



Hydrophilic SOD and LTA membranes for membrane-supported methanol, dimethylether and dimethylcarbonate synthesis



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ABSTRACT

Hydrophilic LTA and SOD membranes have been tested in the selective water removal from methanol (MeOH), dimethylcarbonate (DMC) and dimethylether (DME) thus simulating their synthesis in membrane reactors with CO₂ as feed. To further improve the pervaporation selectivity of LTA membranes for an aqueous MeOH solution, Na⁺ ions located in the 8-membered oxygen ring of LTA were ion-exchanged with larger K⁺ ions in a KNO₃ solution, leading to an improvement of the pervaporation separation factor of the H₂O/MeOH mixture from 2.8 to 7.4 at room temperature. Furthermore, the selective removal of steam from the organic compounds MeOH, DME and DMC on supported SOD membranes was investigated at high temperatures by steam permeation. The separation performances of SOD membranes for equimolar mixtures of steam with H₂, CO₂, MeOH, DME or DMC, were evaluated in the temperature range from 125 to 200 °C. The mixture separation factors for steam from DME and DMC through the SOD membrane were found to be higher than 200 and 1000, respectively.

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1. Introduction

Zeolite membranes have attracted widespread attention due to their great potential in the separation of gas or liquid mixtures. Among them, the fabrication of LTA-type zeolite membranes has been extensively studied, and supported LTA membranes have also been successfully prepared [1–6]. Because of the strong hydrophilicity and suitable pore size, zeolite LTA membranes were first commercialized in the dehydration of alcohol/water mixtures by steam permeation [7–12].

While past decades had witnessed great progress made in LTA membranes, some problems still existed, which had hindered the improvement of the dehydration performance. One critical problem encountered is the pore size control. Usually LTA membranes are synthesized in the Na⁺ form. However, their pore size of about 4 Å is not small enough for the molecular sieving of H₂O/MeOH (kinetic diameters about 2.6 Å and 3.8 Å, respectively) mixtures. One possible solution of pore size-engineering is ion-exchange of the Na⁺ with bigger K⁺ ions. The formula of one cubo-octaheder Na₁₂[Si₁₂Al₁₂O₄₈] represents one large cavity. 8 of the 12 Na⁺ are

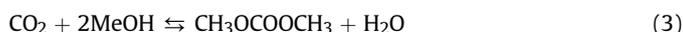
located inside the large cavity near to the eight six-rings. 3 of remaining 4 Na⁺ ions are located in the 8-membered oxygen rings between the large cavities thus hindering the molecular passage. The fourth of these remaining Na⁺ is not located. Zeolite Na⁺-LTA has a pore size of about 4.1 Å, when the sodium ions are exchanged with K⁺, the pore size will be narrowed to about 3 Å. Theoretically, when Na⁺ are ion-exchanged with even larger cations like Rb⁺ for Cs⁺, the pore size of LTA is expected to be further reduced [13]. On the contrary, when the Na⁺ are replaced with smaller cations like Li⁺, the pore size of the framework will be increased [14]. If the Na⁺ are replaced by two-valent ions like Ca⁺⁺ or Mg⁺⁺, these ions go into the large cavity and the cation positions in the 8-membered oxygen rings become unoccupied which “opens” the window to about 5 Å [15,16]. Because of the potential industrial applications like water-softening, gas adsorption and gas separation, the ion-exchange behavior of zeolite LTA has been studied extensively [17–23]. It was found that the Li⁺-exchanged LTA can adsorb NO better relative to the Na-LTA [24]. The Rb⁺ and Cs⁺-exchanged LTA was also investigated [16] and the Rb⁺ and Cs⁺-exchanged LTA membranes supported on carbon discs were used for hydrogen purification [13]. However, ion-exchanged LTA membranes have been investigated in only a few gas separation studies [4–6,25]. Morooka et al. [5] found that K-LTA membranes show better separation performance for a H₂/N₂ system compared to the Na-LTA

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and Ca-LTA membranes. Huang et al. [6] used Ca-LTA membranes to separate n-butane (4.3 Å) from i-butane (5.1 Å).

Zeolite SOD is also hydrophilic, but with a higher framework density of 17.2 T/1000 Å³ which shows a higher chemical and thermal stability compared with zeolite LTA (12.9 T/1000 Å³) [26,27]. The small pore size of about 2.7 Å allows molecular sieving, that is to say the permeation of small molecules like H₂O with 2.6 Å through the membrane should be possible while the large molecules are excluded. Therefore, due to their hydrophilicity and molecular sieving properties, SOD membranes are advantageous in the removal of steam under harsh conditions [28–30] and could be used in the synthesis of methanol (MeOH, Eq. (1)), dimethylether (DME, Eq. (2)) and dimethylcarbonate (DMC, Eq. (3)) in catalytic membrane reactors with carbon dioxide, hydrogen or methanol as reagents:



In the present work, the K⁺-exchanged LTA membrane was prepared and exhibited improved H₂O/MeOH pervaporation performance at room temperature in comparison with the as-synthesized Na⁺-LTA membrane. We further studied the pervaporation behavior of SOD membranes in the separation of H₂O/MeOH, H₂O/DME and H₂O/DMC mixtures in the temperature range between 125 and 200 °C.

2. Experimental

2.1. Materials

The following chemicals were used as received: LUDOX AS-40 colloidal silica (40% SiO₂ in water, Aldrich); aluminum foil (Fisher Scientific); sodium hydroxide (>99%, Merck); potassium nitrate (≥99%, Roth); doubly distilled water; 3-aminopropyltriethoxysilane (98%, Abcr); toluene (99.8%, Acros). Porous α-Al₂O₃ disks (Fraunhofer Institute IKTS, former HITK/Inocermic, Hermsdorf, Germany. diameter: 18 mm; thickness: 1.0 mm; pore size: 70 nm) were used as supports.

2.2. Preparation of zeolite LTA membrane

The zeolite LTA membranes were prepared on APTES-functionalized α-Al₂O₃ supports following the procedure reported elsewhere [31,32]. The porous alumina supports were treated with APTES (0.2 mM) in 10 mL toluene at 110 °C for 30 min under argon. A clear synthesis solution with the molar ratio of 50Na₂O:1A-l₂O₃:5SiO₂:1000H₂O was used as precursor solution. The aluminate solution was prepared by adding 0.15 g aluminum foil to 25 g deionized water containing 11.11 g sodium hydroxides at room temperature. The silicate solution was prepared by mixing 2.08 g LUDOX AS-40 colloidal silica and 23.75 g deionized water at 60 °C under stirring. Then the prepared silicate solution was added into the aluminate solution and stirred overnight to produce a clear, homogenous solution. The APTES-functionalized alumina supports were horizontally placed face down in a Teflon-lined stainless steel autoclave and immersed in the precursor solution. After the in-situ growth at 60 °C for 24 h, the solution was decanted off and the membranes were washed with deionized water several times and immersed in deionized water overnight, and then dried in air at 110 °C for characterization and permeation measurement.

To prepare the K⁺-ion-exchanged LTA membranes, as-prepared LTA membranes were immersed into a 1 M KNO₃ solution for 12 h at room temperature. Then the membranes were thoroughly washed with deionized water several times and dried in air at 110 °C overnight.

2.3. Preparation of zeolite SOD membrane

The clear precursor solution with the molar ratio 50Na₂O:1A-l₂O₃:5SiO₂:1005H₂O was prepared according to the procedure reported elsewhere [28]. To prepare the aluminate solution, 11.11 g sodium hydroxides were dissolved in 25 g deionized water at room temperature, then 0.15 g aluminum foil was added into the solution. The silicate solution was prepared by mixing 2.08 g LUDOX AS-40 colloidal silica and 23.75 g deionized water at 60 °C under stirring. The prepared silicate solution was added into the aluminate solution and stirred overnight at room temperature to produce a clear solution. α-Al₂O₃ support was then horizontally placed face down in a Teflon-lined stainless steel autoclave which was filled with synthesis solution. After hydrothermal synthesis over 24 h at 120 °C, the solution was decanted off. The membrane was washed with deionized water and immersed in deionized water overnight, and then dried in air at 110 °C. To prepare a more compact SOD membrane, the dried membrane was subjected to repeated hydrothermal synthesis under identical conditions. Finally, the dried membrane after the repeated synthesis was further characterized and evaluated in gas permeation measurement.

2.4. Characterization of zeolite LTA and SOD membranes

The morphology and thickness of the zeolite LTA and SOD membranes were characterized by scanning electron microscopy (SEM, JEOL JSM-6700F with a cold field emission gun operating at 2 kV and 10 μA). The chemical composition of the cross-section of ion-exchanged LTA-layer was characterized by energy-dispersive X-ray spectroscopy (EDXS) using the same SEM microscope at 10 kV and 20 μA. The phase purity and crystallinity of the zeolite LTA and SOD membrane layers were measured by X-ray diffraction (XRD). XRD patterns were recorded at room temperature under ambient conditions with Bruker D8 ADVANCE X-ray diffractometer using CuK_α radiation at 40 kV and 40 mA.

2.5. Evaluation of pervaporation

Pervaporation performance of prepared LTA membranes were evaluated as follows: The supported LTA membrane was sealed in a home-built permeation cell with silicone O-rings and tested at room temperature by pervaporation. The concentration on the feed side was 5 wt% water against 95 wt% MeOH or DMC. The H₂O/MeOH or H₂O/DMC mixtures were fed to the feed side of the LTA membrane in the membrane model, and the permeate side of the membrane was evacuated with a vacuum pump. The permeate was collected in liquid nitrogen cooled traps. The flux was calculated by weighing before and after pervaporation, and the composition of the permeate were analyzed by gas chromatograph (HP6890). The total flux *J* and the separation factor *α* are defined following Eqs. (4) and (5)

$$J = \frac{W}{\Delta t \cdot A} \quad (4)$$

$$\alpha_{ij} = \frac{x_{ip} \cdot x_{jf}}{x_{if} \cdot x_{jp}} \quad (5)$$

where W is total weight of the permeate (kg), Δt is collecting time (h), A is separation area of the membrane (m^2), x_{ip} is the weight fraction of species i in the permeate and x_{if} is the weight fraction of species i in the feed.

2.6. Evaluation of single gas permeation and mixed gas separation

Both single and mixed gas permeation behaviors of prepared SOD membranes were evaluated as follows: For permeation experiments, the zeolite SOD membranes were sealed in a permeation module with silicone O-rings. On the feed side, deionized water, methanol, DME or DMC was heated to 200 °C in advance and vaporized before the measurements. Then the gas or liquid vapor was given to the permeation cell via a heated pipe. The permeated gases were kept heated until they were injected into gas chromatograph. The volumetric flow rates of the single gases H₂O, methanol, DME and DMC as well as of the equimolar binary mixtures of H₂O with methanol, DME and DMC were measured with the Wicke–Kallenbach technique, as shown in detail elsewhere [25]. The sweep gas N₂ was fed on the permeate side to guarantee enough driving force for permeation. To avoid the condensation of the liquids, the measurements were carried out in the temperature range from 125 °C to 200 °C. Atmospheric pressure was kept on both sides of the membranes. Fluxes of both feed and sweep gases were controlled by mass flow controllers (MFCs) for gases, while the fluxes of feed water, methanol and DMC were controlled by a MFCs for liquids. A calibrated gas chromatograph (HP6890) was used to determine the gas concentrations. The separation factor $\alpha_{i,j}$ of a binary mixture permeation is defined as the quotient of the molar ratios of the components (i,j) in the permeate, divided by the quotient of the molar ratio of the components (i,j) in the retentate, as shown in Eq. (6).

$$\alpha_{i,j} = \frac{y_{i,Perm}/y_{j,Perm}}{y_{i,Ret}/y_{j,Ret}} \quad (6)$$

3. Results and discussion

3.1. Preparation of Na-LTA membrane and ion-exchanged K-LTA membrane

Fig. 1 shows top view and cross-section of the supported K⁺-exchanged LTA membrane. After hydrothermal synthesis for 24 h, a dense and well-intergrown Na-LTA membrane with a thickness of around 3.5 μm was formed on the α -alumina support without any

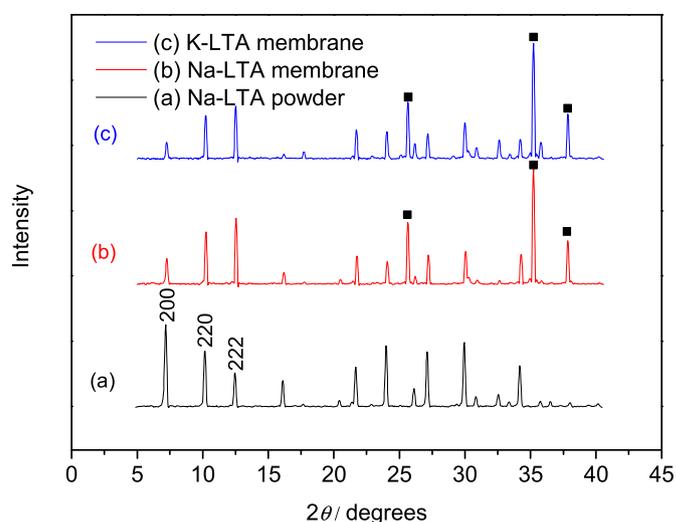


Fig. 2. XRD patterns of the zeolite Na-LTA membrane (b) K-LTA membrane after ion-exchange (c) compared with XRD patterns of the zeolite Na-LTA powder (a). (■): Al₂O₃ support (not marked); zeolite LTA.

macroscopic cracks or pinholes. After the 12 h ion-exchange with potassium ion, the morphology of the zeolite LTA membrane remained unchanged (Fig. 1a). The formation of a phase-pure zeolite LTA membrane with high crystallinity can also be confirmed by XRD patterns (Fig. 2). Referring to the XRD pattern of zeolite LTA powders (Fig. 2a), no other foreign crystalline phase of both Na-LTA and K-LTA membrane was observed, thus indicating that the ion-exchange process did not influence the LTA framework structure. Compared the XRD patterns of the LTA membrane and of LTA powder, the formation of an oriented LTA membrane can be stated. The LTA membrane shows a much stronger (222) peak, while the intensity of the (200) peaks is obviously decreased, which indicates that the LTA crystals are oriented with their diagonal perpendicular to the support surface. In agreement with the evolutionary selection model by van der Drift growth [33,34], the LTA crystals grow with their diagonal of the cube perpendicular to the support surface with {222} as the fastest growth direction. This finding from XRD correlates with the optical impression of the top view of the membrane (Fig. 1a), showing that the corners of the cube-shaped LTA crystals jut out of the membrane surface.

After the ion-exchange in the KNO₃ solution for 12 h, the distribution of the potassium ions in the ion-exchanged K-LTA membrane was investigated by EDXS. Fig. 3a shows the EDXS mapping of

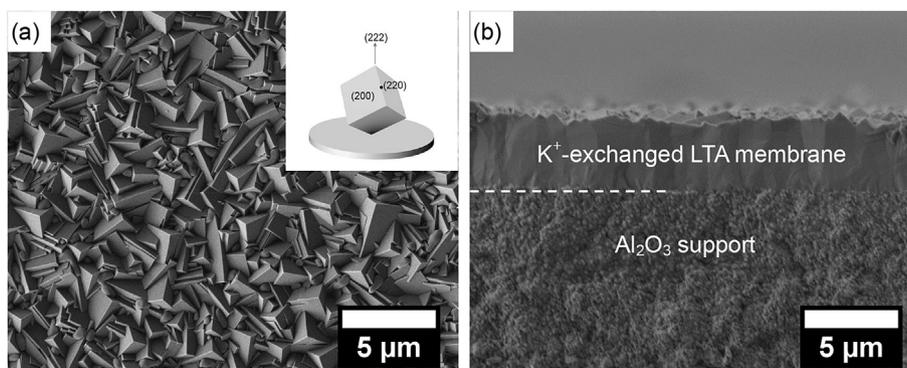


Fig. 1. SEM top views (a) and cross sections (b) of the zeolite LTA membranes on APTES-functionalized alumina supports after the 12 h ion-exchange with potassium ion. The inset of (a) shows the orientation of an individual cubic LTA crystal with (222) perpendicular to the support.

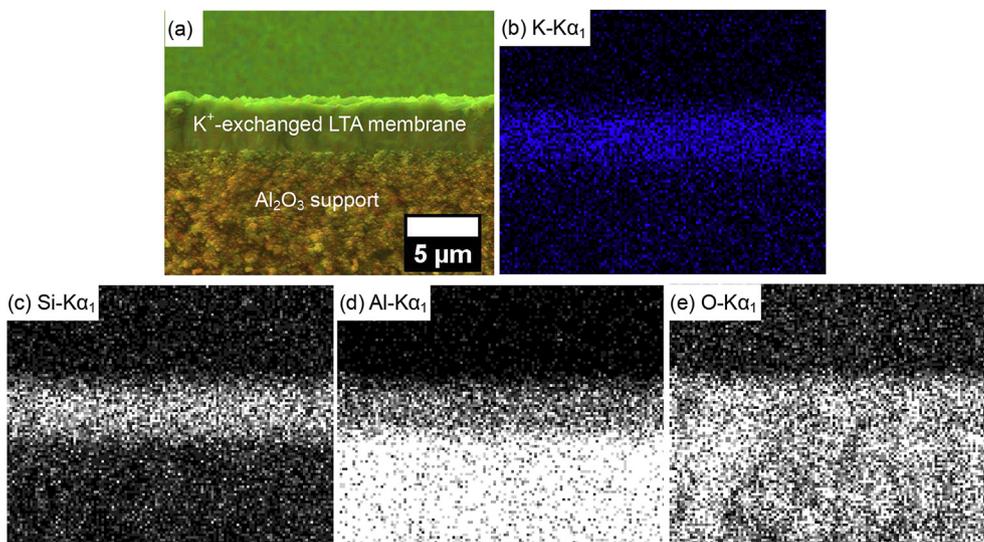


Fig. 3. (a) EDXS mapping of the cross section of ion-exchanged Na-LTA membrane (green: K in the LTA membrane, orange: Al_2O_3 support) after 12 h ion-exchange in KNO_3 solution. (b–e) Element distribution by EDXS of the area shown in (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

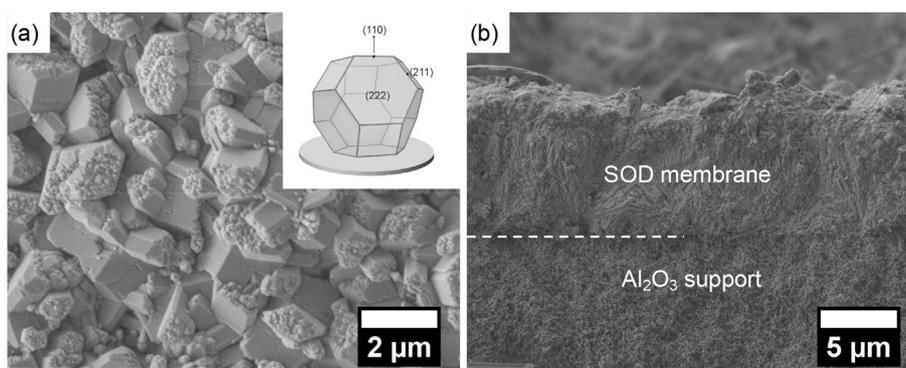


Fig. 4. SEM top view (a) and cross sections (b) of the zeolite SOD membrane by repeated synthesis on alumina support. The inset of (a) shows the orientation of an individual cubo-octahedral SOD crystal with (110) perpendicular to the support.

the cross section of the LTA membrane after K^+ -exchange, and the element distribution of K, Si, Al and O of the same area are shown in Fig. 3b–e, respectively. It can be seen that the K^+ ions (blue color in Fig. 3b) were homogeneously distributed in the whole cross section of the K^+ -LTA layer. Moreover, the element K was also found underneath the porous alumina substrate (comparing Fig. 3c with Fig. 3d), showing that the LTA precursor solution had partially penetrated into the substrate. This was beneficial since the adhesion stability of the LTA membrane to the porous alumina support could thus be strengthened.

3.2. Preparation of zeolite SOD membrane

According to our previous work [35], zeolite SOD membranes were prepared with a repeated synthesis method. Fig. 4 shows the top view and the cross section of a zeolite SOD membrane prepared by repeated synthesis. After two steps of hydrothermal synthesis, the surface of the $\alpha\text{-Al}_2\text{O}_3$ support has been completely covered by a tightly packed SOD layer with a thickness of $8\ \mu\text{m}$, and no visible intercrystalline defects can be observed. The XRD results confirm that a pure zeolite SOD membrane with high crystallinity has formed on the alumina

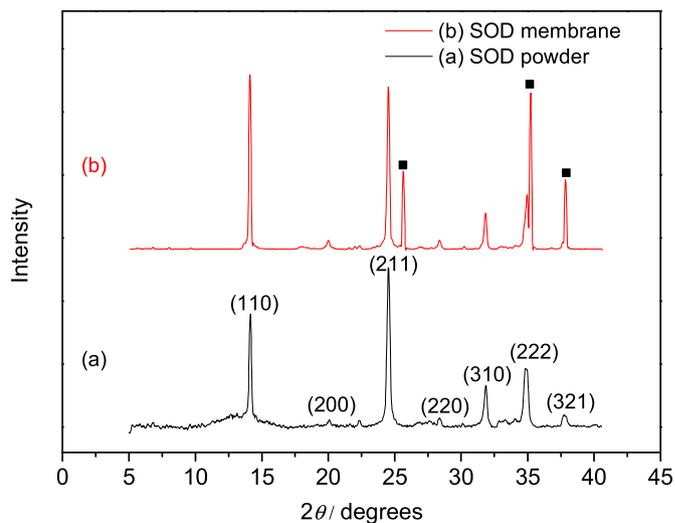


Fig. 5. XRD patterns of the zeolite SOD membrane (b) compared with zeolite SOD powder (a). (■): Al_2O_3 support (not marked): zeolite SOD.

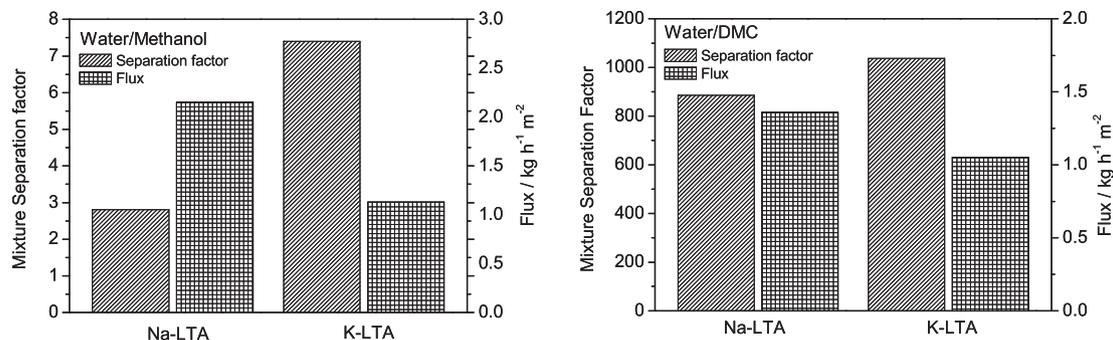


Fig. 6. Mixture separation factors and fluxes of the pervaporation for water against methanol (left) and water against DMC (right) through the supported Na-LTA membrane and ion-exchanged K-LTA membrane at room temperature.

Table 1

Mixture separation factors and fluxes for the pervaporation of water from methanol and DMC through the supported Na⁺-LTA and K⁺-exchanged LTA membrane at room temperature.

Component	Na ⁺ -LTA membrane				K ⁺ -LTA membrane			
	H ₂ O	MeOH	H ₂ O	DMC	H ₂ O	MeOH	H ₂ O	DMC
$x_{\text{feed}}/\text{wt}\%$	5.0	95.0	5.0	95.0	5.0	95.0	5.0	95.0
$x_{\text{permeate}}/\text{wt}\%$	13.1	86.9	97.9	2.1	28.2	71.8	98.2	1.8
Separation factor	2.8		886		7.4		1037	
$J/\text{kg h}^{-1} \text{m}^{-2}$	2.15		1.36		1.13		1.05	

support after the repeated synthesis (Fig. 5), and no foreign phase is present by referring to the XRD. Compared to the XRD patterns SOD powder, the SOD membrane shows an obviously higher (110) peak, which indicates that an oriented SOD membrane was formed on the alumina support with their (110) face perpendicular to the support surface.

3.3. Pervaporation results of LTA membranes before and after K⁺ ion-exchange

Fig. 6 and Table 1 show separation factors and fluxes of the pervaporation experiments for H₂O/MeOH and H₂O/DMC mixtures through supported Na-LTA and K-LTA membranes at room temperature. After K⁺ ion-exchange, the separation factor for the H₂O/MeOH mixture increased from 2.8 to 7.4, while the separation factor for a H₂O/DMC mixture increased from ~800 to ~1000. Simultaneously, the water fluxes through the membranes after K⁺

Table 2

Single gas permeances of H₂O, H₂ and CO₂ as well as mixture separation factors determined for equimolar mixtures acc. to Eq. (5) of H₂O/H₂ and H₂O/CO₂ through the SOD membrane at different temperatures.

Temperature (°C)	Permeance (mol m ⁻² s ⁻¹ Pa ⁻¹)			Mixture separation factor	
	H ₂ O	H ₂	CO ₂	H ₂ O/H ₂	H ₂ O/CO ₂
125	6.37×10^{-8}	1.79×10^{-8}	2.03×10^{-9}	8.1	31.4
150	6.50×10^{-8}	2.13×10^{-8}	2.84×10^{-9}	6.7	28.4
175	6.54×10^{-8}	2.88×10^{-8}	5.56×10^{-9}	5.2	25.2
200	6.59×10^{-8}	3.28×10^{-8}	6.84×10^{-9}	4.6	22.6

ion-exchange decreased. Since the pore size of the zeolite Na⁺-LTA is 4.1 Å, DMC is spontaneously excluded from the LTA cages due to a molecular sieving effect. As a result, a H₂O/DMC mixture separation factor as high as 800 could be obtained on the Na⁺-LTA membrane. However, for the H₂O/MeOH mixture on Na⁺-LTA membrane, a mixture separation factor of $\alpha = 2.8$ was measured, since the kinetic diameter of MeOH (3.8 Å) is smaller than the pore size of Na-LTA (4.1 Å).

3.4. Single and mixed gas permeation of SOD membranes

The single gas permeances of H₂O, H₂ and CO₂ as well as the separation factors of H₂O/H₂ and H₂O/CO₂ mixtures through the SOD membrane were evaluated in the temperature range from 125 to 200 °C. Related results, which were partly reported in our previous work [27], are summarized in Fig. 7 and Table 2.

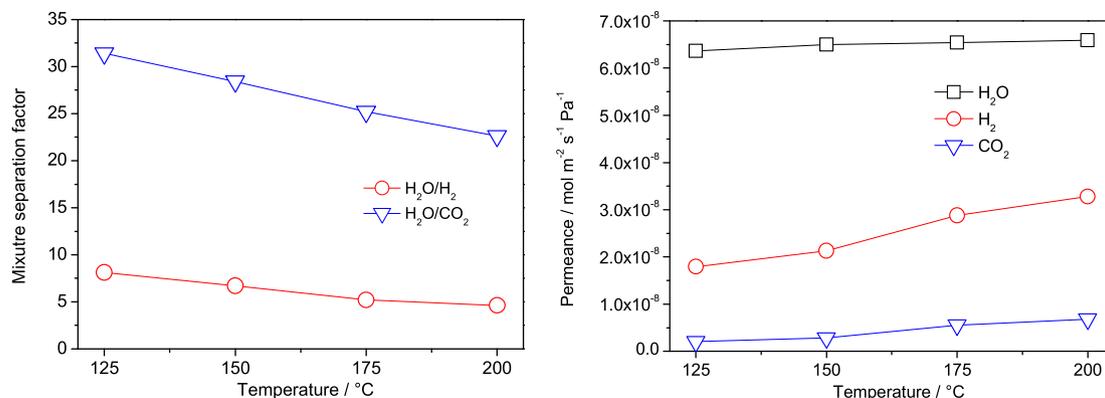


Fig. 7. Mixture separation factors of equimolar mixtures of H₂O/H₂ and H₂O/CO₂ as well as single gas permeances of H₂O, H₂ and CO₂ through a supported zeolite SOD membrane prepared by two-step repeated hydrothermal synthesis as a function of temperature.

Table 3
Single gas permeances of H₂O, MeOH, DME and DMC as well as mixture separation factors of H₂O/MeOH, H₂O/DME and H₂O/DMC through the SOD membrane at different temperatures.

Temperature (°C)	Permeance (mol m ⁻² s ⁻¹ Pa ⁻¹)				Mixture separation factor		
	H ₂ O	MeOH	DME	DMC ^a	H ₂ O/MeOH	H ₂ O/DME	H ₂ O/DMC
125	6.37 × 10 ⁻⁸	3.50 × 10 ⁻¹⁰	2.90 × 10 ⁻¹⁰	<5 × 10 ⁻¹¹	180	220	>1000
150	6.50 × 10 ⁻⁸	2.80 × 10 ⁻¹⁰	2.87 × 10 ⁻¹⁰		228	226	
175	6.54 × 10 ⁻⁸	2.72 × 10 ⁻¹⁰	2.71 × 10 ⁻¹⁰		235	241	
200	6.59 × 10 ⁻⁸	2.75 × 10 ⁻¹⁰	2.60 × 10 ⁻¹⁰		233	253	

^a Since the area of the peaks of DMC, which was detected by gas chromatography was too small to integrate, the permeance of DMC cannot be evaluated exactly, when it was smaller than 5 × 10⁻¹¹.

The hydrophilic zeolite SOD membrane can be not only applied to separate steam from small gas molecules like H₂ and CO₂, but it also works well in the steam separation from larger molecules like MeOH, DME and DMC. Table 3 summarizes the separation performance of our zeolite SOD membrane for H₂O from MeOH, DME and DMC at temperatures from 125 °C to 200 °C. The removal of H₂O from MeOH, DME and DMC is also successful in the whole temperature range due to the hydrophilicity of the SOD membrane additionally supported by the molecular sieving effect. For instance, the separation factors of H₂O against MeOH, DME and DMC at 200 °C were around 230, 250 and >1000, respectively. Different to the steam separation from small molecules, when the temperatures increased from 125 to 200 °C, the mixture separation factors for the separation of H₂O from large molecules were improved, while the H₂O permeance also increased slightly, thus indicating an activated diffusion process. Owing to the extremely small pore size of SOD, large DMC molecules cannot permeate through a dense SOD membrane. The performance of SOD membrane to separate steam from either small gas molecules or large molecules like DME and DMC recommends SOD membrane an ideal candidate for the methanol, DME and DMC synthesis in membrane reactors with water removal.

4. Conclusions

Two hydrophilic zeolite membranes have been evaluated for the water separation from MeOH, DME and DMC: zeolite LTA membrane for pervaporation at room temperature, and zeolite SOD membrane for steam separation at high temperature up to 200 °C. A well-intergrown LTA membrane with a thickness of about 3.5 μm could be obtained on the APTES-modified α-alumina support. After the ion-exchange with K⁺ for 12 h, the structure of the membrane remained unchanged but the free pore diameter of the 8-membered oxygen ring as bottleneck of the LTA membrane was reduced, which resulted in an increase of the selectivity but decrease of the permeance for the separation of water/methanol by pervaporation at room temperature. On the other hand, the LTA membrane was also suitable for the separation of water/DMC by pervaporation showing a high separation performance with a selectivity of around 800 and 1000, before and after ion-exchange, respectively.

With a repeated hydrothermal synthesis, a dense SOD membrane with a thickness of about 8 μm could be formed on the alumina support. The hydrophilic SOD membrane was also water selective, and displayed a high performance for the separation of steam from small gas molecules like H₂ and CO₂, which participated in the synthesis of DME and DMC. Moreover, water could also be separated successfully from MeOH, DME and DMC at high temperatures from 125 to 200 °C by using the SOD membrane.

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