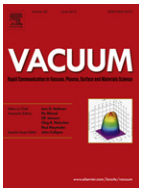
Vacuum 92 (2013) 70–76

Contents lists available at SciVerse ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum



# High performance dehydration of ethyl acetate/water mixture by pervaporation using NaA zeolite membrane synthesized by vacuum seeding method

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## ARTICLE INFO

*Article history:*
Received 2 April 2012
Received in revised form
9 November 2012
Accepted 30 November 2012

*Keywords:*
Aging time
Ethyl acetate
NaA zeolite membrane
Pervaporation
Vacuum seeding

## ABSTRACT

High quality NaA zeolite membranes were prepared by vacuum assisted secondary growth. At the first stage in which NaA powder was synthesized, increasing the aging time led to formation of impure and smaller crystals. However, at the aging time of 48 h, pure NaA zeolite particles with average particle size of 1.5 μm were obtained. In the second stage, the outer surface of porous $\alpha$-$Al_2O_3$ tubular supports were seeded by vacuum method using 1.5 μm NaA particles. The most stable and uniform seeded layer was obtained at seeding time and suspension concentration of 90 s and 5 g $L^{-1}$, respectively. Then, 6 h of secondary growth of the zeolite layer on the seeded surface was carried out at 373 K three times. The XRD and SEM results showed the formation of a uniform and dense layer of pure NaA zeolite with an average thickness of 45 μm. Dehydration experiments were conducted on ethyl acetate/water mixtures with 2 wt% water content. The average total fluxes were 0.147, 0.208, and 0.315 kg $m^{-2}$ $h^{-1}$ at 303, 313, and 323 K, respectively. The separation factor was 163,000. This parameter did not change with temperature and it was due to very close activation energies of ethyl acetate and water.

## 1. Introduction

Pervaporation is an effective and energy-efficient membrane process which can be used for some liquid–liquid separation applications. This process is a promising candidate for cases in which separation encounters difficulties due to liquid physical and chemical properties where it is difficult to achieve desirable results by conventional separation processes such as distillation and extraction [1–3]. During pervaporation process, a liquid feed mixture is contacted with the active side of a dense membrane and one component passes through the membrane to the other side. This is due to the selectivity of the membrane under the act of vacuum. Implementing vacuum force causes the passing species to be evaporated, leaving the membrane body as vapor phase to be later condensed in a cold trap [3–5]. This environmentally clean and economic technology can be used for many applications such as dehydration of aqueous–organic mixtures, removal of volatile organic compounds from aqueous solutions, and organic–organic separations [3–8]. Polymeric membranes are widely used for many pervaporation applications [1–3,9]. However, one major drawback of the polymeric membranes which limits their practical applications is their insufficient chemical and thermal stability [1–3,9–11]. Furthermore, swelling of the polymeric membranes generally leads to higher permeability and lower selectivity [1,12]. On the other hand, being free from swelling effect and having good thermal and chemical stabilities of inorganic membranes make them proper candidates for a broad range of separation applications [1,5,12]. Among them, zeolite membranes take advantage of the unique properties of zeolites such as—highly crystalline ordered structure and having molecular-sized pores [3,13]. These traits are very suitable for separating liquid-phase mixtures via pervaporation process. Basically, molecular transport and separation of different molecules through zeolite pores are based on differences in their adsorption and diffusion properties [13].

Various synthesis strategies and methods have been investigated for synthesis of the zeolite membranes [14]. Coating of the zeolite seeds on the surface of a porous support before hydrothermal synthesis, known as secondary growth method, is an effective approach to synthesizing a high quality zeolite membrane [15–19]. In general, synthesis with seeds gives a better control of membrane formation process [15,20,21]. In addition, the secondary growth method facilitates the growth of the zeolite crystals on the support surface (by heterogeneous nucleation) rather than in the bulk of synthesis solution, which in turn prevents transformation of

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0042-207X/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.vacuum.2012.11.019

the zeolite phase into other undesired phases [15]. However, preparing zeolite suspensions and coating the zeolite seeds on a porous support to obtain a uniform seeding layer is still a challenge [15,19]. Several seeding methods such as—rub coating, dip coating, spray and spin coating, and slip casting—are being used for coating the supports. Also, vacuum seeding is a simple and effective method for support seeding. In this method a uniform seeding layer is formed on the support by adjusting the seeding parameters such as vacuum intensity, seeding time and suspension concentration [15,17].

Due to its low toxicity, ethyl acetate is widely used in industrial processes. Therefore, ethyl acetate purification and dehydration during its production process is an important issue [21]. Zeolite membranes, especially NaA membranes (due to their high hydrophilic nature) are good candidates for dehydration of organic solvents [7]. To our knowledge, there are few published reports on dehydration of highly concentrated ethyl acetate/water mixtures. Dehydration of ethyl actetate/water mixtures by pervaporation process using poly (vinyl alcohol) membranes cross-linked with tartaric acid was studied by Salt and co-workers. Their experiments were conducted at 30, 40, and 50 °C with the feed mixtures containing 1–2.5 wt% water. According to their results, water and ethyl acetate fluxes varied in range of 0.008–0.065 and 0.0001–0.0015 kg $m^{-2}$ $h^{-1}$, respectively. The separation factor was in order of $10^3$–$10^4$ [4]. Tian and Jiang used solvent-cast poly (vinylidene fluoride-co-hexafluoropropene) membranes in a pervaporation system for ethyl acetate separation from its aqueous solution. In this work, the concentration of ethyl acetate in the feed mixture was in range of 1.5–3.0 wt% and their membranes showed relatively high flux for this species, ranging from 0.2 to 2 kg $m^{-2}$ $h^{-1}$. However, the reported separation factor of about $10^2$ was low [22]. Zhu et al. used Poly (VDF-co-HFP)/PP composite membranes to separate ethyl acetate from aqueous solution. Their membranes showed low separation factors varying from 50 to 200 [23]. Also, Shah et al. separated ethyl acetate from water solution containing 5 wt% ethyl acetate by using commercial NaA zeolite membranes (Mitsui Engineering and Shipbuilding, Japan) at 60 °C. The water flux was very high (2.65 kg $m^{-2}$ $h^{-1}$) and the separation factor was in the moderate range of 200–500 [24]. Recently, dehydration of ethyl acetate/water mixtures using PVA/ceramic composite pervaporation membrane has been reported by Xia and co-workers. Using mixtures containing 5.1 wt% water, they obtained the maximum separation factor of 625 [25]. It is seen that in most cases the separation factor for dehydration of ethyl acetate has been in range of a few hundreds, indicating that making membranes with improved performance is an essential task.

In this study, the NaA zeolite membrane was synthesized by vacuum assisted secondary growth method and used for dehydration of an ethyl acetate/water mixture containing 98 wt% of ethyl acetate. The main purpose of this work was to achieve simultaneous desirable separation factor and permeate flux. To this aim, the micrometer size NaA powder was synthesized and then the zeolite layer was grown on a porous alumina support. During the experiments, the effects of some parameters —such as seeding conditions and number of zeolite layers grown on the porous support—on the performance of the membranes were investigated. Also, the effect of temperature on the fluxes of water and ethyl acetate was studied.

## 2. Experimental section

### 2.1. Synthesis of NaA zeolite seeds

NaA zeolite particles were synthesized by conventional heating method in an oven under air atmosphere. The initial aqueous gel for zeolite synthesis was prepared with molar composition of 1.0 $Al_2O_3$: 1.92 $SiO_2$: 3.16 $Na_2O$: 134 $H_2O$. Sodium silicate solution (25–28% $SiO_2$, 7–8%$Na_2O$, 63% $H_2O$, MERCK), aluminium hydroxide (>99%, MERCK), and sodium hydroxide pellets (>98%, MERCK) were used as source materials for Si, Al, and Na elements, respectively. The alumina solution was prepared by dissolving an adequate amount of aluminium hydroxide powder in hot aqueous sodium hydroxide solution at 373 K. Almost half of the total amount of water was used in this stage. On the other hand, the silica solution was prepared by dissolving the necessary amount of sodium silicate in the remaining water. Then, the Si solution was added to the Al solution in a polypropylene bottle and the mixtures were agitated for 15 min to obtain homogeneous gels. Prior to hydrothermal synthesis, the synthesis gels were aged at room temperature for different times. After aging, the NaA powder was synthesized by placing the gels in the oven at 373 K for 3 h. The synthesized powders were thoroughly washed with distilled water followed by centrifuging for several times till the pH of the resultant mixture was lower than 9.

### 2.2. Synthesis of the zeolite membranes

Homemade porous $\alpha$-$Al_2O_3$ tubes (12 mm O.D. and 6 mm I.D.) with average surface pore size of 0.5 μm and porosity of about 43% were used as supports. Before seeding, the surface of each support was polished with sand-paper and cleaned with deionized water in an ultrasonic cleaner bath for 10 min. Finally the clean supports were calcinated at 673 K for 3 h. To proceed with the membrane synthesis process, each pre-treated support was vertically fixed in a Teflon holder. The bottom end of the support was sealed and the upper was connected to a vacuum pump. Then, the support was immersed in a beaker containing the suspension of zeolite NaA seeds. At this stage, the vacuum was applied for a given time to coat the surface of the support with NaA particles as initial seeds for zeolite membrane synthesis. A simple schematic of the system is shown in Fig. 1(a). Due to vacuuming, the suspension of seeds was continuously driven to the surface of support so that a uniform seeding layer was formed on the outer surface of support. After seeding, the support was dried at 383 K at low heating and cooling rate of one K $min^{-1}$ to protect the seed layer from cracking. The membrane synthesis was completed by conventional hydrothermal synthesis method in an oven. For this purpose, at first a synthesis gel with the molar composition of 1 $Al_2O_3$: 2 $SiO_2$: 3 $Na_2O$: 200 $H_2O$ was prepared. Then, the two ends of the support were sealed by Teflon caps to prevent the contact of the gel with the inner surface of the tubular support. The support was placed vertically in a stainless-steel Teflon-lined autoclave and the synthesis gel was carefully poured into the autoclave. The autoclave was placed in the oven for 6 h at 378 K. After synthesis, the membrane was washed with distilled water until neutral, followed by drying at 383 K for 3 h at a heating and cooling rate of one K $min^{-1}$.

### 2.3. Pervaporation experiments

Pervaporation experiments were conducted on 2 wt% water containing ethyl acetate/water binary mixtures at 303, 313, and 323 K. Analytical grade ethyl acetate was purchased from Arman Sina Co. (Iran). Pervaporation experiments were carried out using a simple system shown in Fig. 1(b). The membrane was positioned in a Teflon holder. The upper part of the holder was connected to the vacuum line via a glass tube and the whole set was placed in a sealed glass flask containing 400 ml of the feed mixture. The pressure at the permeate side was adjusted at 0.8 mbar. The condensed permeate was collected in a U-shape tube placed in a cold trap. Since the total volume of the collected permeate was