



Full Length Article

Fabrication of high-flux SAPO-34 membrane on α -Al₂O₃ four-channel hollow fibers for CO₂ capture from CH₄

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ABSTRACT

High-performance SAPO-34 membranes were synthesized on α -Al₂O₃ four-channel hollow fibers (4CHF) for CO₂ capture. Original and nano-size ball-milled seeds were adopted to induce SAPO-34 membranes. The effects of synthesis temperature and synthesis time were investigated. A uniform seed layer could be readily formed on external surface of the support by dip-coating with ball-milled seeds. The ball-milled seeds could accelerate the growth of SAPO-34 membrane due to small particle size and surface lattice defects. With induction of ball-milled seeds, high-quality zeolite membrane could be reproducibly prepared with reduced synthesis time. The separation performances of 4CHF supported SAPO-34 membranes were evaluated for separation of CO₂/CH₄ binary mixture. High separation performance with a CO₂/CH₄ separation selectivity of 160 and CO₂ permeance of $1.18 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ was achieved on a membrane induced with ball-milled seeds at 453 K for 18 h.

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1. Introduction

Carbon dioxide capture has been a worldwide concern on reducing global greenhouse gas emission. Separation of CO₂ from CH₄ is important for natural gas processing because CO₂ reduces the energy content and corrodes transportation pipes and storage systems in presence of water [1]. Membrane separation technology is of great interest in CO₂ capture due to its high efficiency and low cost compared to conventional separation technologies such as amine adsorption [2]. Zeolite membrane has been a promising strategy for gas separation due to its high thermal, mechanical and chemical stability. During past years, great efforts have been made to develop CO₂ selective membranes such as T-type [3,4], DDR [5,6], MFI [7], FAU [8], AIPO-18 [9,10] and SAPO-34 membranes [11–28]. Among these membrane materials, SAPO-34 membrane that possesses an analogue structure of chabazite and a pore diameter of 0.38 nm is more appropriate for CO₂/CH₄ separation due to its remarkable properties of molecular sieving and competitive CO₂ adsorption.

Zhang et al. [11] first prepared SAPO-34 membranes on alumina disks by *in-situ* synthesis. They repeated the crystallization process four times to acquire a defect-free membrane layer, which showed single gas permeations in the order: H₂ > CO₂ > N₂ > n-C₄H₁₀. Li et al.

[12] also *in-situ* synthesized a SAPO-34 membrane on tubular stainless steel support, which exhibited a CO₂ permeance of $1.2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ with a CO₂/CH₄ separation selectivity of 170 at 297 K under the feed pressure of 0.2 MPa. However, the *in-situ* hydrothermal synthesis needed to repeat for several times to form a dense membrane layer, which caused high fabrication cost and a thick membrane layer with low gas permeance. To address this issue, the secondary growth method was developed for preparation of SAPO-34 membrane. Li et al. [13] prepared SAPO-34 membranes with TEOH as the structure-directing agent and repeated hydrothermal synthesis for two times at 493 K, the prepared membrane exhibited a CO₂/CH₄ selectivity of 115 and a CO₂ permeance of $4.0 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 295 K. Carreon et al. [14] reduced the crystallization time to 6 h by using multiple structure-directing agent, the obtained membrane showed a CO₂/CH₄ selectivity of 106 and a CO₂ permeance of $1.9 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at the feed pressure of 0.2 MPa. Mohammadi et al. [15] tried to reduce the synthesis temperature at 455 K for 24 h but repeated hydrothermal synthesis was still necessary; the as-prepared membrane showed an ideal selectivity of 51 for CO₂/CH₄ as well as a single CO₂ permeance of $8.2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$.

To date, SAPO-34 membranes were mainly prepared on disk-shaped or tubular supports [12,25–27]. These supports essentially provide low packing density for the membrane modules. Since the processing amount of natural gas is really huge, it is necessary for

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developing high-efficiency membrane separation equipment with low fabrication cost. Porous ceramic hollow fibers have been demonstrated as excellent supports for preparation of zeolite membranes, such as NaA zeolite membrane [29], T zeolite membrane [30]. Due to small diameter, the membranes could provide very high membrane packing density of up to 1000 m² m⁻³ [31], which could reduce fabrication cost of membrane module largely. Moreover, the thin substrate thickness and finger-like structure of hollow fiber supports could reduce transfer resistance for component permeation, which is beneficial to improve permeation flux through the zeolite membranes. However, the fracture load of conventional single-channel ceramic hollow fiber has not yet satisfied the requirement of practical application.

Recently, we successfully prepared a novel α -Al₂O₃ four-channel hollow fiber (4CHF), which showed greater mechanical strength and higher permeability compared to conventional single-channel hollow fiber [31]. We synthesize NaA zeolite membranes on the 4CHF supports, which showed very high permeation flux as well as separation factor for dehydration of ethanol/water solution [32]. In this work, we aimed to prepare high-performance 4CHF-supported SAPO-34 membranes for CO₂/CH₄ binary separation by induction of ball-milled SAPO-34 seeds. We will demonstrate that high-quality SAPO-34 membranes could be formed on 4CHF supports by once hydrothermal synthesis under a mild condition, which provide the feasibility of large-scale production for SAPO-34 membrane.

2. Experimental

2.1. Preparation of SAPO-34 seeds

SAPO-34 seeds were hydrothermally synthesized as referred to [13]. H₃PO₄ (85 wt% aqueous solution, Sigma-Aldrich) and deionized water were first mixed and stirred for 5 min. Al(*i*-C₃H₇O)₃ (98 wt%, Sigma-Aldrich) was then added into the solution. After stirring for 2 h, Ludox AS-40 colloidal silica (40 wt% aqueous suspension, Sigma-Aldrich) was added and the mixture solution was further stirred for 1 h. Organic template tetraethyl ammonium hydroxide (TEAOH, 35 wt% aqueous solution, Sigma-Aldrich) was added finally. The solution was stirred continuously for 48 h at room temperature and loaded in an autoclave for hydrothermal crystallization at 453 K for 24 h. After cooling down, the crystallization product was separated by centrifugation and washed with deionized water. The resulting SAPO-34 seeds were dried overnight and calcined at 823 K for 10 h to remove the occluded template. Two synthesis solutions with molar compositions of 1.0 Al₂O₃: 1.0 P₂O₅: 0.6 SiO₂: 1.2 TEAOH: 55H₂O and 1.0 Al₂O₃: 1.0 P₂O₅: 0.6 SiO₂: 2.0 TEAOH: 55H₂O were used to prepare original SAPO-34 zeolite seeds of S1 and S2, respectively, which had different average particle sizes. S1 particles were further ground to produce S3 particles with a high-energy planetary ball miller (Retsch. Ind. Ltd., PM-100) using zirconium oxide balls as grinding media. The milling treatment was operated for 3 h at a rotating speed of 450 rpm.

2.2. Synthesis of SAPO-34 membranes

SAPO-34 membranes were hydrothermally synthesized on external surface of home-made α -Al₂O₃ 4CHF supports by secondary growth method. The 4CHF supports were prepared by the phase-inversion method described in our previous work [31]. The obtained supports have an average pore size of ~1.0 μ m and outer diameter/inner diameter (O.D./I.D.) of 3.4 mm/0.9 mm. Before membrane synthesis, the α -Al₂O₃ 4CHF supports were ultrasonically cleaned by deionized water and then dried at 373 K overnight. Seeding suspensions were prepared by dispersing 0.5 g

SAPO-34 zeolite into 100 mL of aqueous solution containing 0.05 wt% hydroxypropyl cellulose (HPC, Sigma-Aldrich). The immersing time for dip-coating process was 10–15 s. The seeded supports were dried in an oven at 353 K overnight and then calcined at 673 K for 4 h to improve the binding between seeds and support surface. The synthesis gel was prepared by mixing H₃PO₄ (85 wt% aqueous solution, Sigma-Aldrich), Al(*i*-C₃H₇O)₃ (98 wt%, Sigma-Aldrich) and deionized water, and stirring the mixture for 3 h. The Ludox AS-40 colloidal silica (40 wt% aqueous suspension, Sigma-Aldrich) was added and the mixture stirred again for 2 h. The TEAOH (35 wt% aqueous solution, Sigma-Aldrich) was added, and stirring the mixture for an additional 1 h. Finally, the second organic template DPA (dipropylamine, 99 wt% aqueous solution, Sigma-Aldrich) was added, and then the solution was stirred for 48 h at room temperature. The synthesis gel for SAPO-34 membrane had a molar ratio of 1.0 Al₂O₃: 1.0 P₂O₅: 0.45 SiO₂: 1.2 TEAOH: 1.6 DPA: 100H₂O, which was similar to the procedure reported by literature [19]. The seeded supports were put into the synthesis solution loaded with an autoclave vertically for hydrothermal crystallization. The hydrothermal synthesis was carried out at 433–493 K for 6–24 h. After synthesis, the membranes were rinsed with deionized water and dried at 353 K overnight. The obtained membranes were then calcined at 673 K for 10 h with heating and cooling rates of 0.7 K·min⁻¹ to remove organic template occluded in the membranes.

2.3. Gas separation

Fig. 1 shows the schematic diagram of the experimental apparatus used for gas separation. The SAPO-34 membrane with effective length of 7 cm was sealed with a silicone O-ring at each end and mounted in a stainless steel module. The membrane module was placed in a tubular furnace with a thermocouple to monitor separation temperature. The operation pressure at feed side was controlled by a back pressure regulator and the permeate pressure was kept at atmospheric pressure. For the measurement of CO₂/CH₄ binary separation, an equimolar CO₂/CH₄ feed gas with a flow rate of about 800 mL·min⁻¹ was introduced to the membrane side and a helium stream with a gas flow rate of 200 mL·min⁻¹ was used to sweep the support side. The gas flow rates were measured by a soap film bubble flowmeters. The permeate gas was analyzed by a gas chromatography (GC, GC-2014, Shimadzu) equipped with thermal conductivity detector and a packed column of HAYESEp-D. The gas permeance of component *i* (*P*_{*i*}) is defined as:

$$P_i = \frac{J_i}{\Delta p_i} \quad (1)$$

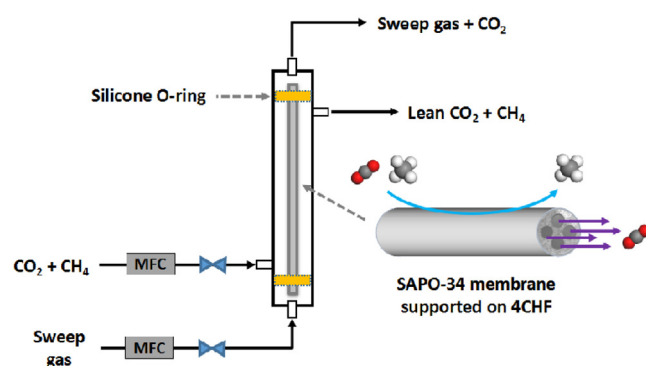


Fig. 1. Schematic diagram of the experimental apparatus for CO₂/CH₄ gas separation.

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