



Facile synthesis of zeolite FAU molecular sieve membranes on bio-adhesive polydopamine modified Al₂O₃ tubes

Chen Zhou^a, Chenfang Yuan^a, Yaqiong Zhu^a, Jürgen Caro^b, Aisheng Huang^{a,*}

^a Institute of New Energy Technology, Ningbo Institute of Materials Technology and Engineering, CAS, 1219 Zhongguan Road, 315201 Ningbo, PR China

^b Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Callinstrasse 3-3A, D-30167 Hannover, Germany

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ABSTRACT

A seeding-free synthesis strategy was developed for the preparation of dense and phase-pure zeolite FAU membranes through mussel-inspired polydopamine (PDA) modification of porous Al₂O₃ tubes. Zeolite FAU nutrients can be attracted and bound to the support surface via the formation of strong non-covalent and covalent chemical bonds, thus promoting the nucleation and growth of uniform, well-intergrown and phase-pure zeolite FAU membranes. The SEM and XRD characterizations demonstrate that a relative thin but dense and pure-phase zeolite FAU membrane with a thickness of about 2.3 μm can be obtained on the PDA-modified Al₂O₃ tube after crystallization at 75 °C for 24 h, and no visible cracks, pinholes or other defects are observed on the membrane layer. The zeolite FAU membrane prepared at 75 °C for 24 h was evaluated in single gas permeation and mixed gas separation. For binary mixtures at 50 °C and 1 bar, the mixture separation factors of H₂/CH₄ and H₂/C₃H₈ are 9.9 and 127.7, respectively, which are much higher than the corresponding Knudsen coefficients. And relative high H₂ permeance of about 1.9 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ can be obtained through the FAU membrane due to the thin layer and the relative wide pore size of 0.74 nm, demonstrating a viable direction for promising application of FAU membranes in hydrogen purification and separation.

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1. Introduction

Since zeolites possess uniform pore structures and a high thermal and chemical stability, much attention has been focused on the synthesis of zeolite membranes, which are promising to separate gas or liquid mixtures with “molecular sieving” property, allowing or excluding molecules to pass through the zeolite pores depending on their molecular sizes [1–3]. To date, many types of zeolite membranes have been prepared on porous supports for gas and/or liquid separation [4–31], such as MFI [4–7], DDR [8,9], LTA [10–18], CHA [19,20], and FAU [21–29]. Among these zeolite membranes, zeolite LTA membrane attracts much attention because of its outstanding hydrophilicity, which is potential in dehydration of water–organics mixtures by pervaporation or steam permeation [32–35]. In fact, zeolite LTA has become the first industrial zeolite membrane in 2001 for dewatering of bio-ethanol [36].

The FAU-type zeolite (including NaX with Si/Al ratio of 1.0–1.5, and NaY with Si/Al ratio of 1.5–3.0) membrane, composed of 12-membered oxygen rings of approximately 0.74 nm in diameter, are attractive to separate large molecules which cannot be handled

effectively by MFI or LTA membranes [22–24]. Further, zeolite FAU membranes with low Si/Al ratio also display good hydrophilicity, thus it can be also used for the dehydration of organic solvents by pervaporation or steam permeation [25–27]. Therefore, the synthesis and application of zeolite FAU membranes have attracted much interest in the past two decades.

So far, two methods have been developed for the preparation of supported zeolite FAU membranes. The first method is secondary growth with seeding. Firstly, a packed layer of zeolite seeds is coated on the support surface, and then hydrothermal synthesis is carried out to form dense membrane layers. The secondary growth method is helpful to control the membrane microstructure [37], and thus results in a high reproducibility [12]. However, this preparation method is relative complicated due to the multiple-step preparation, thus a reliable seeding technique is indispensable for large-scale membrane synthesis. The second method is in-situ growth, where the support is immersed into the synthesis solution, and then the expected membrane is directly grown on the support surface by in-situ crystallization. This method is much simpler in comparison with the previous one. However, a dense and phase-pure zeolite FAU membrane is usually difficult to form owing to poor heterogeneous nucleation on the support surface by in-situ growth [29]. Therefore, it is desirable to develop a simple and powerful method to prepare high-quality zeolite FAU

* Corresponding author. Fax: +49 574 86685043.

E-mail address: huangaiseng@nimte.ac.cn (A. Huang).

membranes for hydrophilic separations and gas permeation.

In the recent years, we have developed a novel strategy for the in-situ growth of zeolite membranes by using 3-aminopropyltriethoxysilane (APTES) [38,39], 1,4-diisocyanate (DIC-4) [40], and 3-chloropropyltrimethoxysilane (CPTMS) [41] as covalent linkers between the zeolite layer and support surface. Via the covalent linkers, the zeolite nutrients were attracted and attached to the functionalized support surface, and thus promoting the nucleation and growth of a continuous zeolite membrane. It should be noted these modification processes were usually done under harsh conditions (110 °C in toluene), which restricts the synthesis of zeolite membranes at large-scale and increases the costs of the membrane manufacturing. Therefore, it is high desired to develop a simple and environmentally-friendly modification method for the facile synthesis of zeolite FAU membranes.

Recently, based on the reaction platform of bio-inspired polydopamine (PDA), we developed a simple, versatile and powerful synthesis strategy to prepare highly reproducible molecular sieve membranes. Attributing to its adhesive ability through non-covalent adsorption and covalent reaction [42], PDA is very effective to attach precursor species onto supports for the facile synthesis of dense and selective ZIF-8 membrane [43,44] and zeolite LTA membrane [45]. In the present work, we extend and develop this concept for in-situ growth of dense zeolite FAU molecular sieve membranes on PDA-modified α -Al₂O₃ tubes, as shown in Fig. S1. It can be expected that zeolite FAU membranes prepared on the PDA-modified supports will be more perfect and show higher gas separation performances.

2. Experimental

2.1. Materials

Reagents were used as received: LUDOX AS-40 colloidal silica (40% SiO₂ in water, Sigma-Aldrich); aluminum foil (99.99%, Aladdin); sodium hydroxide (> 98%, Aladdin); dopamine (DPA, 98%, Sigma-Aldrich); tris(hydroxymethyl) aminomethane (Tris-HCl, 99%, Aladdin). Porous α -Al₂O₃ tubes (Jiexi Lishun Technology Co., Guangdong, China: 12 mm outside diameter, 9 mm inside diameter, 75 mm length, ca. 1.0 μ m pore size, 30% porosity) were utilized as supports.

2.2. Porous tubes modification by dopamine

Dopamine (2 mg mL⁻¹) was dissolved in 10 mM Tris-HCl (pH 8.5) in an open watch glass (diameter: 140 mm). Subsequently the surface of the α -Al₂O₃ tubes were treated with dopamine at 20 °C for 20 h, leading to PDA layer with 50–200 nm thickness deposited on the support surface [43,45].

2.3. Synthesis of zeolite FAU membranes

In order to prepare zeolite FAU membrane on the PDA-modified α -Al₂O₃ tube, a clear synthesis solution with the molar ratio of 70 Na₂O:1 Al₂O₃:20 SiO₂:2000 H₂O was prepared according to the procedure reported elsewhere [29]. Typically, the aluminate solution was obtained by dissolving 15.56 g sodium hydroxide in 50 g deionized water, and then 0.15 g aluminum foil was added to the solution at room temperature, the prepared mixture solution was named as mixture A. Meanwhile, 8.34 g LUDOX AS-40 colloidal silica was dissolved in 44.44 g deionized water at room temperature and kept stirring vigorously for 2 h to obtain the silicate solution, and the solution was labeled as mixture B. Then mixture B was mixed with mixture A and stirred for 24 h at room temperature to produce a clear, homogenous solution. The PDA-

modified and non-modified α -Al₂O₃ tubes were vertically placed in a Teflon-lined stainless steel autoclave, and then the synthesis solution was poured into the autoclave. After in-situ growth for a certain time at 75 °C, the solution was decanted off and the zeolite FAU membrane was achieved after washing with deionized water for several times and drying in air at 110 °C over night.

2.4. Characterizations of zeolite FAU membrane

The phase structure analysis of the zeolite FAU membrane was carried out by X-ray diffraction (XRD) at room temperature under ambient pressure. XRD analyses were recorded on a Bruker D8 Advance operating at 40 kV and 40 mA with a Cu K α 1 radiation source ($\lambda=0.154056$ nm) at a stepwise increase of 2° s⁻¹ in the Bragg angle (2 θ) range from 5° to 40°. The Fourier Transform IR (FT-IR) spectra of the non-modified and PDA-modified Al₂O₃ supports were achieved in the absorbance mode in a Bruker Tensor 27 spectrophotometer. Spectra were collected at 4 cm⁻¹ resolution averaging 32 scans. The morphology and thickness of the zeolite FAU membranes were performed by field emission scanning electron microscopy (FESEM). FESEM micrographs were taken on an S-4800 (Hitachi) with a cold field emission gun operating at 4 kV and 10 μ A. Energy-dispersive X-ray spectroscopy (EDXS) was used to characterize the chemical composition of the zeolite FAU membrane at 20 kV and 20 μ A.

2.5. Single gas permeation and mixture gas separation

The zeolite FAU membranes produced on PDA-modified α -Al₂O₃ tubes were evaluated by single gas permeation and mixed gas separation. For the permeation experiments, the obtained FAU membrane was sealed in a permeation module with silicone O-rings. The sweep gas N₂ was fed on the permeate side to maintain the concentration of the permeating gas as low as possible to provide a high driving force for permeation. The flux of the feed and sweep gases were controlled by mass flow controllers. The gas concentrations were analyzed using a calibrated gas chromatograph (Echrom A90). The separation factor α_{ij} of a binary mixture permeation is defined as the quotient of the molar ratios of the components (*i, j*) in the permeate, divided by the quotient of the molar ratio of the components (*i, j*) in the retentate, as shown in Eq. (1)

$$\alpha_{ij} = \frac{y_{i, perm}/y_{j, perm}}{y_{i, ret}/y_{j, ret}} \quad (1)$$

3. Results and discussions

3.1. PDA modification of Al₂O₃ tube

After PDA modification at 20 °C for 20 h, the color of the α -Al₂O₃ tube changed from white to dark brown (Fig. 1), indicating that PDA could easily deposit on the surface of α -Al₂O₃ tube. Moreover, compared with the FT-IR spectrum of non-modified α -Al₂O₃, the FT-IR spectrum of PDA-modified α -Al₂O₃ contains remarkable bands at 1058, 1274, 1510, 2938 cm⁻¹, which match well with the FTIR spectrum of PDA [46,47]. The band at 1058 cm⁻¹ can be assigned to C–O stretching vibrations of carbonyl groups, and the band at 1274 cm⁻¹ indicates C–OH stretching vibrations [48,49]. The band shown at 1510 cm⁻¹ is related to N–H vibration. The absorptions of CH₂ groups of aliphatic chain are observed at high frequency of 2938 cm⁻¹ resulting from the asymmetric and symmetric stretching vibrations. The presence of N–H, C–O, C–OH and –CH₂ as well as the reduction

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