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Fabrication and characterization of highly crystalline mordenite membranes on α-alumina disks via a seeded in situ template-free hydrothermal treatment

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Abstract A template-free seeded short-time in situ hydrothermal treatment was carried out in a brass autoclave to synthesize crystalline mordenite (MOR) membranes on alumina-silicate disk supports with micro-scale pores. According to XRD analysis, MOR was the only zeolitic material present in the membrane layers on the supports. SEM examination of the membranes showed three different layers of the membrane thickness: (i) support sub-layer, (ii) mix penetrated mid-layer, the MOR crystals filling the pores among the support (about 4–5 μm), and (iii) MOR top-layer (about 4–5 μm). The crystalline bonds between MOR crystals of the membrane top-layer and the crystals of the support were clearly observed within the mid-layer. The continuous top-layer of zeolitic membrane was formed by many large and well-shaped crystals. The seeding treatment significantly enhanced the formation of MOR crystals onto the surface of the supports. EDAX analysis showed a Si/Al ratio of 6.8 for the MOR layer of the membrane. Due to their hydrophilic natures, the polycrystalline MOR membranes were found to be selective for continuous dehydration of different EtOH–water mixtures through an adsorption–diffusion–desorption mechanism. Both total permeation flux and separation factor of the membrane were found to increase by increasing temperature and water concentration of feed. The continuity and high crystallinity of the membrane top-layer led to the fairly high dehydration of EtOH. It was found that there was no pinhole within the layer and the morphology of the membrane was almost defect-free.

Keywords Mordenite membranes · Seeded hydrothermal treatment · Aluminasilicate disk supports · Pervaporation · Ethanol dehydration

1 Introduction

Zeolites, microporous aluminosilicate crystals, have widely been used as adsorbents, catalysts, and ion exchangers. In addition to their high thermal, chemical, and structural stability, zeolite micropore (<2 nm) systems uniquely recognize molecules by molecular sieving and/or preferential adsorption. Therefore, researchers have been motivated to apply them to membranes and membrane reactors, as well as a variety of applications ranging from microelectronics to medical diagnosis (Hernandez et al. 2000; McLeary et al. 2006; Matsukata et al. 2008). Zeolite membranes are commonly synthesized by in situ hydrothermal synthesis onto porous supports, with or without a previous seeding step. Seeding of the supports leads to a higher reproducibility in the synthesis of the zeolite membranes (Chau et al. 2000; Ahunbay et al. 2005). LTA-type zeolite membranes having strong hydrophilic nature have industrially been applied to solvent (ethanol and 2-propanol, etc.) dehydration since 1998 (Morigami et al. 2001; Caro et al. 2005). However, application of LTA zeolite membranes is limited to use under mild conditions

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due to its instability in acidic media and at high temperatures. Stability of zeolites can be enhanced with increasing the Si/Al ratio in its framework, trading-off hydrophilicity. However, a siliceous MFI (i.e. silicalite-1)-type zeolite membrane, for example, has no exchangeable cation while being hydrophobic and stable (Lai et al. 2003). Zeolite membranes with medium Si/Al ratios are expected to have both high stability and ability of ion exchange. MOR, having large nano-scale channels of 0.67 × 0.70 nm and small nano-scale channels of 0.26 × 0.56 nm, has medium Si/Al ratios around 5, and shows high stability and large ion exchange capacity. The pore size and adsorption properties of MOR can be controlled by the choice of exchanged cation.

MOR membranes have been prepared by different methods: vapor phase transport method (Nishiyama et al. 1995, 1996, 1997), direct (unseeded) hydrothermal synthesis with (Yamazaki and Tsutsumi 1997a, b; Salomon et al. 1998; Piera et al. 1998; Bernal et al. 2000) or without (Suzuki et al. 1990; Yamazaki and Tsutsumi 1995, 1997a, b; Gump et al. 2001; Li et al. 2001) template, and seeded hydrothermal synthesis (Lin et al. 2000; Matsukata 2001). In 1990, a MOR membrane was first synthesized on a porous silica-alumina plate by in situ hydrothermal synthesis (Suzuki et al. 1990; Kazemimoghaddam and Mohammadi 2010). In 1995, a defect-free MOR membrane was synthesized on a porous α-alumina disk by vapor-phase transport method (Nishiyama et al. 1995, 1996). This membrane showed a good separation factor of 160 for PV of a benzene/p-xylene mixture. MOR membranes on a tubular α-alumina support were also synthesized using in situ hydrothermal synthesis, using tetraethylammonium hydroxide (TEAOH) as a structure-directing agent (SDA) (Salomon et al. 1998; Piera et al. 1998). Some MOR membranes, under organic SDA-free conditions, were synthesized on α-alumina tubular supports and the effect of seeding was also studied (Lin et al. 2000; Matsukata 2001). When synthesizing a membrane on a support seeded with MOR nano-crystals, the membrane exhibited a very high separation factor of 3360 for a water–isopropyl alcohol mixture (Matsukata 2001), whereas a MOR membrane that was formed on an unseeded support attained a separation factor of only 192. MOR membranes were also fabricated using seeded template-free in situ hydrothermal treatment on cylindrical mullite supports (Asghari et al. 2008). MOR was the only crystalline phase in the membrane and its Si/Al ratio was 6. Small inter-crystalline defects and a pin-hole-free structure of the membrane layer led to high water selectivity of the membranes in water/ethanol PV.

As mentioned, some attempts were made for preparation of MOR membranes by direct hydrothermal synthesis without using SDA (or template) (Suzuki et al. 1990). This is interesting because template-free membranes do not require calcination at high temperatures to remove the template, and this helps to preserve integrity of the membranes and presence of surface OH groups, that contribute strongly to their adsorption characteristics.

Mordenite crystals and layers were typically synthesized in long durations via in situ hydrothermal treatments, such as 24 h (Navajas et al. 2002; Li et al. 2005), 48 h (Li et al. 2007a, b), 3 days (Lu et al. 2004), and 6 days (Mohamed and Katib 2006). In this work, an uncomplicated seeded short-time (14 h) in situ template-free hydrothermal treatment was developed to fabricate a high crystalline layer of MOR on aluminasilicate disk supports. In addition to structural characterization, such as XRD, SEM and EDAX, PV properties of the membranes were evaluated. Since PV has become one of the most promising candidates for efficient and energy-saving separation processes, especially for dehydration of aqueous solutions (Hu et al. 2007; Sato et al. 2011), the dehydration of aqueous ethanol was assessed to operationally characterize the MOR membranes.

2 Experimental methods

2.1 Materials

Asymmetric aluminasilicate disks containing micro-pores (diameter: 20 mm, thickness: 1.2 mm, average pore size: 0.5–2.0 μm, porosity: 30–50) were used as ceramic supports to provide the membranes with high mechanical strength. A commercial high-silica H-mordenite (CBV-90A, Lot Number 1822-42, Zeolyst Corp., Valley Forge Pa, Si/Al = 45) was used as seed for hydrothermal treatment in order to promote the crystallinity of the zeolite layer. Sodium silicate solution (Merck), sodium aluminate powder (Merck), and deionized (D.I) water were the reagents used for preparation of the MOR membranes.

2.2 Membrane preparation

For a rubbed seeding treatment, the milled powder of the commercial H-mordenite was added to D.I. water to make a 2–5 weight percent suspension. The suspension was then placed in an ultrasonic bath for 1–2 h so that the probably flocculated grains were separated into parts. The suspension was then dried in a flat plate overnight. The remaining powder was used for seeding treatment. One side of the support was polished and the smoothed surface was rubbed using the fine powder. The disk was knocked on the cupboard several times to release larger grains of the powder from the surface. The other side of the support was wrapped with Teflon tape to avoid adhesion and growth of the zeolite crystals during the hydrothermal treatment. The support was then ready to use in the in situ hydrothermal treatment.

The in situ hydrothermal treatment was arranged to synthesize the MOR membranes. The synthesis gel was a homogeneous solution including the molar ratios of $SiO_2/Al_2O_3 = 32$, $H_2O/SiO_2 = 23$ and $NaOH/Al_2O_3 = 21$. The Si and Al source solutions were individually prepared in separate pots. The silica source solution was then added quickly to the alumina source solution accompanied by vigorous stirring. As an aging treatment, this parent solution was stirred at 298 K for 30 min.

For the in situ hydrothermal treatment, the seeded disk was stuck to a Teflon holder and fixed vertically into a brass autoclave. The aged parent synthesis solution was then poured into the autoclave to soak the disk support. The autoclave was then placed vertically in an oven at 443 K. After the 14 h crystallization, the autoclave was gently cooled in the off oven, then in air for a few hours. The disk MOR membrane was washed with plenty of D.I. water and dried at 383 K. The crystalline powder product that precipitated at the bottom of the autoclave was also collected, filtered, washed and dried at 383 K overnight.

2.3 Membrane characterization

SEM examinations were used to observe morphologies of the membranes and the crystals. Thicknesses of the membrane top-layers and the mix penetrated mid-layers were also observed and determined using SEM. XRD analyses were also applied for phase identification of the mordenitic layers of the composite MOR membranes. The compositions of the membranes were also determined using EDAX analysis.

2.4 Assessment of PV properties

Dehydration properties of the MOR membranes were determined using PV of EtOH–water feeds. A PV continuous system, including a polyethylene module, was used to perform the assessment. Vacuum of ~110–120 mmHg (abs.) was applied to the permeate side of the module. The permeate (vapor) in the vacuum stream condensed and was collected.

Prior to each run at a given feed composition, the membranes were dried at 393 K for about 12 h under a temperature-programmed condition (heating and cooling rates of 0.5 K/min) to remove any contaminants. Binary EtOH–water mixtures were used as feed. The collected permeate samples in each PV run were weighed. The PV fluxes (kg/m^2 h) of the membranes were calculated as follows:

$$J = w/(S \cdot t)$$

where w is the permeate weight, S is the effective permeable area of the membrane, and t is duration of the PV run. Separation factors of the membranes were also determined as follows:

$$\alpha_{water/EtOH} = (y_{water}/y_{EtOH})/(x_{water}/x_{EtOH})$$

where x and y are the molar fractions of the components in the feed and the permeate, respectively.

3 Results and discussion

Concluding EDAX analysis, Si/Al ratio of the MOR top-layer of the composite membrane was about 6.8.

The XRD of the scratched zeolite is identical with the XRD of MOR. The surface and cross-sectional SEM images of the MOR membrane are presented in Fig. 1. The images reveal the presence of a homogeneous and intergrown layer of well developed, small (about 2–3 μm) MOR crystals on the surface of the disk support. As observed in the image of the membrane surface in Fig. 1a, a layer of MOR crystals continuously covered the surface

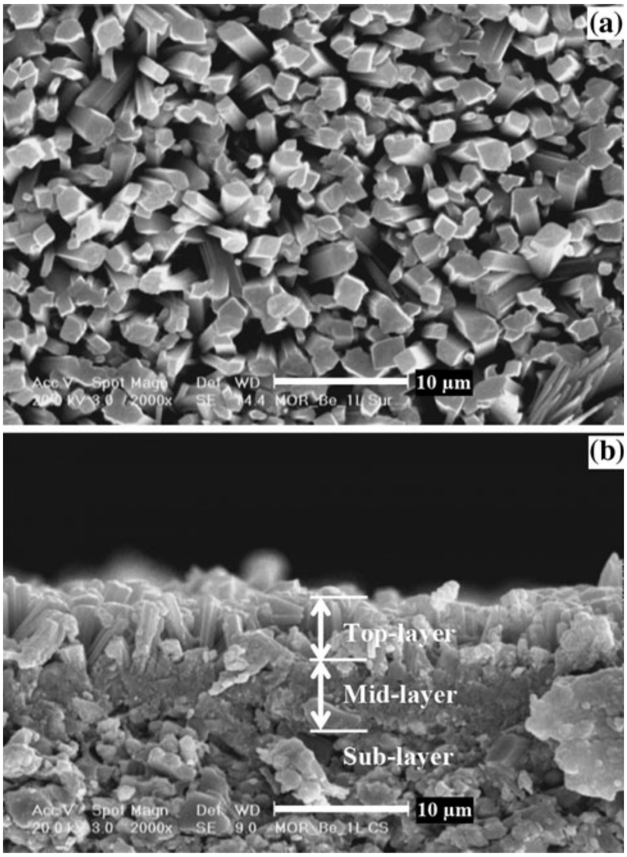

Fig. 1 SEM images of the MOR membrane: **a** surface **b** cross-section

of the disk. It is obvious that the uniform tetrahedral MOR crystals stood vertically, in parallel queues, close to each other. This special manner of crystal growth may be due to the prior MOR seeding treatment. The cross-sectional SEM image of the membrane in Fig. 1b shows three obviously different ceramic layers including: (i) ceramic support sub-layer, (ii) mix penetrated crystalline underlying mid-layer, and (iii) highly crystalline MOR top-layer. As seen in the image, the MOR crystals penetrated through the micro-scale pores of the support about 4–5 µm in depth. The formation of the mid-layer where the MOR deposition is abundant can be due to the penetration of the synthesis gel into the support and, as a result, the subsequent synthesis inside the pores (Bernal et al. 2001; Casado et al. 2003; Asghari et al. 2008; Dutournie et al. 2011). The penetration of MOR crystals made this mix mid-layer continuous and highly dense. Therefore, one can conclude that there is no pinhole (defect) in the surface. Also, the adhesive crystallinity of the MOR layer onto the support led to close intergrowth between the zeolite top-layer and the pores of the support. As observed in the figure, the prismatic MOR crystals twisted into each other and formed the polycrystalline top-layer of the membrane with a thickness of 4–5 µm. As seen, there is not any aggregate (Casado et al. 2003), with lumps of randomly oriented crystals, probably nucleated in the bulk of the liquid phase and then precipitation on the zeolite film. It means that the seeding treatment can reliably accelerate zeolite crystallization on the surface of the support, in comparison with nucleation in the bulk of the liquid phase.

The well-shaped, uniform crystals in the top-layer, in comparison with the various crystals collected from the bottom of the autoclave, can also be due to the seeding treatment. The fine MOR seeds on the surface and in the pores of the disk support led to an accelerated nucleation during the in situ hydrothermal treatment. On the other hand, the nucleation phenomenon in the bulk, far from the surface, took place randomly without any seed motivation. As a result, there is no harmony between the crystals nucleated and grown in the bulk; not only in shape, but also in size.

As mentioned before, the MOR membranes supported using seeded disks, via the in situ hydrothermal treatment, were evaluated in PV dehydration of EtOH–water mixtures. The operational conditions, permeation fluxes and separation factors of the membranes for different feed mixtures are listed in Table 1. Acceptable separation factors were obtained in the EtOH dehydration processes for all feed compositions. It can be concluded that the membranes have negligible intercrystalline pores and pinholes, and are almost defect-free. The relatively low permeation fluxes confirm the defect-free structure of the membranes. The hydrophilic nature of the MOR membranes is believed to be responsible for the dehydrations.

Table 1 PV dehydration experiments of EtOH–water feed mixtures using the MOR membranes

Feed		Permeate		
EtOH (w %)	Temperature (K)	Pressure (abs. mmHg)	J (kg/m^2 h)	$\alpha_{\mathrm{Water/EtOH}}$
50	298	120	0.42	13.8
50	325	120	0.65	27.0
70	298	110	0.23	9.3
70	320	110	0.35	19.1

Vacuum pressures of the PV dehydration experiments are also listed in Table 1. Figure 2 shows variations of the dehydration fluxes versus EtOH composition in the feed at different feed temperatures. As observed, the permeation fluxes at a constant temperature decrease by increasing EtOH composition. The coverage of the zeolitic pores by EtOH might be the reason (Asghari et al. 2008). MOR is a hydrophilic zeolite and tends to adsorb and pass water molecules. Conversely, availabilities of the mordenitic sites for permeating water molecules are limited by increasing EtOH molecules near the adsorption sites of the hydrophilic MOR zeolite. As a result, the adsorption and passage of the water molecules are influenced. As a matter of fact, the more coverage of the sites by EtOH molecules led to the less adsorption and passage of water molecules through the MOR layer. Consequently, the total permeation flux (including water and EtOH fluxes) decreases due to the more coverage of the hydrophilic sites of the MOR layer by EtOH molecules.

Upon closer inspection of Fig. 2, it is also found out that the total permeation flux at a constant feed composition increased due to increasing temperature. Two main factors

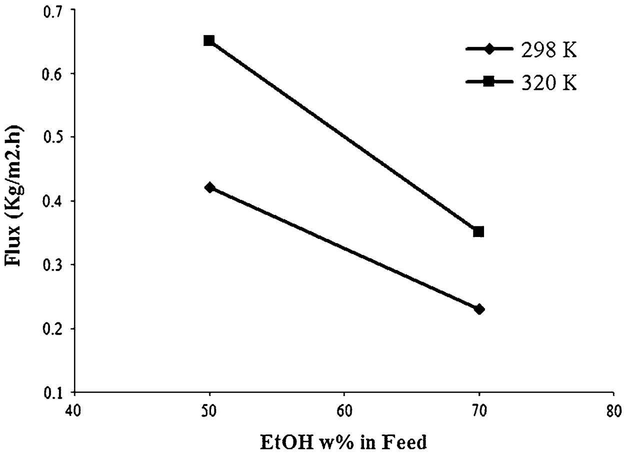

Fig. 2 Dehydration fluxes versus EtOH concentration at different feed temperatures

may lead to this elevation. Increasing temperature causes the adsorption phenomenon on the mordenitic sites to be promoted. Since the evaporation phenomenon takes place through the membrane layers during PV, increasing temperature and being closer to the boiling points of the constituting components in the feed under given circumstances may affect and promote pervaporative properties of the zeolitic membrane in total flux and separation factor. This means that the total permeation flux of the membrane increases with temperature.

In comparison to other works, the performance of MOR zeolite membrane of this study was better than LTA zeolite membrane of Li et al. (Li et al. 2007a, b). The concentration of water in PV permeate of LTA membrane was more than that of the MOR membrane. On the other hand, the EtOH concentration of permeate in this study in flux of 0.2 was about 20 wt% and lower than that of Cho et al. (Cho et al. 2010).

Separation factors of the MOR membranes versus EtOH composition in the feed at different feed temperatures are presented in Fig. 3. It is obvious that the separation factor decreased by increasing EtOH composition in feed. As mentioned above, the coverage of the membrane layer by either EtOH or water molecules is the major factor influencing the membrane selectivity. In other words, the more the hydrophilic sites of the membrane are exposed to water molecules, the more adsorption of water onto the sites can occur due to their hydrophilicity, and the less adsorption of EtOH. This means that the water selectivity of the membrane layer may become limited if the water coverage decreases or the EtOH coverage increases.

Figure 3 shows that the separation factor increases with increasing temperature in a given feed composition. As known, the governing mechanisms of zeolitic PV systems are adsorption-diffusion and molecular sieving. While temperature increases, diffusion rate is promoted. As a result, the water selectivity of the membrane is enhanced with increasing temperature.

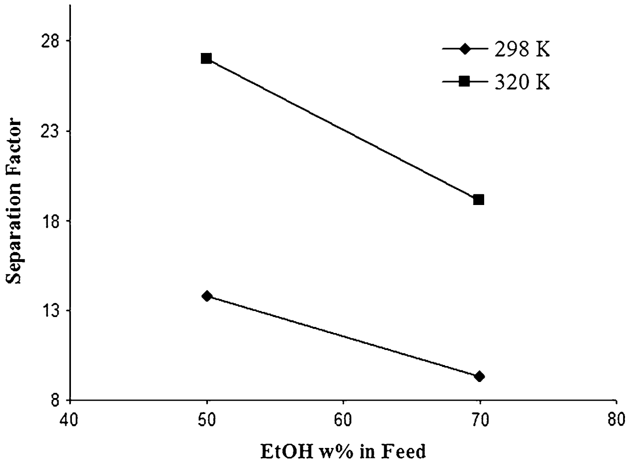

Fig. 3 Dehydration separation factors versus EtOH concentration at different feed temperatures

4 Conclusion

A seeded short-time in situ hydrothermal treatment was used to fabricate composite MOR membranes on pretreated disk supports. The MOR phase, as a single phase, was observed in the powders scraped from the membrane surface and collected from the bottom of the autoclave, as a single phase with no other crystalline phases in parallel. Also, cross-sectional SEM images of the membranes showed three clearly different layers of the composite MOR membranes: (i) ceramic support sub-layer (ii) mix (penetrated MOR within support pores) underlying mid-layer, and (iii) highly dense crystalline MOR top-layer. Large, intergrown, prismatic crystals—as a continuous polycrystalline zeolite layer grown from the seeds deposited on the support, without any aggregation onto the zeolite film—were clear when observed in the SEM images. It also revealed that the seeding treatment can reliably accelerate zeolite crystallization on the support surface. The SEM images showed that the MOR crystals penetrated through the micro-scale pores of the support about 4–5 μm in depth and the prismatic MOR crystals twisted into each other and formed the polycrystalline top-layer of the membrane with a thickness of 4–5 μm.

Due to their hydrophilic natures, the polycrystalline MOR membranes were found to be selective for continuous dehydration PV of different EtOH–water mixtures through an adsorption–diffusion–desorption mechanism. In this mechanism, preferential water adsorption occurs, while permeation of alcohol through zeolitic and small non-zeolitic pores is hindered. Thus, those conditions that favor the adsorption of water molecules, and/or enhance the mobility of adsorbed molecules, led to maximum separation factors. Both total permeation flux and separation factor of the membranes were found to increase by increasing feed temperature and water concentration in feed.

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