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Scale-up of high performance mordenite membranes for dehydration of water-acetic acid mixtures

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ABSTRACT

Mordenite membranes have been successfully synthesized on 80-cm-long mullite supports by secondary growth method. The morphology and quality of mordenite membrane were greatly affected by fluoride concentration, water content and crystallization mode. Compact and high-flux mordenite membranes were obtained with the addition of NaF in precursor gel, which also exhibited a long-term acid stability for a 90 wt% HAc/H_2O mixture at 75 °C. Typically, 80-cm-long mordenite membrane prepared with transverse crystallization displayed a permeation flux of ca. 0.97 kg m^{-2} h^{-1} and separation factor of ca. 1200 for separating a 90 wt% HAc/H_2O mixture at 75 °C. The pervaporation performance was better than that of membranes prepared with vertical crystallization due to the negligible impact of gravity and temperature gradients. These scaled-up mordenite membranes with high reproducibility showed a promising industrial application for dehydration of water-acetic acid mixtures.

1. Introduction

Acetic acid is of great importance as a basic organic chemical material in acetic acid related chemical industries [1]. The current azeotropic distillation and extractive distillation for acetic acid dehydration have energy-intensive, low efficiency and close volatility between water and acetic acid [2]. By comparison with conventional dehydration processes, membrane pervaporation has attracted widespread attention due to easy control, efficiency and energy saving [3,4]. Especially, zeolite membranes with tunable hydrophilicity and acid resistance have wide prospects for dehydration of water-acetic acid mixtures [5–7].

NaA zeolite membrane firstly prepared from a lab-scale to an industrial-scale is the only commercialized zeolite membrane for ethanol dehydration in the actual industrial production [8,9]. In the past two decades, many efforts have been made for scale-up of various zeolite membranes including CHA [10,11], T [12], NaY [13], SAPO-34 [14], DDR [15] and MFI [16,17] for the purpose of industrial application. However, these above membranes mainly applied to alcohol dehydration and gas separation are constrained in acidic solution dehydration application due to their poor acid resistance and low fluxes. Recently, highly acid-stable mordenite membranes for dehydration of water-acetic acid mixtures have attracted extensive attention [18–32]. Mordenite membranes, with a moderate Si/Al ratio (3–10) and regular pore size (6.5 × 7.0 Å), show excellent acidic-resistant property and hydrophilicity, which is a potential candidate for separating water from acetic acid solutions [18,32].

Generally, the synthesis methods of mordenite membranes can be summarized into two main strategies: (i) the fluoride-free system, i.e., no fluoride anions are introduced into the precursor gel [19–26] and (ii) the fluoride-containing system [27–32]. In the former fluoride-free system, the application of mordenite membranes was mainly for dehydration of water-ethanol mixtures [19–23]. Only a few literatures reported that mordenite membranes applied to the separation of low concentration acetic acid solution showed well separation performance [24–26]. Alternatively, high-quality and acid-stable mordenite membranes were easier to obtain when the precursor solution contained fluoride anions [27–32]. Chen et al. [27] showed that fluoride anions played a role of structural guide agent, which could promote defect-free mordenite membrane fabrication. Subsequently, mordenite membranes prepared by Li et al. [28] in a fluoride-containing dilute solution by microwave synthesis, exhibited a high flux of 0.87 kg m^{-2} h^{-1} for 90 wt% HAc/H_2O at 75 °C. In our previous studies [29–31], mordenite

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membranes fabricated from fluoride-containing precursor gel showed excellent performance for dehydration of water-ethanol and water-acetic acid solutions. Recently, a reproducible and acid-stable mordenite membrane rapidly prepared by conventional hydrothermal secondary synthesis displayed a total flux of 0.84 kg m^{-2} h^{-1} for 90 wt% HAc/H_2O at 75 °C [32]. By comparison with the industrialized NaA membrane, however, the relatively low flux of mordenite membrane is far away from the request of industrial application. Therefore, the enhancement of flux as well as high reproducibility are still the main challenges for industrial application of mordenite membranes.

In this work, mordenite membranes were rapidly prepared on macroporous mullite supports in a fluoride-containing precursor gel by secondary growth method. The effects of NaF/SiO_2 ratio and H_2O/SiO_2 ratio in gels were investigated systematically to improve the permeation flux of mordenite membranes. Long-term acid resistance was studied by continuous dehydration of acetic acid of mordenite membranes. Furthermore, mordenite membranes scaled-up from 10 cm to an industrial scale of 80 cm with different crystallization modes were analyzed in detail. The pervaporation performance and reproducibility of 80-cm-long mordenite membranes were extensively studied for dehydration of water-acetic acid mixtures.

2. Experimental

2.1. Preparation of mordenite membranes

Mordenite membranes were prepared on 10-cm-long mullite supports (Noritake, inner diameter = 9 mm, out diameter = 12 mm, pore diameter = 1.3 μm) in a fluoride-containing precursor gel by secondary growth method. The mordenite seed crystals (HS-642, SiAl = 9, Wako) were used as seed and the detailed seeding process was described in our previous studies [30–32]. The synthesis solution had a molar composition of SiO_2: 0.08Al_2O_3: 0.25Na_2O: xNaF: yH_2O. The sodium aluminate ($NaAlO_2$, Al/NaOH = 0.77, Wako) and sodium hydroxide (NaOH, 97 wt%, Wako) were dissolved in deionized (DI) water to obtain the aluminate solution. The silicate solution was prepared by diluting colloidal silica (AS-40, 40 wt%, Aldrich) with DI water. The fluoride solution was prepared by dissolving sodium fluoride (NaF, 99 wt%, Wako) into DI water. The final precursor gel obtained by mixing three solutions and aging for 6 h at room temperature and then poured into a stainless steel autoclave. The hydrothermal crystallization was performed in an air oven at 170 °C for 5 h [32]. After synthesis, the as-synthesized membranes were repeatedly washed with DI water and dried overnight. For comparison, mordenite membranes were prepared in the fluoride-free gel under optimal synthesis procedure.

80-cm-long mordenite membranes were fabricated on mullite supports under optimal synthesis conditions as discussed above. The seeding process and the preparation procedure of precursor gel were identical to those of 10-cm-long mordenite membranes. All reagents of the precursor gel were replaced with low-cost industrial-grade chemicals, which required only 2% prices of the analytical reagents. Four seeded supports were placed vertically in a big stainless steel autoclave containing synthesis gel and then put into a large oven for hydrothermal synthesis. In this work, two kinds of large ovens were used (as shown in Graphical Abstract). After crystallization, the as-synthesized 80-cm-long mordenite membranes were repeatedly washed with DI water and dried.

2.2. Membrane characterization and pervaporation (PV) test

The structures and crystallinity of mordenite membranes were characterized by X-ray diffraction (XRD, Ultima IV, Rigaku) using a Cu-Kα radiation in the 2θ range of 5–45°. The morphologies and thickness of as-synthesized membranes were observed by cold field emission scanning electron microscopy (FE-SEM, SU8020, Hitachi). ^{19}F MAS NMR spectra of the powders were collected on a spectrometer (Advance III 400 WB, Bruker) at 376.4 MHz with 22 kHz magic angle spinning, 4 μs pulses, 10 s recycle delay and 4.96 scans. $CFCl_3$ was used as chemical shift reference. The elemental analysis and Si/Al ratios of mordenite layers were carried out by energy dispersive X-ray (EDX, Q200, Bruker) equipped in the SU8020 machine.

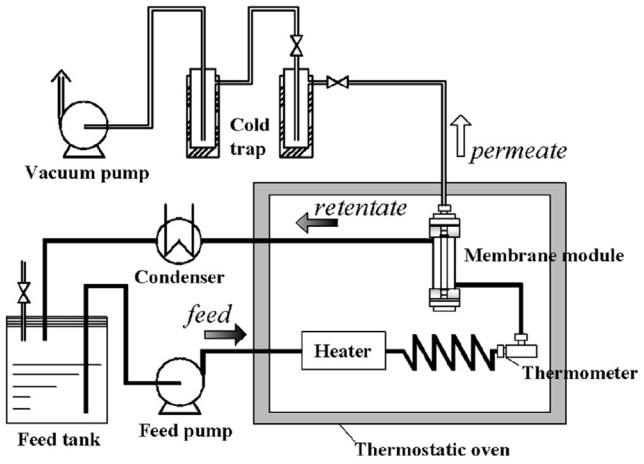

Fig. 1. Schematic diagram of the apparatus for evaluating 80-cm-long mordenite membranes.

PV performance of 10-cm-long mordenite membrane was evaluated by separation for a HAc/H_2O mixture using a PV experimental apparatus described previously [30,32]. The dehydration performance of 80-cm-long mordenite membrane was measured using an apparatus as shown in Fig. 1. The apparatus was illustrated detailedly in our previous study [33]. The feed solution was pumped into a heater for heating to a given temperature before being introduced into membrane module and was then circulated into the feed tank after condensation by liquid nitrogen. The concentrations of feed and permeation were analyzed by a gas chromatograph (GC-14C, Shimadzu) equipped with a TCD detector and a 3 m packed column. PV performance of the membrane was evaluated by the permeation flux (J) and the separation factor (α), defined by equations in the following:

$$J = m/(A \times t)$$

$$\alpha H_2O/HAc = (Y_w/Y_a)/(X_w/X_a)$$

where m, A and t denoted the weight of permeation (kg), the effective membrane area (m^2) and the test time (h), respectively; X_w, X_a, Y_w, and Y_a corresponded to the mass fractions of components w (water) and a (acetic acid) in the feed and permeate, respectively.

3. Results and discussion

3.1. Preparation of high-flux mordenite membranes

3.1.1. Effect of NaF/SiO_2 ratio

Mordenite membranes were prepared in the fluoride-free and fluoride-containing precursor gels, respectively. In order to study the effect of F^-/SiO_2 ratio on mordenite membrane synthesis, NaF as the fluoride source was added into the precursor gel in this study. The surface and cross-sectional SEM images of mordenite membranes prepared with different NaF/SiO_2 ratios are shown in Fig. 2 and their corresponding XRD patterns are shown in Fig. S1. All kinds of zeolite membranes had the characteristic peaks of pure mordenite zeolite in addition to the characteristic peaks of mullite support (Fig. S1). The characteristic peaks intensities of mordenite membranes enhanced with extending NaF/SiO_2 ratios (Fig. S1b–d). In a fluoride-free system, plenty of ellipsoidal crystals were loosely scattered on the poorly intergrown membrane surface (Fig. 2a). The uneven zeolite layer with numerous aggregates of ellipsoidal crystals could be also seen from the