



Low temperature synthesis of NaA zeolite membranes: The effect of primary and secondary crystallizations

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Abstract

NaA zeolite membranes were prepared on porous α -alumina support tubes (inner side) by primary (*in-situ*) and secondary (*ex-situ*) crystallization processes at 65 °C for 6 h, 12 h and 24 h each. For secondary crystallization process, poly(ethyleneimine) (PEI) was used as a buffer layer for proper attachment of the NaA seed crystals (prepared at 65 °C/2 h) onto the alumina support surface. The membranes prepared by primary crystallization process showed thicknesses of about 10 μm , 20 μm and 30 μm for growth times of 6 h, 12 h and 24 h, respectively, while the membranes prepared by secondary crystallization process rendered the corresponding thicknesses of 25 μm , 35 μm and 70 μm , respectively. PEI coating rendered good quality of membrane for secondary crystallization process with lower growth time (6 h). The better quality of membrane which had interlocked dense structure with minimum defects was obtained for primary crystallization at 65 °C for 12 h growth time. Pervaporation study for ethanol/water mixture was performed with the prepared membranes.

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1. Introduction

During the past decades, membrane-based technology has gained widespread acceptance in various applications. Pervaporation is a promising membrane-based process for the separation of liquid chemical mixtures, especially in azeotropic or close-boiling solutions [1]. It is an effective process in terms of energy saving, economic and environmental protection, and so on. Pervaporation is governed by a membrane barrier between liquid and vapor phase with mass transfer occurring selectively across the barrier to the vapor side. Separation *via* pervaporation is determined by the physico-chemical properties of the membranes. Zeolite membranes, in particular, have received considerable attention because of their better thermal, mechanical and chemical stability compared to polymeric membranes [2,3]. Because of unique pore structures, zeolites have a great potential to separate mixture of molecules by both adsorption and molecular sieving.

A typical zeolite membrane is prepared by depositing polycrystalline intergrown layers of zeolite crystals synthesized on the porous ceramic or metal supports. Due to hydrophilic nature and relative ease of preparation, NaA zeolite membrane is of special interest for the selective separation of hydrophilic/hydrophobic liquid mixtures [4,5]. There are many reports on the formation of zeolite membranes like, heterogeneous gel systems [6], clear solution [7], pre-seeding technique [8], microwave assisted crystallization [9], multi-stage hydrothermal process [10], etc. Secondary growth method is widely used [11–14] for the preparation of zeolite membranes. In the secondary growth method, the seed particles act as nuclei for the growth of zeolite crystals. In this case, the properties like crystal size of seed particles, thickness, density, and continuity of the seed layers are important toward the separation performance of the prepared zeolite membranes. Proper anchoring and adhesion of seed crystals with high surface coverage on the support surface are very much important for the preparation of defect-free membranes. We prepared silicalite-1 zeolite membrane using 3-aminopropyltriethoxysilane (APTES) as a surface modifier [15]. The NaA zeolite membranes were prepared by applying polyvinylpyrrolidone (PVP) [16], silica [17] and poly

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(ethyleneimine) (PEI) [18] as intermediate buffer layers. There are few reports on the formation of zeolite membranes by a primary growth process [19,20]. The random nuclei formation resulting in non-homogeneity of surface crystallization is the main disadvantage of the primary growth process. However, we prepared silicalite-1 zeolite membranes by both the primary growth and secondary growth techniques, and studied the single gas permeation with the prepared membranes [21].

With the motivation of previous works, the objective of the present research was to study the preparation of NaA zeolite membranes *via* primary growth and secondary growth techniques by varying the growth times. In this work, the NaA zeolite membranes were prepared at low temperature (65 °C) which is important in terms of energy saving as well as optimization of membrane thickness, and particle compactness towards separation/pervaporation performance. The performance of the prepared membranes was examined by pervaporation behavior of ethanol/alcohol mixture.

2. Experimental

For the preparation of NaA zeolite membranes, two techniques, *i.e.*, primary crystallization and secondary crystallization were applied. In the secondary crystallization process, NaA zeolite seed crystals were required to pre-coat the support surface.

2.1. Synthesis of NaA zeolite seed crystals

Sodium hydroxide (G.R., Merck, India, purity > 98%), aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) (S.D. Fine Chem, India, purity > 98%), and sodium metasilicate nonahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) (Qualigens Fine Chem, India, purity > 99%) were used as the precursor materials. In a typical experiment, 1.33 g NaOH and 23.67 g $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 150 mL water (solution A). In another set, 3.4 g $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 150 mL water (solution B). Solution A was added slowly into solution B under stirring with magnetic stirrer. The stirring was continued for 30 min at room temperature (30 °C) to obtain a clear solution. The molar composition of the solution was maintained as $6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:5\text{SiO}_2:1000\text{H}_2\text{O}$. The solution was transferred into a Teflon-lined stainless steel autoclave. It was then aged at 65 °C for 2 h followed by cooling down to room temperature (30 °C). The synthesized particles were collected by centrifugation and washing followed by aging at 60 °C for 4 h.

2.2. Preparation of NaA zeolite membrane by primary crystallization

The α -alumina-based support tube (70 mm (*L*) \times 10 mm (OD) \times 7 mm (ID)) with an average pore size of 100 nm (purchased from Inopor GmbH, Germany) was used for the preparation of membranes. The outer surface of the tube was masked by Teflon tape. The precursor solution for membrane was prepared as mentioned in Section 2.1. The solution was

poured into the Teflon-lined stainless steel autoclave. The support tube was dipped vertically into the precursor solution. The autoclave containing the precursor solution and support tube was placed in an air oven at 65 °C for 3 h. The NaA zeolite film was grown inside the tube. For uniform growth of the particles in the membrane throughout the tube, it was again placed into the freshly prepared precursor solution in an inverted position (top-side down and bottom-side up) for another 3 h. The total growth time was 6 h (3+3 h). After the experiment, the masked Teflon tape was removed from the outer surface of the tube. The as-prepared NaA film (membrane) formed onto the inner surface of the tube was washed with DI water until the washing liquid became almost neutral. Other sets of experiments were performed following the same procedure with (6+6 h) and (12+12) h growth times. After washing, all the NaA membranes were dried at 60 °C for 6 h. Fig. 1 shows schematically the formation of NaA zeolite membrane.

2.3. Preparation of NaA zeolite membrane by secondary crystallization

In this process, an intermediate buffer layer of poly(ethyleneimine), PEI ($M_w=25,000$) (Aldrich, Steinheim, Germany) was applied between the inner surface of support and the NaA zeolite particles. The PEI coating was used for proper anchoring of NaA zeolite particles onto the support surface.

The outer surface of the tube was masked by the Teflon tape. Then, the tube was dip-coated with 20 wt% PEI solution in ethanol (Merck, Darmstadt, Germany, > 99%) with a withdrawing speed of 7.5 cm/min followed by drying at 30 °C for 2 h. The synthesized NaA seed particles were rubbed onto the PEI-coated tubes (inner surface) by rolling with a glass rod. The seed particles were adhered with PEI coating. The precursor solution for membrane was prepared as mentioned in Section 2.1. The solution was poured into the Teflon-lined stainless steel autoclave. The PEI-modified NaA seed-coated support tube was dipped vertically into the precursor solution. The autoclave containing the precursor solution and PEI-modified NaA seed-coated support tube was placed in the air oven at 65 °C for 3 h for secondary growth of the particles. The NaA zeolite film was grown inside the tube. For uniform growth of the particles in the membrane throughout the tube, it was again placed into the freshly prepared precursor solution in an inverted position (top-side down and bottom-side up) for another 3 h. The total growth time was 6 h (3+3 h). After the experiment, the masked Teflon tape was removed from the outer surface of the tube. The as-prepared NaA film (membrane) formed by secondary crystallization onto the inner surface of the tube was washed with DI water until the washing liquid became almost neutral. Other sets of experiments were performed following the same secondary growth procedure with (6+6) h and (12+12) h growth times. After washing, all the NaA membranes were dried at 60 °C for 6 h. The formation of NaA zeolite membrane by secondary growth process is illustrated in Fig. 1.

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