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Synthesis of zeolite NaA membranes with high performance and high reproducibility on coarse macroporous supports

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ABSTRACT

Pilot-scale zeolite NaA membranes with high PV performance supported on cheap coarse macroporous supports were prepared by one single secondary growth using varying temperature hot dip-coating seeding method (VTHD). Through the VTHD method, a thin, dense and pinhole-free asymmetric NaA seed layer composed of large and small NaA seeds could be manipulated onto the surface of a coarse macroporous support. The large NaA seeds mainly acted as fillers to reduce the pore sizes of the support while the small NaA seeds acted as nuclei to provide sites for NaA crystal growth. The effects of the seed suspension concentrations, the seed sizes and coating temperature on the morphology of the seed layer and the separation performance of the resulting NaA membranes were investigated. The reproducibility of the VTHD method was as high as 70%. The zeolite NaA membrane prepared by the VTHD method showed a water flux of 2.85 kg m^{-2} h^{-1} with a separation factor over 10,000 in dehydrating the 90 wt% ethanol/10 wt% water mixture at 343 K. The use of a cheap macroporous support and the high reproducibility of the VTHD method provide the feasibility for large-scale commercial production of low cost zeolite NaA membranes, promoting the broad application of zeolite NaA membranes.

1. Introduction

Zeolites have been widely used as catalysts [1,2], ion exchangers [3] and adsorbents [4]. Due to their ordered structures, uniform pore sizes, good thermal stability, mechanical strength and chemical resistance, they have shown a great potential for membrane-based applications. In the past two decades, a variety of zeolite membranes, such as LTA [5–10], MFI [11–13], DDR [14], FAU [15] membranes, have been intensively studied as separators [16], reactors [17] and sensors [18]. Among these zeolite membranes, zeolite LTA membranes proved ideally suited for the dehydration of organics by pervaporation or vapor permeation because of their high hydrophilicity and small crystal-graphic pore size. In 1999, Mitsui Engineering &Shipbuilding Co. firstly put zeolite LTA membranes into industrilization for dehydration of alcohol/water mixtures [19]. Recently, the Nano-Research Institute Inc., a 100% subsidiary of Mitsui &Co., has installed vapor permeation units in Brazil (3000 l/d) and India (30,000 l/d) at an operation temperature of 403 K for the dewatering of bioethanol using LTA membranes [20]. Besides, many efforts were focused on development of zeolite NaA membranes with high performance to extend implementation of zeolite NaA membranes into industrial applications [21–23]. Particularly, hollow ceramic fiber supported NaA membranes exhibit an extremely high water flux of about 9.0 kg m^{-2} h^{-1} with a selectivity of 10,000 for dehydrating the 90 wt% ethanol/10 wt% water mixture at 348 K were reported [5].

Secondary growth method, coating zeolite crystals on a support surface before hydrothermal synthesis, is widely accepted as a highly efficient method to fabricate high quality zeolite membranes due to its decoupling nucleation and crystal growth process. The seeds act as nuclei for the growth of zeolite crystals, thus the properties of a seed layer including the seed size, continuity, density and thickness are crucial to the properties and the separation performance of the resulting zeolite membranes. Therefore, one of the key steps of secondary growth method is the formation of uniform and continuous seed layer on the outer surface of a support. Many approaches, such as dip-coating [24], rub-coating [25], spin coating [26], vacuum seeding [27] dip-coating-wiping [5], cationic polymer treatment [28] etc., have been explored to coat zeolite seeds on a substrate surface and pinhole-free zeolite membranes were prepared successfully by these methods. However, the supports were generally of low surface roughness and small pore sizes (smaller than 1 μm [5,8,10,27–31]), and they are comfortable for the formation of good quality seed layer.

Compared to polymer membranes, the high cost of a zeolite NaA membrane is the main obstacle for its broad application in

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industry [20,32]. Caro et al. [20] pointed out that the price of a zeolite membrane was governed by the production cost of supports (about 70%) rather than by the zeolite layer. Cheap macroporous supports are desirable for industrial applications due to the low cost and the potential high flux of the resulting zeolite membrane. However, it may be more difficult to gain a high performance zeolite membrane on such a macroporous support because the larger the pore size of the support is, the higher the risk of forming defects will be.

In our previous work [33,34], we developed a varying temperature hot dip-coating method (VTHD) for the preparation of high performance zeolite T and MFI membranes on cheap coarse macroporous supports. The VTHD method is mainly composed of three steps: (1) hot dip-coating of seeds at higher temperature; (2) rubbing off the excessive seeds; and (3) hot dip-coating of seeds at lower temperature. This method is found flexible and effective for combined control over the seed suspension concentration, seeding temperature and seed size. In the present work, high performance zeolite NaA membranes in pilot-scale were prepared on low cost coarse macroporous α-Al_2O_3 tubes with a mean pore size of 2~3 μm and some large defect pores up to 20 μm using the VTHD seeding method. The use of coarse macroporous supports aimed at reducing the production cost of zeolite NaA membranes. Combined manipulation over the seed size, thickness, coverage and defect of the seed layer were carried out using VTHD seeding method to obtain a thin, compact and pinhole-free NaA seed layer that was proven significant for the achievement of a high performance zeolite NaA membrane. Besides, the reproducibility of the VTHD method was examined.

2. Experimental

2.1. Materials

As shown in Fig. 1a two types (denoted as A and B) of coarse macroporous alumina tubes with an average pore size of 2–3 μm (OD:13 mm, ID: 9 mm, length: 500 mm, Foshan Ceramics Research Institute, China) were used as substrates. If not stated otherwise, type A tubes were used as the supports. Sodium hydroxide (>98 wt%, Tianjin Kermel Chemical Reagent Co., Ltd), tetramethylammomium hydroxide (TMAOH, >99 wt%, RudongZhenfengYiyang Chemical Co., Ltd), aluminum isopropoxide (>99.5 wt%, Tianjin Chem reagent Institute), colloidal silica (SiO_2: 25 wt%, Na_2O: 0.3 wt %, Qingdao Haiyang Chemical Co., Ltd), sodium aluminate (Al_2O_3: 41 wt%, Na_2O: 24.92 wt%, Sinopharm Chemical Reagent Co., Ltd) were obtained commercially as reagent chemicals and used as received without purification. The deionized water was home-made.

2.2. Synthesis of submicron-size NaA crystal seeds

0.4 μm NaA crystals were hydrothermally prepared according to the previously published procedure [35] with molar composition of 0.32 Na_2O: 3.4 SiO_2: Al_2O_3: 8.4 TMAOH: 257H_2O. The synthesis solution was prepared by adding 0.544 g of sodium hydroxide and 71.668 g of tetramethylammomium hydroxide into 152.252 g of deionized water, followed by adding 19.108 g of aluminum isopropoxide into the above solution at 313 K. Then 38.112 g of colloidal silica was added dropwise until the mixture was clear. The resultant synthesis solution was sealed into a Teflon-lined stainless steel autoclave at 373 K for 12 h after aging at room temperature for 12 h under vigorous stirring.

After the products were recovered by repeated centrifugation and washing with deionized water, dried at 393 K overnight, and finally calcined in air at 773 K for 6 h to remove the templates. The pure phase of the zeolite NaA crystals was confirmed by XRD, and the size and shape were obtained by SEM observation (not shown in this article).

2.3. Synthesis of zeolite NaA membranes

2.3.1. Preparation of seed layers on macroporous substrates

The SEM images of the support (Fig. 1b and c) revealed that the pore size of the support is quite large, of 2–3 μm even with some big defects of about 20 μm as marked with red circles in Fig. 1b, and the surface of the support is quite rough. In order to form a continuous, compact and pinhole-free zeolite NaA seed layer on such a coarse support, the VTHD seeding method was applied. The deposition

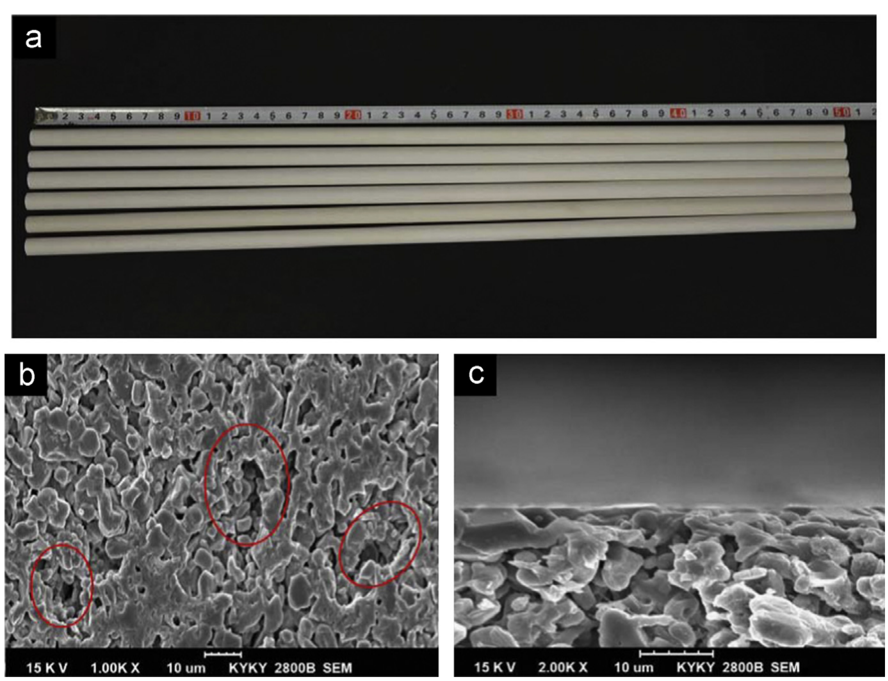

Fig. 1. Optical photo (a) and SEM (b and c) images of the coarse macroporous substrate (inserted red circles: large defect pores). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)