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The preparation of zeolite NaA membranes on the inner surface of hollow fiber supports

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ABSTRACT

Zeolite NaA membranes with excellent water/ethanol separation factors are successfully prepared on the inner surface of hollow fibers in a rotating autoclave for the first time. NaA/PES composite hollow fibers (CHF) are first used to investigate the effects of different synthesis conditions such as synthesis composition, synthesis time and synthesis method (static and dynamic) because there are uniform seed crystals on the inner surface of CHF supports. The seeded growth of zeolite NaA membranes on the inner surface of alumina hollow fibers (AHF) supports (1.0 mm i.d.) are carried out at 373 K. The optimal synthesis conditions obtained are applied to AHF supports to investigate the effects of seed suspensions by the dip-coating seeding method. The effects of the synthesis conditions for AHF supports on the membrane morphology and properties are also investigated. The synthesized membranes are characterized by scanning electron microscopy. The separation properties of the membranes are evaluated by pervaporation of 90 wt.% ethanol/water mixture at 348 K. Zeolite membranes with high separation factor up to 10,000 can be obtained under the conditions: synthesis composition of $7.5Na_2O{:}2SiO_2{:}Al_2O_3{:}600H_2O$, synthesis time of 5 h, using a rotating autoclave (30 rpm).

1. Introduction

Zeolite membranes have been intensively investigated and shown interesting properties in gas permeation and pervaporation. Zeolite NaA membranes have been used for dewatering of bio-ethanol due to its strong hydrophilic nature in combination with small pore size [1].

Zeolite membranes are usually synthesized on the external surfaces of the tubular supports [2]. Only a few studies have been reported in literature regarding the preparation of zeolite membranes on the inner surfaces of the tubular supports [3–8]. Growing a zeolite layer on the inner surface of the tubular support is attractive from the viewpoint of industrial application because the membrane layer is better protected from mechanical damage. On the other hand, in order to increase the flux of zeolite membranes and decrease the volume of the modules, multi-channel supports [9] and hollow fiber supports [10] are greatly preferred for zeolite membrane preparation. The zeolite membrane layers can only be synthesized on the internal surfaces of multi-channel supports. The zeolite membrane layers are better synthesized on the inner surface of hollow fiber supports because of the expected decrease of the flux with the length of the supports due to the pressure loss of vacuum in the lumen of the support in the case of the outer zeolite membrane. Among the different preparation methods for the development of zeolite membranes (e.g. in situ hydrothermal synthesis [11], secondary (seeded) growth [12], multi-stage synthesis [13], microwave heating [14–16], and adding additional covalent linker to develop an intermediate layer [17–19]), zeolite NaA membranes have been usually synthesized by the seeded growth method due to the advantage of this technique: better control of the membrane formation process by decoupling the nucleation and growth steps. In order to obtain a high-performance zeolite membrane, the seeding process has been considered crucial [20,21]. Until now, a lot of seeding methods have been reported, such as dip-coating [22], spin-coating [23], rub-coating [10], laser ablation [24], cross-flow filtration [3] and vacuum seeding [25].

However, not all these methods are applicable for all kinds of supports, especially for the inner surface of tubular supports, and some techniques cannot be used due to the restricted accessibility to the lumen of hollow fiber supports. The preparation of zeolite membranes on the inner surfaces also makes it hard to maintain sufficient nutrient for crystal growth, which would be easier to achieve when the crystals grow on the outer surfaces. In order to overcome these limitations, some techniques have been suggested. Pera-Titus et al. [3] prepared zeolite NaA membrane on the internal surface of porous α-alumina tubular supports (10 mm o.d., 7 mm

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i.d.) by means of a cross-filtration seeding technique. The separation factors of the as-synthesized membrane was up to 600 at fluxes of 0.5 kg/(m^2 h) in the pervaporation of 92 wt.% ethanol/water mixtures at 323 K. With the same seeding technique, they [5] also reported the preparation of inner side zeolite NaA membranes with separation factors up to 16,000 and fluxes of 0.50 kg/(m^2 h) at 323 K in the pervaporation of 90 wt.% ethanol/water mixtures using a semi-continuous synthesis system where the synthesis solution inside the tubes was periodically renewed. Tiscareno-Lechuga et al. [6] developed a novel device to prepare inner side zeolite NaA membranes under a centrifugal force field. The synthesized membrane showed a separation factor higher than 130 at water fluxes over 2.5 kg/(m^2 h) when used for pervaporation of 90.8 wt.% ethanol aqueous solution at 366 K. Some authors reported the use of a flow system for zeolite NaA membrane synthesis to ensure a continuous supply of reactants to the support surface. The synthesis of zeolite NaA membranes on the inner side of porous titania (rutile) asymmetric tubular support in a flow system was performed by the action of gravity [8]. The membrane showed great ability to dehydrate 92 wt.% ethanol/water mixtures by pervaporation with separation factors and fluxes, respectively, up to 8500 and 1.2 kg/(m^2 h) at 323 K. More recently, Aguado et al. [4] proposed the preparation of zeolite NaA membranes on the inner surfaces of tubular supports by in situ hydrothermal continuous synthesis in a flow system. The membrane of 5 μm in thickness showed a N_2 permeance of 5×10^{-7} to 1×10^{-6} mol/(m^2 s Pa). Rotating autoclave was also introduced to prepare zeolite NaA membranes on the inner surface of α-Al_2O_3 tubes [7].

In these previous studies, most of the efforts have been focused on the preparation of inner side zeolite NaA membranes on tubular supports with inner diameter (i.d.) larger than 7 mm, no studies have reported the preparation of zeolite NaA membranes on the inner surfaces of hollow fiber supports with inner diameter less than 2 mm, which is obviously more challenging.

In this article, we study the synthesis of zeolite NaA membranes on the inner surface of hollow fibers with inner diameter of ~1.0 mm by seeded growth method. There are no effects of the seeding process on the properties of zeolite membranes due to the existence of the uniform seed crystals on the inner surface of NaA/PES composite hollow fibers (CHF). Therefore, in order to obtain optimum synthesis conditions for the synthesis of zeolite membranes on alumina (α-Al_2O_3) hollow fibers (AHF), the CHF supports are first used to investigate the effects of synthesis conditions including synthesis composition, synthesis time and synthesis method (static synthesis and dynamic synthesis). Then the optimized conditions are used for the AHF supports to find a suitable seeding method. The influences of synthesis composition, synthesis time and synthesis method on the membrane morphology and properties on AHF supports are also investigated.

2. Experimental

2.1. Materials

Sodium metasilicate nonahydrate (Jinling Chemicals, China) as Si source, sodium aluminate (Sinopharm Chemical Reagent Co. Ltd.) as Al source, sodium hydroxide (>96%, Sinopharm Chemical Reagent Co. Ltd.), ethanol (>99.7%, Sinopharm Chemical Reagent Co. Ltd.), deionized water.

Two kinds of supports were used to prepare zeolite NaA membranes: NaA/PES (polyethylene sulphone) composite hollow fiber (CHF) supports (~2.0 mm o.d. and ~1.0 mm i.d., the weight ratio of NaA/PES was 75/25) [26] and porous alumina (α-Al_2O_3) hollow fibers (homemade, ~1.5 mm o.d. and ~1.0 mm i.d.) [2]. The mechanical strength of the alumina hollow fibers (AHF) was 200–250 MPa. The outer surface of the AHF supports was wrapped with Teflon tape prior to the seeding process.

2.2. Seeding the support

Zeolite NaA seed crystals were prepared according to the literature [2]. The average size (90 nm) of the crystals was measured by dynamic light scattering (DLS, Malvern, ZEN 3600). Three kinds of seed suspensions were used: suspension A was an aqueous seed suspension with 90 nm NaA crystals (1.10 wt.%); suspension B was prepared as follows: a clear solution (solid content, 5.5 wt.%) obtained by centrifuging the synthesis mixture with molar composition of $7.5Na_2O{:}2SiO_2{:}Al_2O_3{:}600H_2O$ (aged at room temperature for 3 h) at a speed of 2000 rpm for 15 min, was added into 1.02 wt.% 90 nm seed suspension with a solution weight ratio of 1/15, and the solid content of the suspension B was 1.30 wt.%; suspension C was obtained by mixing the clear solution with an aqueous seed suspension with 90 nm (1.70 wt.%) in a ratio of 1/9, and the solid content of the suspension C was 2.08 wt.%. The AHF support was dipped in the seed suspension for 10 s to deposit a seed layer onto its internal surface. After dipping, the seed-coated support was dried at 333 K for 1 h.

2.3. Membrane preparation

All supports were wrapped with Teflon tape on their outer surfaces before put into the synthesis mixture to avoid any zeolitic deposition on the outer surfaces. The length of the supports is generally ~5 cm, unless otherwise specified. The zeolite NaA membrane layers were formed on the supports by hydrothermal crystallization. The synthesis mixture with molar composition of $x Na_2O{:}2SiO_2{:}Al_2O_3{:}600H_2O$ was prepared by adding an aluminate solution to a silicate solution under vigorous stirring. The aluminate solution was prepared by dissolving certain amount of sodium aluminate in deionized water at room temperature. The silicate solution was prepared by mixing sodium metasilicate nonahydrate and deionized water at room temperature, then sodium hydroxide was added after the sodium metasilicate nonahydrate was completely dissolved. The resulting synthesis mixture was aged at ambient temperature for 3 h. The synthesis mixture was poured into an autoclave (50 ml), the support was added vertically, and the autoclave was sealed.

Dynamic synthesis: The crystallization was carried out in a rotating oven same as Ref. [27] at 373 K with a rotation of 30 rpm. After the crystallization, the solution was decanted off and the membrane was dried at 333 K after washed with deionized water several times. The membranes synthesized by dynamic synthesis was denoted as "Dn", where n is the membrane number.

Static synthesis: The crystallization was carried out in a convectional oven at 373 K. After the crystallization, the solution was decanted off and the membrane was dried at 333 K after washed with deionized water several times. The membranes synthesized by static synthesis was denoted as "Sn", where n is the membrane number.

2.4. Membrane characterization

The morphology of the membrane was observed with a field-emission scanning electron microscopy (FE-SEM), using a HITACHI SU-70 microscope. The dehydration performance of the as-synthesized membranes was studied by vacuum pervaporation for the separation of 90 wt.% ethanol/water mixture at 348 K. The pervaporation setup is shown in Fig. 1. The zeolite membrane prepared on CHF support was pasted to a stainless steel pipe and then connected to the connector 14 shown in Fig. 1 to measure the pressure in the pemeate side (denoted as vacuum pressure). The zeolite