

Preparation of a non-hydrothermal NaA zeolite membrane and defect elimination by vacuum-inhalation repair method



Meng-xue Xu^a, Yan He^{a,*}, Yi-pin Wang^a, Xue-min Cui^{a,b,**}

^a School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, PR China

^b Guangxi Key Lab of Petrochemical Resource Processing and Process Intensification Technology, Guangxi University, Nanning 530004, PR China

ARTICLE INFO

Keywords:

Geopolymer
NaA zeolite membrane
Non-hydrothermal
Pervaporation
Vacuum-inhalation repair method

ABSTRACT

This work reports the preparation of a non-hydrothermal NaA zeolite and its stainless steel-supported membrane using geopolymer-gel-thermal-conversion (GGTC) combined with a dip-coating method, which does not require hydrothermal processing. The XRD and high-resolution transmission electron microscopy (HRTEM) analyses indicate that the $1.1\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-2\text{SiO}_2-8\text{H}_2\text{O}$ geopolymer gels cured at 25 °C nucleate in the geopolymerization stage. After heat-treatment above 60 °C, the crystal nuclei in the geopolymer gels continue to grow and transform into NaA zeolite crystals with good crystallinity. To improve the separation efficiency of the stainless steel-supported NaA zeolite membrane in the pervaporation (PV) process of an ethanol/water mixture, this paper reports a simple vacuum-inhalation repair method for non-zeolitic pores or other defects in the NaA zeolite membrane. After vacuum-inhalation repair of the non-hydrothermal NaA zeolite membrane with sodium alginate solutions and CaCl_2 solutions, in that order, the repaired NaA zeolite membrane exhibited a separation factor that was enhanced approximately 7- to 14-fold over that of the unrepaired NaA zeolite membrane.

1. Introduction

In recent decades, zeolite membranes have been intensively investigated and observed to exhibit interesting dehydration, gas permeation, and pervaporation (PV) separation properties. NaA zeolite membranes are ideally suited for the dehydration of aqueous organic solutions by pervaporation, due to their high hydrophilicity and pore size of 0.4 nm (Sander and Soukup, 1988; Coronas, 2010; Liu et al., 2006; Braunbarth et al., 2000; Ge et al., 2009; Ju et al., 2006). For use as separation filters, NaA zeolite membranes must have good mechanical strength without mesoscopic or macroscopic defects. In general, two types of NaA zeolite membranes are considered. The first type includes (1) thin NaA zeolite films supported by a porous material (e.g., alumina, silica, or stainless steel) (Sander and Soukup, 1988; Coronas, 2010; Liu et al., 2006; Braunbarth et al., 2000; Ge et al., 2009; Ju et al., 2006). Currently, a secondary crystal growth method, which coats zeolite crystal seeds on a support surface prior to hydrothermal synthesis, is widely accepted as a highly efficient method for the fabrication of zeolite membranes due to its decoupled nucleation and crystal growth processes. (2) Thick polycrystalline NaA zeolite films (free-standing or self-supported) are the second type. However, self-

supported zeolite membranes lack strength and are highly fragile. Therefore, their separation performance has not been extensively studied (Wang et al., 2002). In previous work (Cui et al., 2011; He et al., 2012, 2013; Zhang et al., 2014), a self-supported NaA zeolite membrane was successfully prepared using a hydrothermal process with a chemosynthetic $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-2\text{SiO}_2$ geopolymer gel. Although the results indicated that the self-supported NaA zeolite membrane possesses good strength and a high permeation flux, it has a lower separation factor. Therefore, in order to maintain their advantages, processes for improving the separation factor of zeolites membranes should first be considered.

In previous studies, dip-coating (Zhu et al., 2011; Lai et al., 2012; Shao et al., 2007), rub-coating (Kusakabe et al., 1997), spin-coating (Tosheva et al., 2008), and dip-coating-wiping (Wang et al., 2009) have been explored as methods to coat zeolite seeds on a substrate surface, and pinhole-free zeolite membranes have been successfully prepared using these methods. However, the seeding method involves a complex process for synthesizing zeolite membranes with large areas, and results in the formation of macropores, cracks, and/or grain boundary defects (Choi et al., 2009) during the thermal treatment required for removing templating agents from zeolitic pores. Such defect structures

* Corresponding author.

** Corresponding author at: School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, PR China.
E-mail addresses: 568158886@qq.com (Y. He), cui-xm@tsinghua.edu.cn (X.-m. Cui).

are believed to degrade the separation performances of zeolite membranes by introducing nonzeolitic pores or micro-cracks. Macro-pores and mesopores are major non-zeolitic defects formed in the fabrication process of zeolite membranes. Successful approaches for the repair of these cracks and the minimization of their effect on membrane performance rely on compositional optimization and repeated hydrothermal treatment during membrane fabrication (Choi et al., 2009; Yan et al., 1997). However, this is a complex and highly costly form of processing.

The results from previous studies (Cui et al., 2011; He et al., 2012, 2013; Zhang et al., 2014; Provis et al., 2005; Liu et al., 2013) show that increasing the alkalinity of the geopolymer gel from $\text{Na}/\text{Si}=1.0$ to $1.25 > \text{Na}/\text{Si} > 1.0$ can lead to direct transformation of the NaA zeolite from the amorphous geopolymer phase, without any hydrothermal processing and templating agents, and only a simple heat-curing method at 60°C or above would need to be used. The method would successfully reduce the effects of grain boundaries, developed during zeolite membrane formation, on the membrane performance.

Sodium alginate has excellent water solubility and can quickly create an ionic cross-linked hydrogel under mild conditions (Yeom and Lee, 1998). Huang et al. (1999) prepared an evaporation membrane by cross-linking with Ca^{2+} cations. In order to make sodium alginate molecules as much as possible into the nonzeolitic pores and to fill the macroporous or mesoporous defects, the vacuum-inhalation method is more effective way than impregnation method (Zhang and Lu, 2010). Compare with the impregnation method, the vacuum inhalation method provided a greater penetration driving force.

In this work, we successfully prepared a NaA zeolite membrane by coating the geopolymer paste onto sheet stainless steel supports using a dip-coating process. The key factor demonstrating the success of this method is the elimination or reduction of non-zeolitic defects in the zeolite membranes. This is the main objective of this paper.

2. Experimental procedure

2.1. Preparation of NaA zeolite membrane supports via a non-hydrothermal process

The starting Al_2O_3 - SiO_2 powder materials were synthesized using a

sol-gel method with tetraethylorthosilicate (TEOS) and aluminium nitrate nonahydrate (ANN). A sodium silicate solution (modulus=0.9) was obtained with industrial waterglass (solid mass fraction 39%; modulus=3.15) and sodium hydroxide. The geopolymer specimens were prepared using chemosynthesized Al_2O_3 - SiO_2 powders, sodium silicate solution (with different modulus ($\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio)=0.7, 0.8, 0.9, or 1.0), and distilled water by mechanically mixing the solid silicon (in aluminosilicate powders) with the liquid silicon (silicon in sodium silicate solution) in a molar ratio of 1.0. The molar composition of the resulting geopolymer paste was $n\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-2\text{SiO}_2-x\text{H}_2\text{O}$. After mechanical stirring of the geopolymer slurry, the homogeneous geopolymer paste was cast into disk-shaped moulds or coated on the supports. The planar moulds or stainless steel membrane-supports with the geopolymer paste were sealed and heat-treated at designated temperatures (NaA zeolite bulk @25, 40, 50, 60, and 90°C , membrane-supports @ 60°C) for various periods of time. The $\text{H}_2\text{O}/\text{Na}_2\text{O}$ molar ratio of the geopolymer paste was varied from 6 to 10 (NaA zeolite bulk with $\text{H}_2\text{O}/\text{Na}_2\text{O}=6, 7, 8, 9$, and 10, membrane-supports with $\text{H}_2\text{O}/\text{Na}_2\text{O}=8$). After the geopolymer gel thermal conversion (GGTC) process, the polycrystalline NaA bulk or membrane was obtained.

The stainless steel planchet supports (diameter=40 mm, thickness=2.0 mm) were fabricated using a 200×200 -mesh stainless steel wire web as a raw material, which was pressed using a dense woven mesh with a pore size of approximately $74\ \mu\text{m}$. The supported NaA zeolite membrane was fabricated by coating the geopolymer paste onto sheet stainless steel supports, by what is known as the dip-coating process, as shown in Fig. 1. First, stable $1.1\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-2\text{SiO}_2-8\text{H}_2\text{O}$ coating pastes were prepared with different $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratios. The designed geopolymer slurry was degassed by mechanical stirring in preparation for dip-coating. The viscosity of the slurry was adjusted to approximately $1.0\ \text{Pa}\cdot\text{s}$ at $398.15\ \text{K}$. Dip-coating of the stainless steel disk support was conducted by vertically placing the support in a container, which was then filled with the slurry. After a dipping time of 30 s for contact between the immobile paste and the surface of the support, the paste was discharged from the bottom at a withdrawal speed of $30\ \text{mm}\cdot\text{s}^{-1}$. The designed zeolite membrane layer thickness (0.2 – $1.0\ \text{mm}$) was determined by dip-coating number and withdrawal speed. For reducing the zeolite membrane thickness, it was left only one side of geopolymer paste on the stainless steel support.

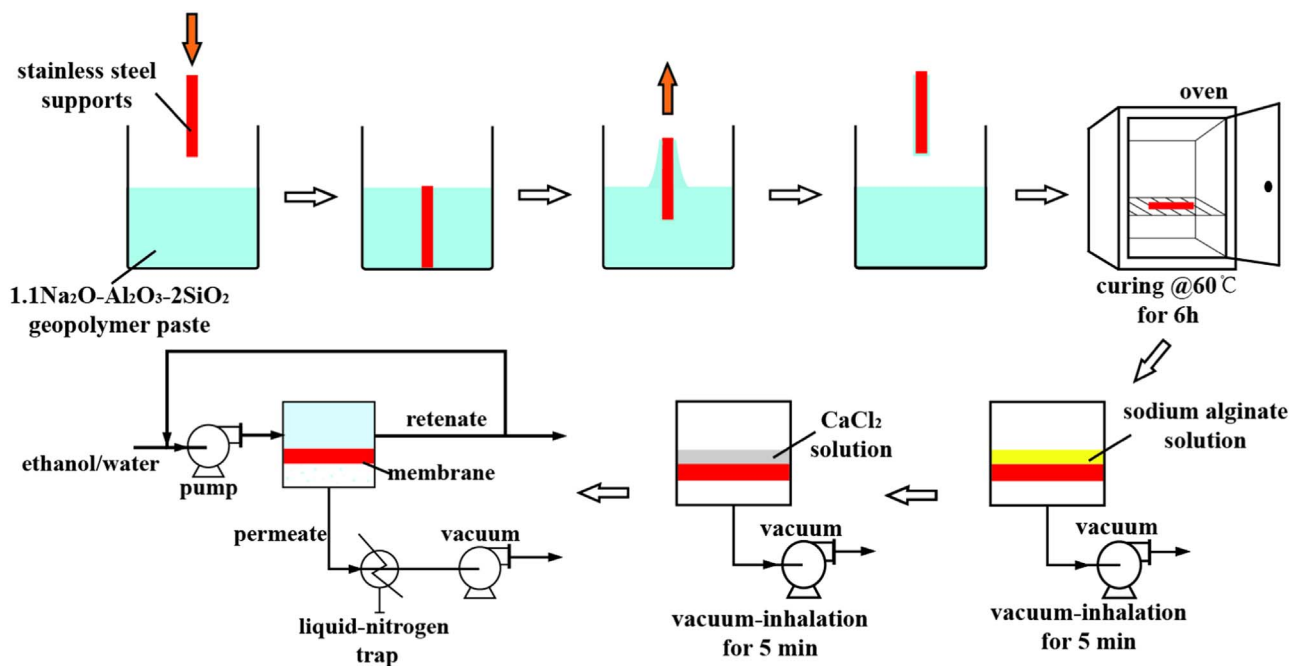


Fig. 1. Schematic representation of the dip-coating and patching process of the stainless steel-supported NaA zeolite membrane combined with the vacuum-inhalation repair of the non-zeolitic interstitial pores using a non-hydrothermal method.

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