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# Effect of seeding methods on growth of NaA zeolite membranes

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ABSTRACT

NaA zeolite membranes were prepared by secondary growth on the outer surface of tubular mullite supports. Support surface was found to have obvious effect on the quality of as-made NaA zeolite membranes. Three seeding methods were compared for the quality of as-made NaA zeolite membranes, which included dip-coating, rubbing, and the combination of rubbing and dip-coating. The dip-coating treatment could provide well-distributed seeds on flat area of support surface, but poor coverage on dents and pinholes. Rubbing treatment with seed paste, however, could preferentially provide seeds into the defects but non-uniform coverage on the flat area. The combined seeding approach was better than the former two seeding methods, which produced high performance membranes with high reproducibility.



## 1. Introduction

Pervaporation (PV) is a promising highly-efficient separation technique for solvent dehydration and organic separation, especially for the separation of azeotropes and close-boiling mixtures [1–3]. Polymeric membranes have been industrially used for pervaporation separation, but the inherent property of membrane materials in terms of thermal, mechanical and chemical stabilities have limited their applications out of harsh environments. By contrast, zeolite membranes exhibit better stability and the relevant pervaporation can be extended to more industrial processes [3–5]. MFI, FAU, DDR and LTA zeolite membranes have been widely investigated for dehydration of organics [6–9].

Due to small pore diameter (~0.41 nm) and high hydrophilism, NaA zeolite membrane exhibits highly selective to water. It has been shown excellent separation performance for NaA zeolite membrane in dehydration of ethanol, acetone, methanol and tert-butyl alcohol [10,11]. Moreover, the membranes have advantages of high permeation flux and possibility of utilization under feed conditions of higher pressures and temperatures up to 140 °C and 570 kPa, respectively [4,12]. The first large-scale pervaporation plant using NaA zeolite membrane was reported in 2001 by Mitsui Engineering and Shipbuilding Co. Ltd. This plant could produce 530 l/h of solvents at less than 0.2 wt.% of water from 90 wt.% solvent at 120 °C [13]. Although successful application has been realized in Japan, the dehydration technique has not been popular world widely so far. High cost for fabrication of zeolite NaA membrane is one of the main hurdles for industrial utilizations.

Since the first report about zeolite NaA membrane, many efforts have been made to reduce the membrane cost. These include the use of cheap synthetic materials and the improvement of synthesis procedure. After comparison of supports including α-alumina, mullite and cristobalite, Kondo et al. [14] suggested that using mullite support with Si/Al < 70 wt.% for NaA zeolite membranes synthesis could reduce the membrane cost significantly. Chen et al. [15] recently developed an in situ reaction sintering method to further reduce the cost of mullite support. Xu et al. [16] developed a microwave synthesis technique for NaA zeolite membrane synthesis, which could effectively cut down the membrane synthesis time. On the other hand, researchers also focused on the improvement of membrane synthesis to increase permeation flux. Sato and Nakane [17] developed a synthesis method for preparing NaA zeolite membranes with high flux. Tubular α-alumina support was seeded with a dip-coating technique, and then treated hydrothermally at 100 °C for 4 h. Permeation flux up to 5.6 kg $m^{-2}$ $h^{-1}$ was achieved for PV tests at 75 °C using a feed of 90 wt.% ethanol solution. Recently, Wang et al. [18] reported a high flux (9.0 kg $m^{-2}$ $h^{-1}$) of zeolite NaA membrane synthesized on α-alumina hollow fiber support.

For industrial production, however, the reproducibility of membrane fabrication is also very important factor to dominate membrane cost. Secondary hydrothermal growth with seed induction was commonly used in the synthesis of NaA zeolite membranes. The seeding quality has been found to affect the membrane

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performance, which is essential to influent the reproducibility of membrane synthesis. It was documented that good seeding approaches could produce higher quality of zeolite membranes [17–20]. The general seeding methods used for zeolite membrane synthesis include dip-coating [17], vacuum suction [21], and rub-coating method [22]. The dip-coating method could produce the membranes with good quality, but it generally requires very smooth and uniform surface of supports. However, some pinholes and dents exist inevitably on the surface of supports for the industrial production, which could significantly affect membrane quality. The drawback of vacuum suction method is that it needs auxiliary equipment and is inconvenient to operate on large-scale production. For rub-coating, it is easy to coat seeds on support surface but it is difficult to achieve uniform coverage, which could result in low-quality membrane growth. However, the rubbing method could be effective to mend the pinholes and dents on support surface.

In this work, we investigated the effect of seeding methods on the quality of as-made zeolite membranes. A combined rubbing and dip-coating method was used to plant NaA seeds on mullite supports for NaA zeolite membrane synthesis. The rubbing treatment with seed paste was conducted with the purpose to mend the pinholes and dents, which was then followed by dip-coating treatment with seed suspension. We will show in this paper that the combined seeding method could produce high quality NaA zeolite membranes with high reproducibility even on rough support surfaces.

## 2. Experimental

### 2.1. Membrane preparation

NaA zeolite membranes were hydrothermally synthesized on the out surface of tubular mullite supports by secondary growth method. Porous mullite tubes with dimensions of 1.2 cm o.d. and 0.7 cm i.d. were provided by Nanjing Jiusi High-Tech. Co. Ltd. The tubes have a mean pore size of 1 μm and a porosity of 40%. The materials used for the synthesis were solvable sodium aluminate, water glass and sodium hydroxide (supplied by commercial companies in China) and deionized water. Prior to synthesis, the supports were cut to 7 cm long and polished with 320–1200 grit SiC sandpapers under running water. After polishing treatment, the supports were further treated by ultrasound for about 30 s in deionized water.

Three seeding methods were employed to plant home-made NaA seeds with an average particle size of about 2.1 μm (Mastersizer 2000, Malvern Instruments Ltd.) on the polished supports, including dip-coating, rubbing, and the combination of rubbing and dip-coating. For dip-coating method, the supports were immersed vertically into 0.5–3.0 wt.% seeds suspension for 3–5 s. For rubbing method, NaA seed paste was first prepared by mixing NaA seeds with deionized water at the mass ratio of 1:10. The seed paste was rubbed on the surface along axis direction thrice with a brush. The combined method was carried out by rubbing support with NaA seed paste first and then dip-coating with 1.0 wt.% seeds suspension for 3–5 s. Prior to dip-coating treatment, the seeded supports by rubbing were dried at 100 °C for 2 h. The seeded supports were dried at 50 °C for 12 h before membrane synthesis. The pretreatment conditions and seeding methods for the supports used for membrane synthesis are summarized in Table 1.

A synthesis solution was prepared by dissolving sodium aluminate, water glass and sodium hydroxide in deionized water at room temperature. The composition of synthesis solution had the molar ratio of $Al_2O_3$:$SiO_2$:$Na_2O$:$H_2O$ = 1:2:2:120. The synthesis solution was stirred intensively for 30 min and then poured into a PTFE-lined stainless steel autoclave. The seeded mullite supports were immersed into the solution vertically. Hydrothermal crystallization was performed at 100 °C for 3.5 h. To improve membrane quality, hydrothermal synthesis was repeated once.

### 2.2. Pervaporation and characterizations

The separation performances of as-made membranes were evaluated by pervaporation tests. NaA zeolite membrane was sealed in a membrane module with silicon O-rings. Ethanol solution with flow rate of 15 ml/s was introduced through outside of membrane tube at atmospheric pressure. The inside of membrane was evacuated with a vacuum pump through a vacuum line, which maintained the downstream pressure below 200 Pa throughout the operation. Pervaporation experiments were carried out at a temperature range of about 50–75 °C. The permeated vapor mixture was collected by two liquid nitrogen traps in parallel. The hot retentate was recycled back to feed tank. The compositions of the feed and permeate were analyzed by a gas chromatography (GC-8A, Shimadzu) equipped with a thermal conductivity detector (TCD) and a packed column of Parapak-Q. The separation factor ($\alpha$) for water over ethanol is defined as:

$$\alpha = \frac{y_W/y_E}{x_W/x_E} \tag{1}$$

where $y_W/y_E$ is the weight ratio of water over ethanol in permeates and $x_W/x_E$ is the ratio in feed. The permeation flux ($J$) and flux of component ($J_i$) through NaA zeolite membrane can be calculated respectively by Eqs. (2) and (3) as follows:

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

and

$$J_i = J \cdot y_i \tag{3}$$

where $m$ is the total mass of permeate, $A$ the effective area of membranes, $t$ permeate time and $y_i$ the weight percentage of component $i$ in permeate.

The roughness of support surfaces were measured by a precise surface roughometer (JB-4C, Shanghai Taiming Optical Instrument Co. Ltd.). Average result was calculated based on nine parallel test data. The morphology of samples was examined by scanning electron microscopy (SEM, Quanta200, FEI).

## 3. Results and discussion

### 3.1. Seeding by dip-coating method

Since NaA zeolite layers are generally less than 20 μm, the roughness of support surface exhibits significant effect on membrane quality. To investigate the effect, the outer surfaces of mullite tubes were polished with 320, 500, 800 and 1200 grit sandpapers, respectively. Roughness pictures of the support surfaces before and after polishing are shown in Fig. 1. Without pretreatment, the supports were quite rough with an average roughness ($Ra$) of 3.44 μm and some contaminations adhered on the surface. Pinholes and dents were observable on some surface area, which could be indicated by valleys on roughness line (Fig. 1a). After polished with sandpapers, the support surface became cleaner and smoother. The roughness decreased to 2.10, 1.75, 1.32 and 0.92 μm for the polishing treatments by 320, 500, 800 and 1200 grit sandpapers, respectively. It was noted that although support surface became smooth after polishing treatment some small pinholes were unavoidable on some areas of surface. As shown in Fig. 1d–e, some deep valleys on the roughness lines were