Preparation and characterization of high performance CHA zeolite membranes from clear solution

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ABSTRACT

CHA zeolite membranes with Si/Al ratio of 2–3 have been successfully synthesized on the outer surface of yttria-stabilized zirconia (YSZ) hollow fibers from clear solution for the first time. The influence of synthesis parameters, such as precursor alkalinity, crystallization time and temperature, on the morphologies and dehydration performance of CHA zeolite membrane, were extensively investigated. Pervaporation (PV) results indicated that the separation performances of obtained CHA membranes were strongly influenced by the morphology of the membranes. The optimal synthesis condition was 140 °C for 16 h in the precursor of 22 SiO_2: 1 Al_2O_3: 15 K_2O: 1 Na_2O: 4400 H_2O. The as-synthesized membranes composed of flake-like grains exhibited a water permeation flux of 13.3 kg m^{-2} h^{-1} with separation factor of 6000 for the PV dehydration of 90 wt% ethanol/water mixture at 75 °C. The long-term (> 550 h) acid resistance of the as-synthesized CHA zeolite membranes ensures them the most promising candidate for PV dehydration of organic solvents containing acids.

1. Introduction

Pervaporation (PV) using zeolite membranes, with the advantage of low energy consumptions compared to conventional distillation, has attracted increasing attentions in the separation of organic solvents, especially for azeotropes and close-boiling mixtures [1–5]. In particular, NaA-type zeolite membranes show excellent dehydration performance for mixtures of water and alcohols [6,7]. However, the poor acid stability of NaA zeolite membrane originated from the large aluminum content in the framework (Si/Al =1) confined its applications in neutral systems [8–10]. Although several types of zeolite membranes with higher Si/Al ratio, such as FAU [11], T-type [12,13], MOR [14,15] and MFI (ZSM-5) [16], have been prepared to improve the acid resistance, their dehydration performances (productivity and selectivity) are not comparable to that of NaA zeolite membrane.

CHA zeolite featured with eight-membered-ring channels and large cavities is a promising building block for PV dehydration membranes [17–26]. Specially, the acid resistance of CHA zeolite membrane could be significantly improved because of the tunable Si/Al ratio (2–∞) [17,18,21,25]. In the past few years, many efforts have been made on preparation of CHA zeolite membranes [17–31]. The CHA zeolite membranes with Si/Al ratio of 8 or higher have been synthesized using N,N,N-trimethyl-adamantammonium cation (TMAda⁺) as the struc-

ture-directing agent (SDA) [22,27,28,30]. The strategy of interzeolite conversion has been applied to the fabrication of CHA zeolite membranes to reduce the cost. CHA zeolite membrane with Si/Al ratio of 2–21 has been prepared by secondary growth method using the FAU-type or T-type zeolite directed CHA zeolite seeds in present of organic cation, such as benzyltrimethylammonium cation [21] as well as inorganic cation, such as strontium [17,19,20,24,26]. These CHA zeolite membranes have shown good dehydration performance and excellent acid stability for various organic solvent/water mixtures. A synthetic medium by the use of individual K⁺ as SDA was also developed to fabricate CHA zeolite membranes to further reduce the fabrication cost [18,23]. However, the preparation of pure phase CHA zeolite membranes in milk-like gel is still a challenge in the K⁺ individually controlled synthetic medium as MER crystals could be readily generated in the synthesis process.

Recently, we developed a ball-milled seeding method to prepare CHA zeolite membranes from a synthesis gel containing K⁺ on mullite tube supports [18]. The reduced particle size and lattice defects accelerated the nucleation and intergrowth of CHA zeolite crystals and thus inhibited the generation of MER zeolite crystals. The synthesized membranes exhibited a separation factor of 2980 and a water permeation flux of 2.5 kg m^{-2} h^{-1} for PV dehydration of 90 wt% ethanol solution at 348 K. Previous study showed that the membrane

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permeation flux was significantly influenced by the membrane thickness as well as the support structure [32]. In this work, we try to synthesis CHA zeolite membranes from clear solution to reduce the thickness. Meanwhile, the permeation flux could be further enhanced by the hollow fiber supports due to the large finger-like pores and thinner wall thickness [6,12,24,33,34].

Clear solution synthesis has been widely used to study the nucleation and growth of zeolite [35–38]. Typically, a silica source, is hydrolysed at room temperature in high alkalinity medium to form a transparent suspension, referred to as 'the clear solution'. The state of the precursor liquid varies with the silicon over hydroxide ratio (Si/OH) from a true solution to a transparent sol. Both time and temperature lead to further aggregation, followed by condensation of the species into nanoparticles, which ultimately crystalize into the final zeolite structure. The main difference between syntheses from heterogeneous hydrogels and from clear sols is the presence of the amorphous solid phase during the initial stage of crystallization in hydrogels, which has a direct impact on the crystallization pathways [38]. Some investigations for the zeolite membranes synthesis show that, generally, the milk-like gel with high viscosity would lead to a relatively thicker membrane layer of > 10 μm [18,22,23]. Clear solution synthesis, however, has been proved to be an effective approach to synthesize thinner zeolite membranes [39–46]. Several types of zeolite membranes, including NaA [43,46], T [42,45], FER [44] and MFI [39–41], have been synthesized from clear solutions. Most of these zeolite membranes synthesized using clear solutions possessed thinner layers and higher PV performances compared with those synthesized in milk-like gels [13,33,42]. Solubility of zeolite crystals and the presence of more silica ions for the secondary growth of seeded crystals in high alkalinity medium were expected to provide smaller crystals and consequently increase the possibility of thin zeolite membrane manufacturing [43,45].

Herein, high-flux CHA zeolite membranes were fabricated on yttria-stabilized zirconia (YSZ) hollow fibers from clear solution for the first time. Ball-milled submicron CHA crystals were used as seeds to induce the formation of well-intergrown CHA zeolite membranes. The effects of synthesis parameters, such as precursor alkalinity, crystallization time and temperature, on the morphologies and dehydration performance of CHA zeolite membranes, were investigated extensively. Furthermore, the long-term acid stability of the as-synthesized CHA zeolite membranes was evaluated.

2. Experimental

2.1. Membranes preparation

CHA zeolite membranes were hydrothermally synthesized on homemade YSZ hollow fiber supports by the secondary growth method. The supports had outer/inner diameters of 1.8/1.0 mm, average pore size of ~1.0 μm and porosity of ~36%. Prior to hydrothermal synthesis, ball-milled submicron CHA zeolite particles (ca. 0.22 μm in average particle size) were planted onto the outer surface of a hollow fiber support by vacuum-coating method. Detailed information about seed preparation and ball-mill treatment were described in our previous work [18]. For the vacuum-coating method, one end of support was sealed with a silicone cap and the other end was connected to a pump with vacuum degree of 10 kPa. The support was firstly immersed into D.I. water to remove the gas and then immersed into 0.5 wt% seed suspension for 5 s. After being dried at 75 °C for 2 h, the seeded supports were applied for membranes synthesis. For the secondary growth, the precursor was prepared by mixing sodium aluminate (NaAlO₂, 41 wt% Al₂O₃, Sinopharm Chemical Reagent Co., Ltd, China), potassium hydroxide (KOH, 85%, Shanghai Lingfeng Chemical Reagent Co., Ltd, China), colloidal silica (Ludox SM-30, Sigma-Aldrich), and deionized water. The synthesis precursor was prepared by dissolving potassium hydroxide and sodium aluminate
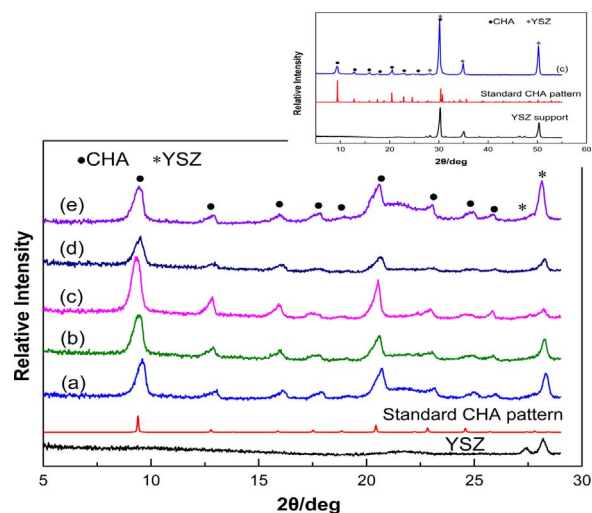

Fig. 1. XRD results of CHA zeolite membranes synthesized at different alkalinity, $K_2O/H_2O=5/4400$ (a), 10/4400 (b), 15/4400 (c), 30/4400 (d), 40/4400 (e).

into deionized water until a homogenous solution was obtained. Then colloidal silica was poured into the solution slowly. The mixture was stirred at 20 °C for 1 h. The molar composition of synthesis solution was 22 SiO_2 : 1 Al_2O_3 : x K_2O : 1 Na_2O : 4400 H_2O, where x was variable from 5 to 45 to get clear synthesis solution. Hydrothermal synthesis was carried out at 130–150 °C for 8–16 h. The as-synthesized membranes were washed with deionized water and dried in an oven overnight before PV tests.

2.2. PV experiments

The as-synthesized membranes were tested for separation of methanol/water, ethanol/water and isopropanol/water mixture by PV experiments. The PV apparatus was illustrated schematically in our previous paper [12]. One end of the membrane was sealed with silicone rubber and the other end was connected to a vacuum line. The membrane was immersed into a feed solution and the lumen side was evacuated by a vacuum pump through the vacuum line, which maintained a downstream pressure of below 200 Pa throughout the operation. The tested membranes had an effective length of about 5 cm unless otherwise stated. The permeated vapor was collected with cold traps cooled by liquid nitrogen. Both of the feed and permeate was analyzed by a gas chromatograph (GC, GC-2014A, Shimadzu) equipped with a thermal conductivity detector. The membrane performance was determined by separation factor (α) and permeation flux (J), which were respectively defined as follows:

$$\alpha_{i/j} = \frac{y_i/y_j}{x_i/x_j} \tag{1}$$

$$J = \frac{w}{A \cdot t} \tag{2}$$

Where x_i and x_j are weight fractions of component i and component j in the feed; y_i and y_j are the corresponding weight fractions in the permeate; w is the total weight of the permeate water, kg; t is the collecting time, h; A is the effective separation area of the membrane.

2.3. Characterizations

The volume particle size distributions and the average particle size of CHA zeolite particles were analyzed by a particle size analyzer (NPA152-31A Zetatrac, Microtrac Inc.); detailed data about particle size distribution was available in our previous work [18]. The morphologies of CHA zeolite particles and membranes were observed