -alumina support before hydrothermal secondary growth.

Table 1 Conditions used during membrane fabrication

Sample No.	Molar composition of the synthesis solution	(Si/Al) _{gel} ratio*
Z1	SiO ₂ :0.039Al ₂ O ₃ :0.21Na ₂ O:NaF:51.6H ₂ O	12.8
Z2	SiO ₂ :0.039Al ₂ O ₃ :0.21Na ₂ O:NaF:51.6H ₂ O:0.14T PAOH	12.8
Z3	SiO ₂ :0.039Al ₂ O ₃ :0.21Na ₂ O:NaF:51.6H ₂ O:0.14T PABr	12.8
Z4	SiO ₂ :0.030Al ₂ O ₃ :0.21Na ₂ O:NaF:51.6H ₂ O	16.7
Z5	SiO ₂ :0.043Al ₂ O ₃ :0.21Na ₂ O:NaF:51.6H ₂ O	11.6
Z6	SiO ₂ :0.050Al ₂ O ₃ :0.21Na ₂ O:NaF:51.6H ₂ O	10.0

*(Si/Al)_{gel} ratio: Si/Al ratio of the synthesis gel.

The final seeded support was vertically placed in a PTFE-lined stainless steel autoclave filled with synthesis gel. The organotemplate-free synthesis gel was obtained by mixing sodium hydroxide (NaOH, 96 wt.%, Kermel), sodium fluoride (NaF, 98 wt.%, Sinopharm), aluminum sulfate octadecahydrate (Al₂(SO₄)₃·18H₂O, 99 wt.%, Sinopharm), and colloidal silicon (SiO₂·nH₂O, 25 wt.%, Qiaodao Haiyang Chemical) in deionized water, and vigorously stirring for 2 h at 35 $^{\circ}\text{C}$. The corresponding organotemplate synthesis gels were obtained by adding certain amounts of organic template agents tetrapropylammonium hydroxide (TPAOH, 25 wt.%, Kente) and tetrapropylammonium bromide (TPABr, 96 wt.%, Sinopharm). The detailed parameters of the synthesis gels of all as-synthesized membranes Z1-Z6 are listed in Table 1. The hydrothermal secondary growth was performed in an electrothermal blower oven at 175 $^{\circ}\text{C}$ for 24 h. After synthesis, all as-synthesized membranes Z1-Z6 were thoroughly and repeatedly washed with deionized water and then dried at 80 $^{\circ}\text{C}$ overnight. For membranes Z2 and Z3, the calcination process was carried out at 500 $^{\circ}\text{C}$ for 10 h with rising and cooling rates of 1 $^{\circ}\text{C}/\text{min}$.

2.2 Membrane characterization

The crystal structures and crystallinity of the seeds and membranes were identified by X-ray diffraction (XRD) with a Philips Analytical X-ray diffractometer using Cu K α radiation (30 mA and 40 kV). Scanning electron microscope (SEM) images of the membranes were taken on QUANTA 450 and KYKY-2800B, operating at an acceleration voltage of 30 kV and 15 kV, respectively. Before observations, the samples were sputter-coated with a layer of gold to increase conductivity. The Si/Al ratio of the membrane was determined by an energy dispersive spectrometer (EDS, QUANTA 450 microscope equipped with an X-MAX 20/50 mm²).

2.3 Pervaporation test

The pervaporation performances of the as-synthesized membranes were evaluated by dehydration of binary isopropanol aqueous mixture. The permeate vapors were collected using a cold trap condensed under liquid nitrogen. The compositions of the feed and permeate sides were detected by a gas chromatograph (GC7890T, Techcomp).

The pervaporation performances were determined in terms of the permeation flux (J , kg/(m²·h)) and the separation factors of water/isopropanol ($\alpha_{(w/i)}$) of the membranes, as seen in Eqs. (1) and (2), respectively

$$J = \frac{m}{A \cdot t} \quad (1)$$

$$\alpha_{(w/i)} = \frac{y_w / y_i}{x_w / x_i} \quad (2)$$

where m , A , t , y_w , y_i , x_w and x_i denote the mass of permeate vapor condensed in the cooled trap (kg), effective area of the outer surface of the membrane (m²), test time (h), and mass fractions of water and isopropanol at the permeate and feed sides, respectively.

3. Results and discussion

3.1 ZSM-5 seeds and seed layer

The SEM images of the ZSM-5 seeds are shown in Fig. 1(a) and (b). It can be seen that the sizes of ZSM-5 without and with ball-milling are about 1.5 μm and 500 nm, respectively. Their corresponding XRD patterns are shown in Fig. 2(a) and (b). The intensities of typical peaks of ZSM-5 seeds with ball-milling are weaker than those of the original ZSM-5 seeds. This result is mainly attributed to the reduction in crystal size caused by ball-milling.

Figs. 1(c)–(h) show the SEM images of the tubular α -alumina support before and after the seeding process. Surface and cross-sectional morphologies of the original support are shown in Figs. 1(c) and (d), respectively. The support surface formed by random accumulation of α -alumina particles is rather rough and irregular. The average pore size is \sim 2–3 μm , with some pores exceeding 8 μm . Variable temperature dip coating is an effective seeding method. It can form a continuous and smooth seed layer on the outer surface of the support. The coated seeds act both as fillers to reduce the pore size and surface roughness of the support, and as crystal nuclei to provide sites for crystal growth. Figs. 1(e) and (f) show the surface and cross-sectional morphologies of the intermediate seeded support after the first dip coating, respectively. The support surface was covered with ZSM-5 seeds, which can reduce the roughness of the support surface. However, coverage by the ZSM-5 seeds is not enough because of the existence of bare α -alumina and the uneven surface of the seeded support. The surface and cross-sectional morphologies of the final seeded support after the second dip coating are shown in Figs. 1(g) and (h), respectively. It was found the final seeded layer is quite smooth and continuous, and no ZSM-5 seeds had invaded the interior of the support. The original support and final seeded support were also subjected to XRD analysis, as shown in Figs. 2(c) and (d), respectively. Typical α -alumina characteristic peaks appeared on the XRD patterns. However, 2 theta was within 7–9° and 22–24° in the XRD pattern (Fig. 2(d)), and four significant ZSM-5

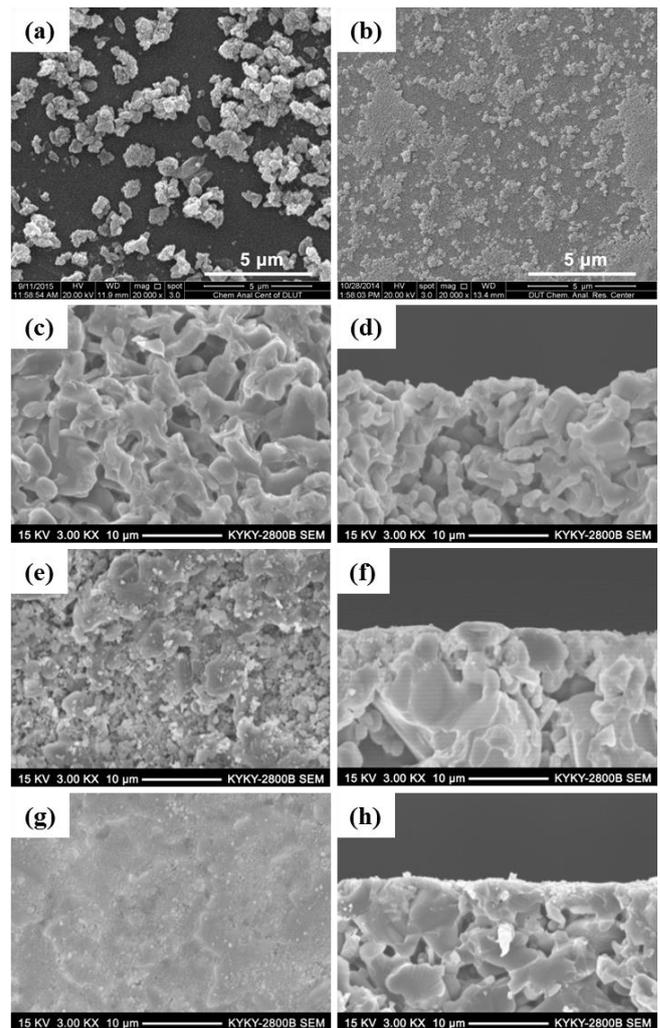


Fig. 1 Typical SEM images of original (commercially available) ZSM-5 seeds (a), small-sized ZSM-5 seeds after ball-milling (b), original α -alumina support (c and d), intermediate seeded support (e and f), and final seeded support (g and h)

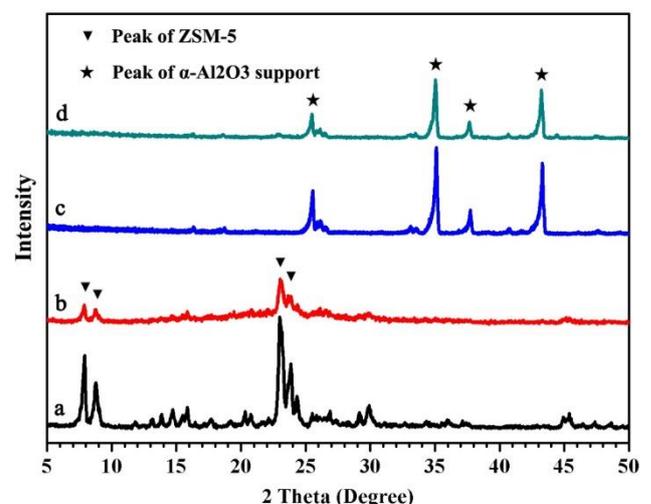


Fig. 2 XRD patterns of original (commercial) ZSM-5 seeds (a), small-sized ZSM-5 seeds after ball-milling (b), original α -alumina support (c), and final seeded support (d)

peaks could not be observed because of a combination of a strong support peak and weak seed peak. This finding may be ascribed mainly to the thin ZSM-5 seed layer on the α -alumina support surface. The thickness of the seed layer was $\sim 1.5 \mu\text{m}$, and thus, the ZSM-5 peaks could hardly be observed in the background of the strong α -alumina support peaks.

3.2 Effect of synthesis route

The synthesis route acts as a critical factor in the formation of hydrophilic ZSM-5 membranes and membrane pervaporation performance pertaining to dehydration of isopropanol. In this work, the membranes were prepared using the organotemplate-free and organotemplate routes. The change in morphology, structure, and Si/Al ratio of these membranes was detected by SEM (Fig. 3), XRD (Fig. 4), and EDS analyses (Table 2).

Figs. 3(a) and (b) show the surface and cross-sectional morphologies of membrane Z1 prepared by the organotemplate-free route. It can be seen that the membrane surface was fully covered with dice-like crystals. Membrane Z1 was thin ($\sim 3.0 \mu\text{m}$). In contrast, membranes Z2 and Z3 were prepared by the organotemplate route, using TPAOH and TPABr as the organic template agents. As per Figs. 3(c)-(f), the surface microphotographs of membranes Z2 and Z3 are markedly different from that of membrane Z1. Membrane Z2 showed columnar crystals and a zeolite layer of \sim approximately $40.0 \mu\text{m}$ had grown on the surface of the support (Figs. 3(c) and (d)). As per Fig. 3(e), membrane Z3 formed on the surface of the support shows a rugged surface morphology. Membrane Z3 was ~ 7.0 - $9.0 \mu\text{m}$ thick (Fig. 3(f)). The thicknesses of membranes Z2 and Z3 are higher than that of membrane Z1. This may be attributed to the presence of TPAOH or TPABr in the solution, which could lead to an increase in the number of nucleation sites, especially in the gel layer near the support surface. This would generate more crystals from the available resources, resulting in an increase in membrane thickness (Berenguer-Murcia *et al.* 2003, Xiao *et al.* 2010). Composite synthesized using TPAOH as an organic template agent has higher thickness than that prepared with TPABr. This may be mainly due to the change in the pH of the reaction mixture caused by the presence of the OH⁻ anion in TPAOH. In addition, crack defects were found on the surface of membranes Z2 and Z3, wherein the crack defects of membrane Z3 were larger than those of membrane Z2. These defects are mainly caused by the presence of the organotemplate during calcination at high temperatures.

According to the XRD patterns in Fig. 4, membranes Z1-Z3 show typical ZSM-5 and α -alumina support characteristic peaks without any other crystalline phase, indicating that pure ZSM-5 membranes were prepared using both synthesis routes. In addition, we carefully analyzed crystallographic preferred orientations (CPO) of the membranes according to literature (Mintova *et al.* 1998, Wang *et al.* 2001). Membrane Z1 is mainly (a, b, c)-oriented, and membranes Z2 and Z3 are random-oriented. The presence of (a, b, c)-oriented crystals in membrane Z1 can be observed in the SEM image in Figure 3a and b. The typical peaks of the XRD pattern in the region of 6 to 25° is consistent with those of a reported (a, b, c)-oriented MFI membrane (Wang *et al.* 2001). Moreover, the Si/Al ratios

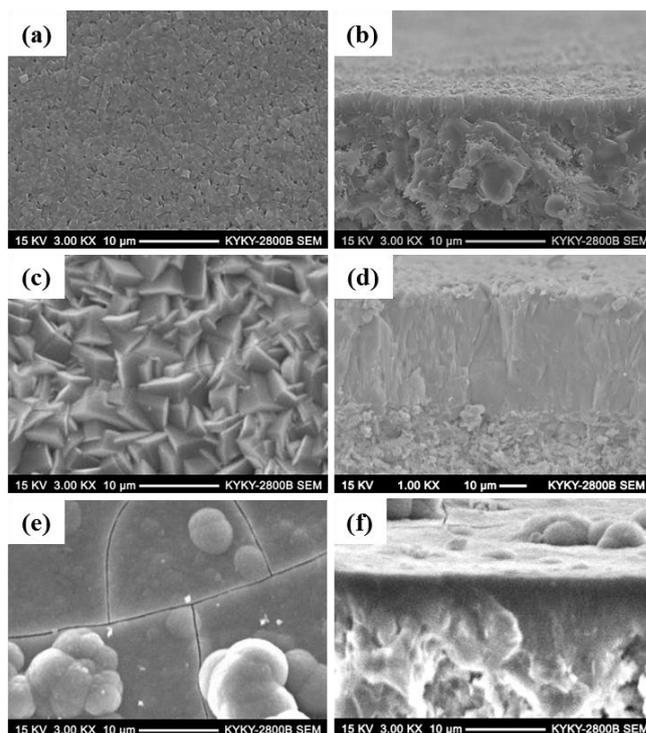


Fig. 3 Surface and cross-sectional SEM images of membranes: Z1 (organotemplate-free) (a and b), Z2 (TPAOH, (c and d)), and Z3 (TPABr, (e and f))

of membranes Z1-Z3 were evaluated by EDS analysis. The Si/Al ratios of membranes Z1-Z3 were 12.0, 47.4, and 65.6, respectively. The results showed that membrane Z1, prepared by the organotemplate-free route, has the lowest Si/Al ratio. It is well known that the lower the Si/Al ratio of the zeolite membrane, the higher its hydrophilicity. Therefore, with its lower Si/Al ratio, membrane ZSM-5 can facilitate high separation performance in the dehydration of isopropanol.

Furthermore, the isopropanol dehydration performances of the membranes were determined by a laboratory-scale batch pervaporation experimental apparatus, using 90 wt.% isopropanol aqueous solution as a feed side mixture. Table 2 shows the isopropanol dehydration performances of membranes Z1-Z3 prepared by different routes for dehydration of isopropanol at 75°C . Membrane Z1 displayed a flux of $2.56 \text{ kg}/(\text{m}^2\cdot\text{h})$ and a separation factor of 2022. As expected, the poor separation performances of membranes Z2 and Z3 were consistent with the observed microphotographs and EDS analysis results. The fluxes of membranes Z2 and Z3 were $1.87 \text{ kg}/(\text{m}^2\cdot\text{h})$ and $3.22 \text{ kg}/(\text{m}^2\cdot\text{h})$, with separation factors of 226 and 21, respectively. This result may be attributed to the higher Si/Al ratio and existence of some cracks or grain boundary defects. The results suggested that organotemplate-free synthesis is conducive to the preparation of high performance ZSM-5 membranes for dehydration of isopropanol.

3.3 Effect of Si/Al ratio of synthesis gel

We also explored the influence of the Si/Al ratio of the synthesis gel on the morphologies and isopropanol dehydration performances of the membranes. A series of experiments were performed to prepare ZSM-5 membranes for different Si/Al

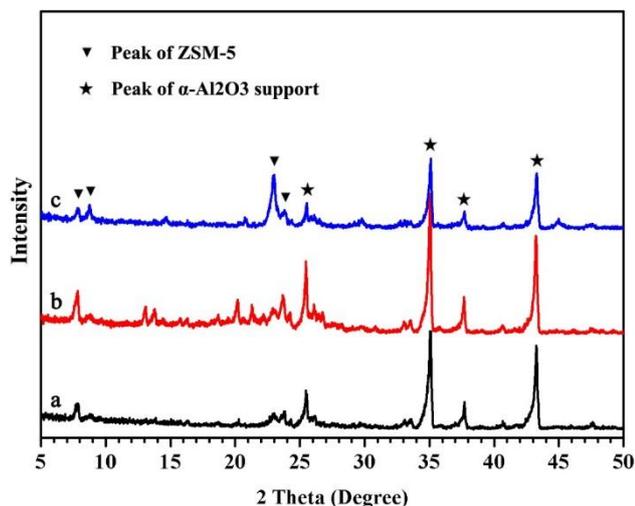


Fig. 4 XRD patterns of the membranes: Z1 (organotemplate-free, (a)), Z2 (TPAOH (b)), and Z3 (TPABr (c))

Table 2 Pervaporation performances of membranes for dehydrating 90 wt.% isopropanol aqueous solution at 75 °C

Sample No.	(Si/Al) _{EDS} ratio*	Flux (kg/(m ² ·h))	Separation factor
Z1	12.0	2.56	2022
Z2	47.4	1.87	226
Z3	65.6	3.22	21
Z4	16.1	1.14	499
Z5	11.2	3.27	> 10000
Z6	10.1	3.92	> 10000

*(Si/Al)_{EDS} ratio: the Si/Al ratio of the as-synthesis membrane by EDS analysis.

ratios of synthesis gels, using different aluminum contents. The detailed synthesis parameters of membranes Z4-Z6 are listed in Table 1. The changes in morphologies and structures of membranes Z4-Z6 were evaluated by surface and cross-sectional SEM images and their XRD patterns (Figs. 5 and 6). Fig. 5 indicates that the membranes exhibited different morphologies depending on the Si/Al ratio of the synthesis gel. According to Figs. 5(a) and (b), the surface of membrane Z4 was fully covered with dice-like crystals, similar to the case of membrane Z1, and the thickness of membrane Z4 was ~6.0 μm (Figs. 5(a) and (b)). For membrane Z5 (Figs. 5(c) and (d)), the surface displayed long rice-like morphology, showing good intergrowth. The membrane thickness was ~3.0-4.0 μm. For membrane Z6 (Fig. 5(e)), the surface was fully covered by many particles but no micro-cracks were visible. Membrane Z6 was ~3.0 μm thick, as shown in Fig. 5(f).

As per the XRD patterns in Fig. 6, membranes Z4-Z6 display typical characteristic peaks of ZSM-5 and α-alumina support without any other crystalline phase, indicating that pure ZSM-5 membranes were obtained using different Si/Al ratios of the synthesis gels. The Si/Al ratios of membranes Z4-Z6 obtained by EDS analysis were 16.1, 11.2, and 10.1, respectively (Table 2). The EDS Si/Al ratios of membranes Z4, Z1, Z5, and Z6 decreased from 16.1 to 10.1 as the Si/Al ratio

Table 3 Comparison of pervaporation performance of membranes for dehydration of isopropanol

Membrane	Feed (wt.%)	Temp. (°C)	Flux (kg/(m ² ·h))	Separation factor	Ref.
ZSM-5	90	75	3.92	>10000	This work
ZSM-5	90	75	3.24	3100	Zhu <i>et al.</i> 2012
SPVA	90	40	0.035	3452	Rachipudi <i>et al.</i> 2011
ZIF-90/P84	85	60	0.109	5668	Hua <i>et al.</i> 2014
PVA/Silicone	90	30	0.0265	1580	Zhang <i>et al.</i> 2007
TFC	85	50	3.10	467	Zuo <i>et al.</i> 2013
PVA/ZIF-8	90	30	0.868	132	Amirilargani <i>et al.</i> 2014
CS-TEOS	90	80	0.284	460	Ma <i>et al.</i> 2009

SPVA: sulfonated-poly(vinyl alcohol); TFC: organic-inorganic hollow fiber; CS-TEOS: chitosan-tetraethoxysilane.

of the synthesis gels decreased from 16.7 to 10.0. These results suggest that controlling the Si/Al ratio of the synthesis gel is an effective way to tune ZSM-5 membranes.

The pervaporation performances of membranes Z4-Z6 are reported in Table 2. The flux of membrane Z4 was 1.14 kg/(m²·h), with a separation factor of 499 for the 90 wt.% isopropanol aqueous solution at 75 °C. The fluxes of membranes Z5 and Z6 were 3.27 kg/(m²·h) and 3.92 kg/(m²·h), respectively, and the separation factors for both were higher than 10000. The excellent selectivities indicate that membranes Z5 and Z6 were of high quality, containing dense and well-intergrown layers, and a very small amount of isopropanol passed through the membrane layers. The fluxes of membranes Z4, Z1, Z5, and Z6 increased from 1.14 kg/(m²·h) to 3.92 kg/(m²·h) as the Si/Al ratio decreased from 16.1 to 10.1. Their corresponding separation factors also increased from 499 to higher than 10000. The results suggest that the water perm-selectivity of the ZSM-5 membrane increases with a decrease in the Si/Al ratio from 16.1 to 10.1. The high water perm-selectivity is mainly attributed to the lower Si/Al ratio (and hence higher hydrophilicity) of the membrane.

3.4 Comparison of pervaporation performance

The results of this study are notable. Table 3 shows a comparison of the pervaporation performance of this work with other studies on pervaporation dehydration of isopropanol. According to Table 3, the flux and separation factor of the as-synthesized ZSM-5 membrane are higher than the corresponding values of the other membranes. It is worth noting that the ZSM-5 membrane with a low Si/Al ratio (about 14) prepared from an aluminum-rich synthesis gel by Zhu *et al.* (2012) showed a flux of 3.24 kg/(m²·h) with a separation factor of 3100 at the same isopropanol feed concentration and operating temperature. In comparison, the ZSM-5 membrane in this work showed better pervaporation performance, which can be mainly attributed to the lower Si/Al ratio of about 10.1.

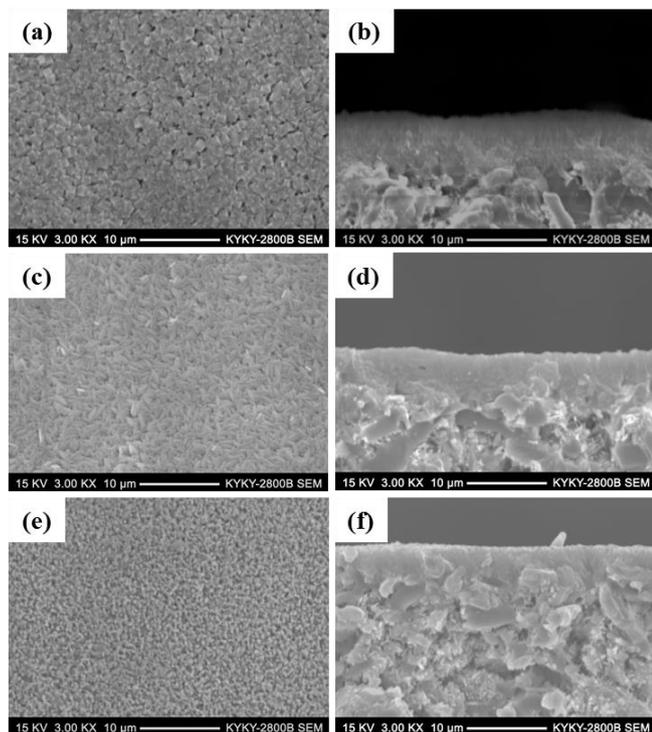


Fig. 5 Surface and cross-sectional SEM images of membranes prepared using synthesis gels of different Si/Al ratios: Z4 (Si/Al ratio of 16.7, (a) and (b)), Z5 (Si/Al ratio of 11.6, (c) and (d)), and Z6 (Si/Al ratio of 10.0, (e) and (f))

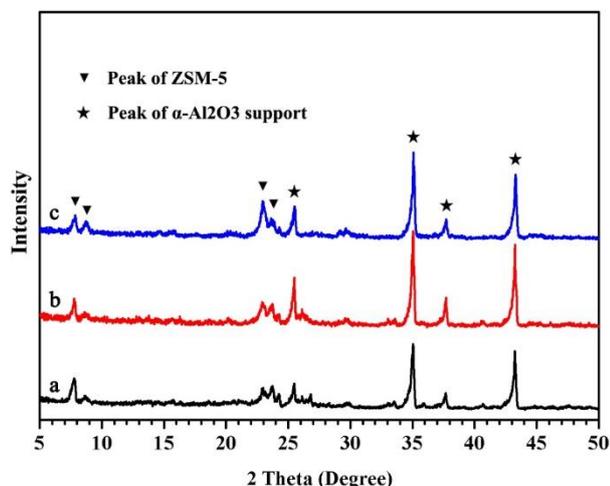


Fig. 6 XRD patterns of membranes prepared using synthesis gels of different Si/Al ratios: Z4 (Si/Al ratio of 16.7, (a)), Z5 (Si/Al ratio of 11.6, (b)), and Z6 (Si/Al ratio of 10.0, (c))

4. Conclusions

In conclusion, a high-quality ZSM-5 membrane with a thickness of ~ 3.0 μm and a low Si/Al ratio of 10.1 was successfully prepared on tubular macroporous α -alumina support using the organotemplate-free synthesis route. The ZSM-5 membrane displayed high water perm-selectivity performance for pervaporation dehydration of 90 wt.% isopropanol/water mixture at 75 $^{\circ}\text{C}$. The permeation flux was 3.92 $\text{kg}/(\text{m}^2\cdot\text{h})$ and the corresponding separation factor was

higher than 10000. These findings suggested that reducing the Si/Al ratio of the membrane is an effective means for modulating the hydrophilicity and acid resistance of ZSM-5 membrane. A ZSM-5 membrane with low Si/Al ratio can not only potentially dehydrate organic acids and other organics in acidic media, but can also be used as a catalytic membrane reactor to facilitate conversion in esterification.

Acknowledgments

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References

- Abedi Koupaei, J. (2001), "The effect of Mashhad landfill on pollution of groundwater resources", *Proceed. 4th Nat. Conf. Environment. Health, Iran*, **1**, 87-97.
- Algieri, C., Bernardo, P. and Barbieri, G. (2009), "A novel seeding procedure for preparing tubular NaY zeolite membranes", *Micropor. Mesopor. Mater.*, **119**(1-3), 129-136. <https://doi.org/10.1016/j.micromeso.2008.10.008>.
- Amirilargani, M. and Sadatnia, B. (2014), "Poly (vinyl alcohol)/zeolitic imidazolate frameworks (ZIF-8) mixed matrix membranes for pervaporation dehydration of isopropanol", *J. Membr. Sci.*, **469**, 1-10. <https://doi.org/10.1016/j.memsci.2014.06.034>.
- Bakker, W.J.W., Kapteijn, F. and Poppe, J. (1996), "Permeation characteristics of a metal-supported silicalite-1 zeolite membrane", *J. Membr. Sci.*, **117**(1-2), 57-78. [https://doi.org/10.1016/0376-7388\(96\)00035-X](https://doi.org/10.1016/0376-7388(96)00035-X).
- Berenguer-Murcia, A., Garcia-Martinez, J. and Cazorla-Amorós, D. (2003), "Silicalite-1 membranes supported on porous carbon discs", *Micropor. Mesopor. Mater.*, **59**(2-3), 147-159. [https://doi.org/10.1016/S1387-1811\(03\)00306-8](https://doi.org/10.1016/S1387-1811(03)00306-8).
- Bhat, S.D. and Aminabhavi, T.M. (2006), "Novel sodium alginate composite membranes incorporated with SBA-15 molecular sieves for the pervaporation dehydration of aqueous mixtures of isopropanol and 1, 4-dioxane at 30 $^{\circ}\text{C}$ ", *Micropor. Mesopor. Materials*, **91**(1-3), 206-214. <https://doi.org/10.1016/j.micromeso.2005.11.044>.
- Caro, J. and Noack, M. (2008) "Zeolite membranes—recent developments and progress", *Micropor. Mesopor. Mater.*, **115**(3), 215-233. <https://doi.org/10.1016/j.micromeso.2008.03.008>.
- Cui, Y., Kita, H., Okamoto, K.I. (2004), "Zeolite T membrane: preparation, characterization, pervaporation of water/organic liquid mixtures and acid stability", *J. Membr. Sci.*, **236**(1-2), 17-27. <https://doi.org/10.1016/j.memsci.2003.12.018>.
- Chen, H., Li, Y., Yang, W. (2007), "Preparation of silicalite-1 membrane by solution-filling method and its alcohol extraction properties", *J. Membr. Sci.*, **296**(1-2), 122-130. <https://doi.org/10.1016/j.memsci.2007.03.021>.
- Chen, H., Yan, Y. and Shao, Y. (2014), "Catalytic activity and stability of porous Co-Cu-Mn mixed oxide modified microfibrillar-structured ZSM-5 membrane/PSSF catalyst for VOCs oxidation", *RSC Adv*, **4**(98), 55202-55209. <https://doi.org/10.1039/C4RA08769K>.
- Chen, X., Wang, J., Yin, D., Yang, J., Lu, J., Zhang, Y. and Chen,

- Z. (2013), "High-performance zeolite T membrane for dehydration of organics by a new varying temperature hot-dip coating method", *AIChE J*, **59**(3), 936-947. <https://doi.org/10.1002/aic.13851>.
- Choi, J., Jeong, H.K. and Snyder, M.A. (2009), "Grain boundary defect elimination in a zeolite membrane by rapid thermal processing", *Science*, **325**(5940), 590-593. <https://doi.org/10.1126/science.1176095>.
- Diban, N., Aguayo, A.T., Bilbao, J., Urriaga, A. and Ortiz, I. (2013), "Membrane reactors for in situ water removal: a review of applications", *Ind. Eng. Chem. Res*, **52**(31), 10342-10354. <https://doi.org/10.1021/ie3029625>.
- Feng, X. and Huang, R.Y. (1997), "Liquid separation by membrane pervaporation: A review", *Ind. Eng. Chem. Res*, **36**(4), 1048-1066. <https://doi.org/10.1021/ie960189g>.
- Gao, X., Zou, X. and Zhang, F. (2013), "Eco-friendly fabrication of hydrophilic ZSM-5 membranes for alcohol upgrading", *Chem. Commun*, **49**(78), 8839-8841. <https://doi.org/10.1039/C3CC44515A>.
- Hua, D., Ong, Y.K. and Wang, Y. (2014), "ZIF-90/P84 mixed matrix membranes for pervaporation dehydration of isopropanol", *J. Membr. Sci*, **453**, 155-167. <https://doi.org/10.1016/j.memsci.2013.10.059>.
- Kittur, A.A., Kulkarni, S.S. and Aralaguppi, M.I. (2005), "Preparation and characterization of novel pervaporation membranes for the separation of water-isopropanol mixtures using chitosan and NaY zeolite", *J. Membr. Sci*, **247**(1-2), 75-86. <https://doi.org/10.1016/j.memsci.2004.09.010>.
- Korelskiy, D., Leppäjärvi, T., Zhou, H., Grahn, M., Tanskanen, J. and Hedlund, J. (2013), "High flux MFI membranes for pervaporation", *J. Membr. Sci*, **427**, 381-389. <https://doi.org/10.1016/j.memsci.2012.10.016>.
- Li G., Kikuchi E. and Matsukata M. (2003), "The control of phase and orientation in zeolite membranes by the secondary growth method", *Micropor. Mesopor. Mater*, **62**(3), 211-220. [https://doi.org/10.1016/S1387-1811\(03\)00407-4](https://doi.org/10.1016/S1387-1811(03)00407-4).
- Li, G., Kikuchi, E. and Matsukata, M. (2003), "Separation of water-acetic acid mixtures by pervaporation using a thin mordenite membrane", *Sep. Purif. Technol*, **32**(1-3), 199-206. [https://doi.org/10.1016/S1383-5866\(03\)00035-2](https://doi.org/10.1016/S1383-5866(03)00035-2).
- Li, L., Yang, J. and Li, J. (2016), "High performance ZSM-5 membranes on coarse macroporous α -Al₂O₃ supports for dehydration of alcohols", *AIChE J*, **62**(8), 2813-2824. <https://doi.org/10.1002/aic.15234>.
- Li, L., Yang, J. and Li, J. (2016), "Synthesis of high performance mordenite membranes from fluoride-containing dilute solution under microwave-assisted heating", *J. Membr. Sci*, **512**, 83-92. <https://doi.org/10.1016/j.memsci.2016.03.056>.
- Li, L., Zhang, W. and Yang, J. (2015), "Preparation and characterization of water perm-selectivity ZSM-5 zeolite membrane using fluoride route", *J. Inorg. Mater*, **30**(11), 1167-1171.
- Lin, X., Kikuchi, E. and Matsukata, M. (2000), "Preparation of mordenite membranes on α -alumina tubular supports for pervaporation of water-isopropyl alcohol mixtures", *Chem. Commun*, **0**(11), 957-958. <https://doi.org/10.1039/A909867D>.
- Lin, Y.S., Kumakiri, I., Nair, B.N. and Alsayouri, H. (2002), "Microporous inorganic membranes", *Sep. Purif. Rev*, **31**(2), 229-379. <https://doi.org/10.1081/SPM-120017009>.
- Lipnizki, F., Field, R.W. and Ten, P.K. (1999), "Pervaporation-based hybrid process: a review of process design, applications and economics", *J. Membr. Sci*, **153**(2), 183-210. [https://doi.org/10.1016/S0376-7388\(98\)00253-1](https://doi.org/10.1016/S0376-7388(98)00253-1).
- Ma, J., Zhang, M. and Lu, L. (2009), "Intensifying esterification reaction between lactic acid and ethanol by pervaporation dehydration using chitosan-TEOS hybrid membranes", *Chem. Eng. J*, **155**(3), 800-809. <https://doi.org/10.1016/j.cej.2009.07.044>.
- Mintova, S., Hedlund, J., Valtchev, V., Schoeman, B.J. and Sterte, J. (1998), "ZSM-5 films prepared from template free precursors", *J. Mater. Chem*, **8**(10), 2217-2221. <https://doi.org/10.1039/A803687J>.
- Morigami, Y., Kondo, M. and Abe, J. (2001), "The first large-scale pervaporation plant using tubular-type module with zeolite NaA membrane", *Sep. Purif. Technol*, **25**(1-3), 251-260. [https://doi.org/10.1016/S1383-5866\(01\)00109-5](https://doi.org/10.1016/S1383-5866(01)00109-5).
- Noack M., Kölsch P. and Caro J. (2000), "MFI membranes of different Si/Al ratios for pervaporation and steam permeation", *Microporous and Mesoporous Materials*, **35**, 253-265. [https://doi.org/10.1016/S1387-1811\(99\)00226-7](https://doi.org/10.1016/S1387-1811(99)00226-7).
- Noack, M., Kölsch, P., Seefeld, V., Toussaint, P., Georgi, G. and Caro, J. (2005), "Influence of the Si/Al-ratio on the permeation properties of MFI-membranes", *Micropor. Mesopor. Mater*, **79**, 329-337. <https://doi.org/10.1016/j.micromeso.2005.01.004>.
- Okamoto, K., Kita, H. and Horii, K. (2001), "Zeolite NaA membrane: preparation, single-gas permeation, and pervaporation and vapor permeation of water/organic liquid mixtures", *Ind. Eng. Chem. Res*, **40**(1), 163-175. <https://doi.org/10.1021/ie0006007>.
- Premakshi, H.G., Ramesh, K. and Kariduraganavar, M.Y. (2015), "Modification of crosslinked chitosan membrane using NaY zeolite for pervaporation separation of water-isopropanol mixtures", *Chem. Eng. Res. Des*, **94**, 32-43. <https://doi.org/10.1016/j.cherd.2014.11.014>.
- Pulyalina, A., Polotskaya, G. and Goikhman, M. (2013), "Study on polybenzoxazinone membrane in pervaporation processes", *J. Appl. Polym. Sci*, **130**(6), 4024-4031. <https://doi.org/10.1002/app.39674>.
- Qiao, X., Chung, T.S. and Guo, W.F. (2005), "Dehydration of isopropanol and its comparison with dehydration of butanol isomers from thermodynamic and molecular aspects", *J. Membr. Sci*, **252**(1-2), 37-49. <https://doi.org/10.1016/j.memsci.2004.11.014>.
- Rachipudi, P.S., Kariduraganavar, M.Y. and Kittur, A.A. (2011), "Synthesis and characterization of sulfonated-poly (vinyl alcohol) membranes for the pervaporation dehydration of isopropanol", *J. Membr. Sci*, **383**(1-2), 224-234. <https://doi.org/10.1016/j.memsci.2011.08.040>.
- Sato, K., Sugimoto, K. and Nakane, T. (2008), "Mass-production of tubular NaY zeolite membranes for industrial purpose and their application to ethanol dehydration by vapor permeation", *J. Membr. Sci*, **319**(1-2), 244-255. <https://doi.org/10.1016/j.memsci.2008.03.041>.
- Tang Z., Kim S.J. and Gu X. (2009), "Microwave synthesis of MFI-type zeolite membranes by seeded secondary growth without the use of organic structure directing agents", *Micropor. Mesopor. Mater*, **118**(1-3), 224-231. <https://doi.org/10.1016/j.micromeso.2008.08.029>.
- Wang, Z. and Yan, Y. (2001), "Controlling crystal orientation in zeolite MFI thin films by direct in situ crystallization", *Chem. Mater*, **13**(3), 1101-1107. <https://doi.org/10.1021/cm000849e>.
- Xiao, W., Yang, J. and Shen, D. (2010), "Synthesis and property of silicalite-1 membranes by restricting growth method with dilute solution", *Micropor. Mesopor. Mater*, **129**(1-2), 22-29. <https://doi.org/10.1016/j.micromeso.2009.08.036>.
- Xu, X., Yang, W. and Liu, J. (2000), "Synthesis of a high-permeance NaA zeolite membrane by microwave heating", *Adv. Mater*, **12**(3), 195-198. [https://doi.org/10.1002/\(SICI\)1521-4095\(200002\)12:3<195::AID-ADMA195>3.0.CO;2-E](https://doi.org/10.1002/(SICI)1521-4095(200002)12:3<195::AID-ADMA195>3.0.CO;2-E).
- Yang, J., Li, L. and Li, W. (2014), "Tuning aluminum spatial distribution in ZSM-5 membranes: a new strategy to fabricate high performance and stable zeolite membranes for dehydration of acetic acid", *Chem. Commun*, **50**(93), 14654-14657. <https://doi.org/10.1039/C4CC04747H>.

- Zhang, Q.G., Liu, Q.L., Chen, Y. (2007), "Dehydration of isopropanol by novel poly (vinyl alcohol)-silicone hybrid membranes", *Ind. Eng. Chem. Res.*, **46**(3), 913-920. <https://doi.org/10.1021/ie0609719>.
- Zhu, M.H., Lu, Z.H., Kumakiri, I. (2012), "Preparation and characterization of highwater perm-selectivity ZSM-5 membrane without organic template", *J. Membr. Sci.*, **415**, 57-65. <https://doi.org/10.1016/j.memsci.2012.04.037>.
- Zuo, J., Wang, Y., Chung, T.S. (2013), "Novel organic-inorganic thin film composite membranes with separation performance surpassing ceramic membranes for isopropanol dehydration", *J. Membr. Sci.*, **433**, 60-71. <https://doi.org/10.1016/j.memsci.2013.01.002>.

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