Facile synthesis of zeolite FAU molecular sieve membranes on bio-adhesive polydopamine modified Al$_2$O$_3$ tubes

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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 Al$_2$O$_3$ 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 Al$_2$O$_3$ 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 H$_2$/CH$_4$ and H$_2$/C$_3$H$_8$ are 9.9 and 127.7, respectively, which are much higher than the corresponding Knudsen coefficients. And relative high H$_2$ 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

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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-aminopropyl-triethoxysilane (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 poly-dopamine (PDA), we developed a simple, versatile and powerful synthesis strategy to prepare highly reproducible molecular sieve membranes. Attributing to its adhesive ability through non-cova-lent 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-Al$_2$O$_3$ 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% SiO$_2$ in water, Sigma-Aldrich); aluminum foil (99.99%, Alad-din); sodium hydroxide (> 98%, Aladdin); dopamine (DPA, 98%, Sigma-Aldrich); tris(hydroxymethyl) aminomethane (Tris–HCl, 99%, Aladdin). Porous α-Al$_2$O$_3$ tubes (Jiexi Lishun Technology Co., Guangdong, China: 12 mm outside diameter, 9 mm inside dia-meter, 75 mm length, ca. 1.0 μm 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-Al$_2$O$_3$ 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-Al$_2$O$_3$ tube, a clear synthesis solution with the molar ratio of 70 Na$_2$O:1 Al$_2$O$_3$:20 SiO$_2$:2000 H$_2$O was prepared according to the procedure reported elsewhere [29]. Typically, the aluminate so-lution 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 col-loidal silica was dissolved in 44.44 g deionized water at room temperature and kept stirring vigorously for 2 h to obtain the si-licate 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-Al$_2$O$_3$ 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 Kα1 radiation source (λ=0.154056 nm) at a stepwise increase of 2° s^{-1} in the Bragg angle (2θ) range from 5° to 40°. The Fourier Transform IR (FT-IR) spectra of the non-modified and PDA-modified Al$_2$O$_3$ 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 op-erating at 4 kV and 10 μA. Energy-dispersive X-ray spectroscopy (EDXS) was used to characterize the chemical composition of the zeolite FAU membrane at 20 kV and 20 μA.

2.5. Single gas permeation and mixture gas separation

The zeolite FAU membranes produced on PDA-modified α-Al$_2$O$_3$ 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 N$_2$ was fed on the permeate side to maintain the concentration of the permeating gas as low as pos-sible 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 $\alpha_{i,j}$ 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)

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

3. Results and discussions

3.1. PDA modification of Al$_2$O$_3$ tube

After PDA modification at 20 °C for 20 h, the color of the α-Al$_2$O$_3$ tube changed from white to dark brown (Fig. 1), indicating that PDA could easily deposit on the surface of α-Al$_2$O$_3$ tube. Moreover, compared with the FT-IR spectrum of non-modified α-Al$_2$O$_3$, the FT-IR spectrum of PDA-modified α-Al$_2$O$_3$ 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 car-bonyl 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 CH$_2$ groups of ali-phatic chain are observed at high frequency of 2938 cm^{-1} re-sulting from the asymmetric and symmetric stretching vibrations. The presence of N–H, C–O, C–OH and –CH$_2$ as well as the reduction
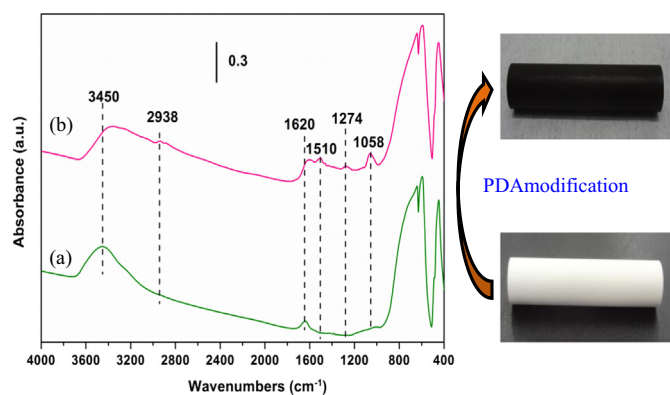
Fig. 1. FT-IR spectra of (a) bare Al_2O_3 support and (b) PDA-modified Al_2O_3 support. The dashed lines indicate the following vibrations: $3450\ cm^{-1}$ and $1620\ cm^{-1}$ (O–H), $2938\ cm^{-1}$ (C–H_2), $1510\ cm^{-1}$ (N–H), $1274\ cm^{-1}$ (C–OH), and $1058\ cm^{-1}$ (C–O).

of O–H at $3450\ cm^{-1}$ after the PDA modification confirms that PDA has been grafted on the surface of Al_2O_3 tube.

The grafting of PDA on the surface of Al_2O_3 tube was further confirmed by XPS. As shown in Fig. S2, after PDA modification, the Al 2p peaks from the Al_2O_3 support were completely covered, and the intensity of C 1s peaks significantly enhances. Further, a new N 1s peak emerges at binding energy of about 399.5 eV, which is in good agreement with the previous reports [42,43].

3.2. Synthesis and characterization of zeolite FAU membrane

Fig. 2a and b shows the FESEM images of the zeolite FAU membrane prepared on α-Al_2O_3 tube without PDA-modification before hydrothermal synthesis. It can be seen that no dense zeolite FAU membrane can be formed when the support surface was not modified with PDA before hydrothermal synthesis, and inter-crystal voids are easily observed on the membrane layer. On the contrary, a dense zeolite FAU membrane is formed if the surface of

the α-Al_2O_3 tube was treated with PDA before hydrothermal synthesis (Fig. 2c and d). It can be seen that a well-intergrown zeolite FAU membrane with a thin thickness of about 2.3 μm is formed on the surface of the α-Al_2O_3 tube, and no visible cracks, pinholes or other defects can be observed on the surface of the membrane. According to the previous reports [25,29], a continuous and phase-pure zeolite FAU membrane is rather difficult to prepare via in-situ hydrothermal synthesis because of the poor heterogeneous nucleation of FAU on the support surface. Therefore, the support surface is usually coated with zeolite seeds to promote the nucleation and growth of the dense FAU layer. In the present work, attributing to the adhesive ability of PDA through non-covalent adsorption and covalent reaction [43,45], the FAU precursors are first attached and then chemically anchored onto the support surface for the nucleation and growth of a continuous zeolite FAU layer. The enhancement of nucleation on the PDA-modified α-Al_2O_3 tube can be deduced from membrane morphology. A large number of small and well intergrown crystals (about 1 μm) are formed on PDA-modified Al_2O_3 tube (Fig. 2c), while larger FAU aggregates (about 5 μm) are found on the non-modified support surface (Fig. 2a).

Figs. 3 and 4 show the FESEM images of the zeolite FAU membranes prepared on PDA-modified α-Al_2O_3 tube at 75 °C for different synthesis time. As shown in Figs. 3a and 4a, in a short synthesis time of 4 h, amorphous phases rather than zeolite FAU crystals are observed on the support surface. After 8 h synthesis (Figs. 3b and 4b), the support surface has been covered with sub-micron zeolite FAU crystals and form a thin layer with a thickness of about 0.9 μm, but observable inter-crystalline gaps are still found between the zeolite FAU crystals. With increasing crystallization time, the FAU crystals grow larger and larger with typically bi-pyramidal morphology. After synthesis time of 16 h at 75 °C, a dense FAU membrane with a thickness of 2.0 μm can be formed (Figs. 3d and 4d). A much denser FAU membrane is formed after 20 h, and correspondingly the thickness of the FAU membrane increases to 2.3 μm (Figs. 3e and 4e). Extending the synthesis time longer than 20 h, the membrane thickness keeps constant (Figs. 4f
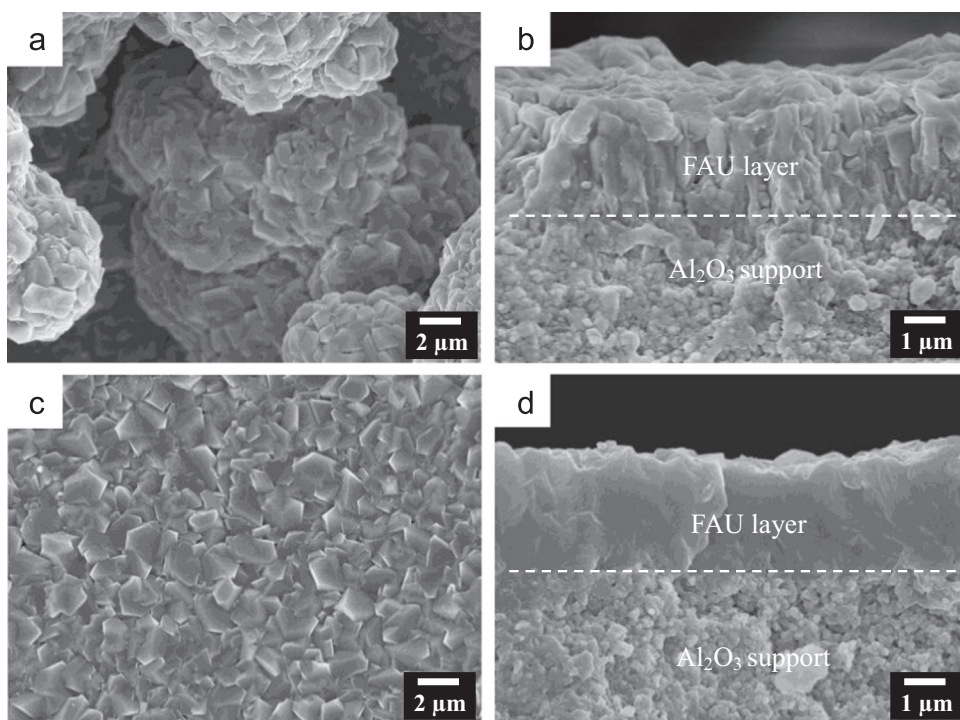

Fig. 2. Top view (a) and cross-section view (b) FESEM images of the zeolite FAU membrane prepared on non-modified α-Al_2O_3 tube; top view (c) and cross-section view (d) FESEM images of the zeolite FAU membrane prepared on PDA-modified α-Al_2O_3 tube.
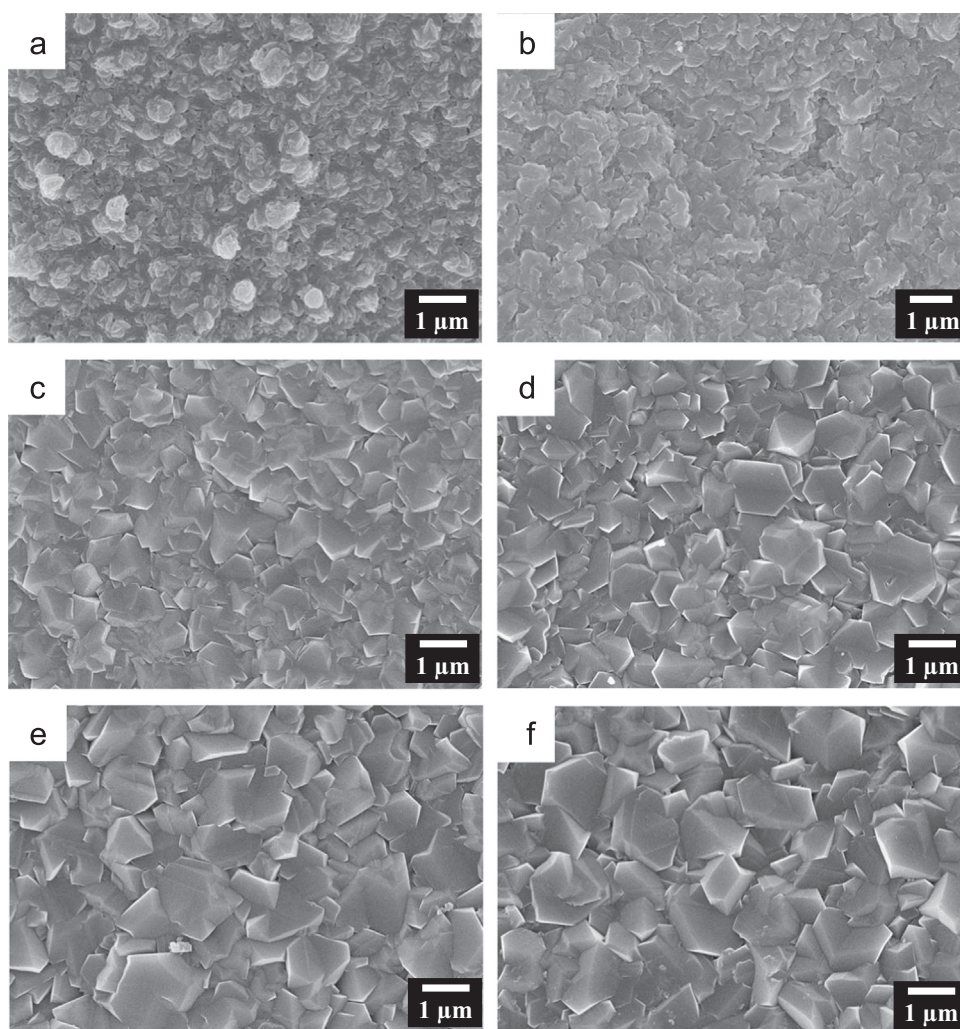
Fig. 3. Top view FESEM images of the zeolite FAU membranes on PDA-modified α-Al$_2$O$_3$ tubes prepared at 75 °C for different synthesis time: (a) 4 h, (b) 8 h, (c) 12 h, (d) 16 h, (e) 20 h, and (f) 24 h.

and 5), indicating that the FAU growth has been completed after 24 h under the present experimental conditions.

These evolvements of membrane growth are in good accordance with the XRD characterization. As shown in Fig. 6, after synthesis of very short time (4 h), only weak FAU phase can be observed. When synthesis time increases to 12 h, clear zeolite FAU has been detected on the support surface. Then the heights of zeolite FAU peaks relative to alumina support increase with synthesis time, indicating that thicker zeolite FAU membranes are formed with longer synthesis time, which is in good agreement with the membrane thickness as shown in Fig. 5. When the synthesis time is longer than 20 h, the heights of zeolite FAU peaks relative to alumina support remain constant, indicating that the crystallization of phase-pure zeolite FAU membrane has been completely achieved. From the EDXS pattern (Fig. S3), the Si/Al ratio of the zeolite FAU membrane is about 1.38, which is in good agreement with our previous report of zeolite FAU membrane [29], further confirming the formation of a phase-pure zeolite FAU membrane.

3.3. Evaluation of single gas permeation and mixture gas separation

The obtained zeolite FAU membrane supported on PDA-modified Al$_2$O$_3$ prepared at 75 °C for 24 h was measured by single gas permeation and mixed gas separation. Fig. 7 shows the permeances of the single gas through the zeolite FAU membrane as a function of the kinetic diameters of the permeating molecules at 50 °C and 1 bar. As shown in Fig. 7, attributing to its smallest molecular diameters (0.29 nm) in comparison with N$_2$ (0.364 nm), CH$_4$ (0.38 nm), C$_3$H$_8$ (0.43 nm), and SF$_6$ (0.55 nm), the H$_2$ permeance of 2.83×10^{-7} mol m^{-2} s^{-1} Pa^{-1} is much higher than the permeances of N$_2$ (2.54×10^{-8} mol m^{-2} s^{-1} Pa^{-1}), CH$_4$ (1.93×10^{-8} mol m^{-2} s^{-1} Pa^{-1}), C$_3$H$_8$ (1.60×10^{-9} mol m^{-2} s^{-1} Pa^{-1}), and SF$_6$ (6.80×10^{-10} mol m^{-2} s^{-1} Pa^{-1}). The single gas permeances of the zeolite FAU membrane follow the sequence: H$_2$ > N$_2$ > CH$_4$ > C$_3$H$_8$ > SF$_6$, completely corresponding to their kinetic diameters. At 50 °C and 1.0 bar, the ideal separation factors of H$_2$/N$_2$, H$_2$/CH$_4$, H$_2$/C$_3$H$_8$, and H$_2$/FS$_6$, determined as the ratio of the single component permeances, are 11.2, 14.7, 177.5 and 416.2, respectively, which by far exceeded the corresponding Knudsen coefficients (3.7, 2.8, 4.7, and 5.9), suggesting that the zeolite FAU membrane prepared on PDA-modified α-Al$_2$O$_3$ tubes displayed high H$_2$ selectivity. It is worth to mention that the single gas permeance through the zeolite FAU membrane which was prepared on the non-modified α-Al$_2$O$_3$ tube cannot be collected because no constant feed pressure of 1.0 bar can be realized, indicating that there are inter-crystal voids in the FAU layer prepared on the non-modified α-Al$_2$O$_3$ support, and that PDA functionalization is indispensable for the growth of high-quality zeolite FAU membrane on the porous Al$_2$O$_3$ tubes.

The gas separation performance of the zeolite FAU membrane prepared on PDA-functionalized α-Al$_2$O$_3$ tube was investigated by the
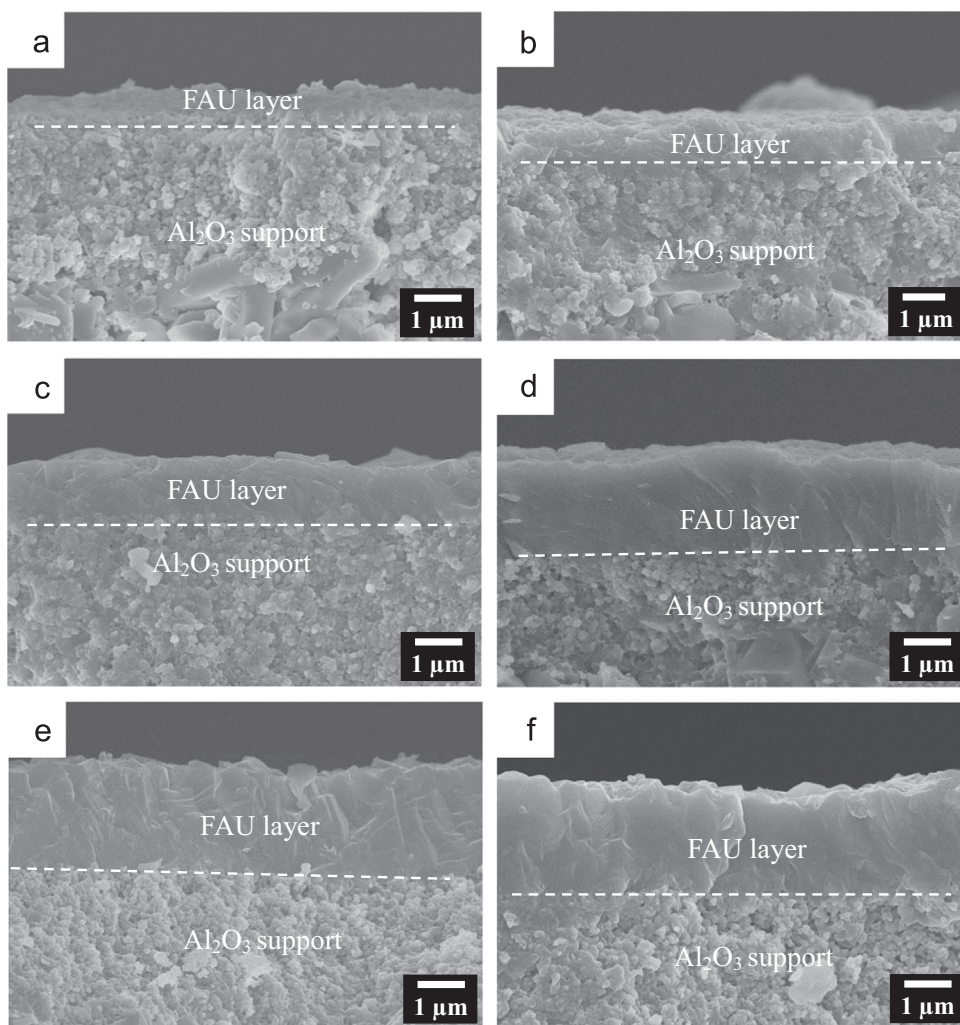
Fig. 4. Cross-section view FESEM images of the zeolite FAU membranes on PDA-modified α-Al₂O₃ tubes prepared at 75 °C for different synthesis time: (a) 4 h, (b) 8 h, (c) 12 h, (d) 16 h, (e) 20 h, and (f) 24 h.
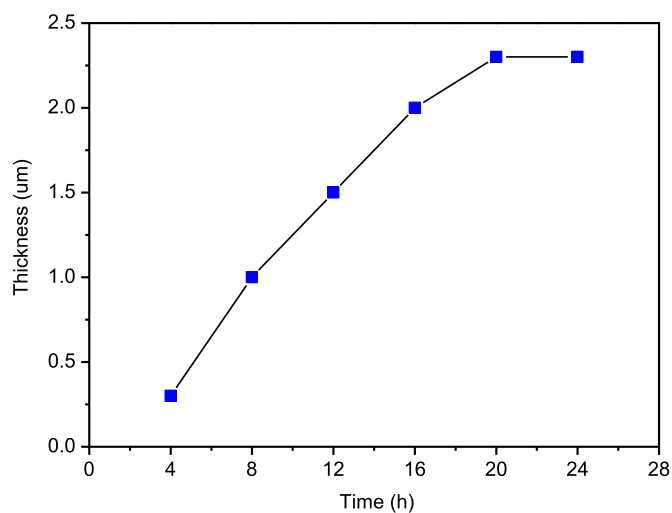

Fig. 5. The thickness of the zeolite FAU membranes prepared on PDA-modified α-Al₂O₃ tubes at 75 °C as a function of synthesis time.
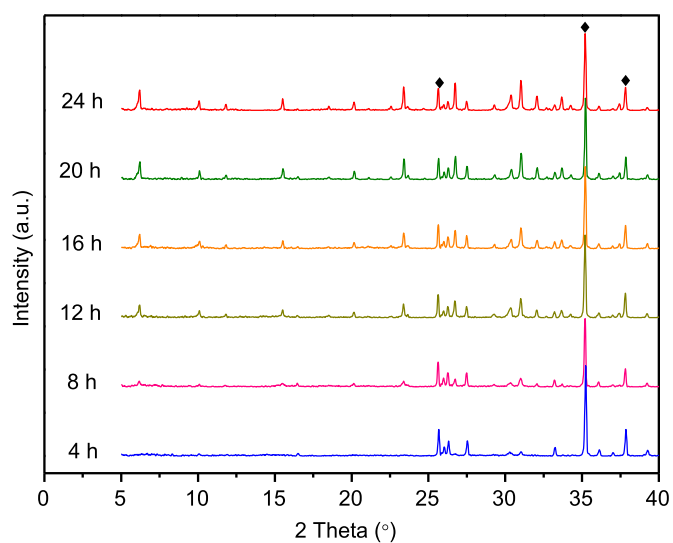

Fig. 6. XRD patterns of the zeolite FAU membranes prepared at 75 °C on PDA-modified α-Al₂O₃ tubes as a function of synthesis time. (♦): Al₂O₃ support, (not marked): zeolite FAU.
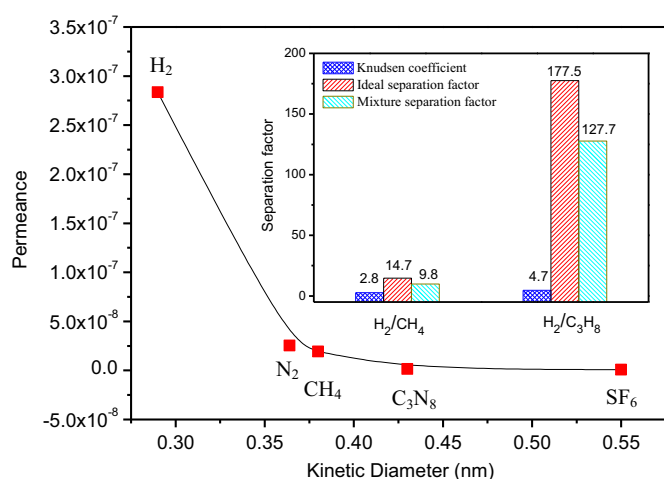
Fig. 7. Single gas permeance of different gases through zeolite FAU membrane prepared on PDA-modified α-Al$_2$O$_3$ tubes as a function of the gas kinetic diameter at 50 °C and 1 bar. The inset shows the ideal and mixture separation factors of the zeolite FAU membrane prepared on PDA-modified α-Al$_2$O$_3$ tubes. The zeolite FAU membrane was prepared at 75 °C for 24 h. The single gas SF$_6$ was measured by using soap-film method.

proposed seeds coating and chemical modification methods, thus the present strategy is helpful to reduce the cost of the membrane preparation.

Table 2 also lists the gas separation performance of the zeolite FAU and other zeolite membranes in previous studies. Although gas separation results from different labs are usually difficult to compare due to different experimental conditions, it can be said that the zeolite FAU membranes prepared on PDA-modified support are among those with the best gas separation performances. However, it has to be admitted that zeolite FAU membranes are not the perfect candidate for the separation of small molecules due to its rather large pore size. Therefore, post-functionalization of the zeolite FAU membrane, as shown in previous reports [54,55], should be helpful to enhance the separation performances of zeolite FAU membrane.

3.4. Stability evaluation of the zeolite FAU membrane

Fig. 8 shows the permeances and H$_2$/CH$_4$ selectivity of the zeolite FAU membrane prepared at 75 °C for 24 h as a function of temperature at 1 bar. It can be seen that the H$_2$ permeance increases from 1.50×10^{-7} mol m^{-2} s^{-1} Pa^{-1} to 2.84×10^{-7} mol m^{-2} s^{-1} Pa^{-1} when the operation temperature

Table 1
Single and mixed gases permeances and separation factors at 50 °C and 1 bar for the zeolite FAU membrane prepared on PDA-modified Al$_2$O$_3$ tube.

Gas$_{i/j}$	Knudsen coefficient	Separation performances of the zeolite FAU membrane grown on PDA-modified Al$_2$O$_3$ tube					
		Single gas			Mixed gases		
		Permeances (i) (mol m^{-2} s^{-1} Pa^{-1})	Permeances (j) (mol m^{-2} s^{-1} Pa^{-1})	ISF	Permeances (i) (mol m^{-2} s^{-1} Pa^{-1})	Permeances (j) (mol m^{-2} s^{-1} Pa^{-1})	SF
H$_2$/N$_2$	3.7	2.83×10^{-7}	2.54×10^{-8}	11.1	–	–	–
H$_2$/CH$_4$	2.7	2.83×10^{-7}	1.93×10^{-8}	14.7	1.92×10^{-7}	1.94×10^{-8}	9.9
H$_2$/C$_3$H$_8$	4.7	2.83×10^{-7}	1.60×10^{-9}	177.5	1.87×10^{-7}	1.46×10^{-9}	127.7
H$_2$/SF$_6$	5.9	2.83×10^{-7}	6.80×10^{-7}	416.2	–	–	–

ISF: ideal separation factor, which is determined as the ratio of the single component permeances; SF: mixture separation factor, which 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.

separation of equimolar mixtures of H$_2$ with CH$_4$ and C$_3$H$_8$. Compared with the H$_2$ single gas permeance (2.83×10^{-7} mol m^{-2} s^{-1} Pa^{-1}), the H$_2$ permeance ($\sim 1.9 \times 10^{-7}$ mol m^{-2} s^{-1} Pa^{-1}) in the mixture is lower, indicating that the larger molecules (CH$_4$ and C$_3$H$_8$) slow down the permeation of the highly mobile H$_2$. While the permeances of the CH$_4$ and C$_3$H$_8$ in the mixture gases are slightly higher than those of the corresponding single gas permeances (Table 1). For the 1:1 binary mixtures at 50 °C and 1 bar, the mixture separation factors of H$_2$/CH$_4$ and H$_2$/C$_3$H$_8$, determined as the molar ratios in permeate and retentate, are 9.9, 127.7, which are also much higher than the Knudsen coefficients. Recently, we have reported the synthesis of zeolite FAU membrane on the APTES-modified α-Al$_2$O$_3$ disk [29]. Comparing with the zeolite FAU membrane on the APTES-modified support, the zeolite FAU membrane on the PDA-modified α-Al$_2$O$_3$ tube displays higher separation selectivities (Table 2). As mentioned above, the zeolite FAU precursors are facilely attached and then chemically anchored onto the support surface for the nucleation and growth attributing to the adhesive ability of PDA, resulting in the formation of a much denser zeolite FAU membrane on the PDA-modified alumina tube. Further, a strong binding strength between support and FAU layer can be expected due to the adhesive ability of PDA through covalent reaction, leading to the enhancement of the separation selectivity of zeolite FAU membrane. It is worth to mention that the whole modification procedure by PDA is done under a mild environment (simple immersion at room temperature, non-toxic), which is easy and effective in comparison with the previously

increases from 25 °C to 100 °C, while the mixture separation factor of H$_2$/CH$_4$ increases from 9.0 to 10.4. A similar phenomenon was also observed on the zeolite FAU membrane prepared on APTES-modified α-Al$_2$O$_3$ disk [29], which can be explained by the adsorption–diffusion model of permeation. At low temperature, mainly CH$_4$ is adsorbed in the zeolite FAU pores thus blocking the diffusion of the rarely adsorbed but highly mobile H$_2$. With increasing temperature, less CH$_4$ is adsorbed and hence more H$_2$ can diffuse in the resulting free volume, leading to an enhancement of the H$_2$/CH$_4$ selectivity. Further, the zeolite FAU membrane has been tested for the separation of equimolar H$_2$/CH$_4$ mixtures at 100 °C and 1 bar for more than 24 h, and both the H$_2$ permeance and H$_2$/CH$_4$ selectivity remains unchanged (Fig. 9), indicating that the zeolite FAU membrane has a high thermal stability.

4. Conclusion

Inspired by the highly bio-adhesive ability of PDA, we developed a seeding-free synthesis method to prepare dense and phase-pure zeolite FAU membranes on PDA-modified porous α-Al$_2$O$_3$ tubes. PDA facilitated the growth of the zeolite FAU membrane on the α-Al$_2$O$_3$ tubes and shortened the synthesis time for obtaining high-quality zeolite FAU membrane. For the zeolite FAU membrane prepared on PDA-modified α-Al$_2$O$_3$ tube at 75 °C for 24 h, at 50 °C and 1 bar, the mixture separation factors of H$_2$/CH$_4$ and H$_2$/C$_3$H$_8$ were 9.9 and 127.7,

Table 2
Comparison of mixed gas separation performances of the zeolite FAU membranes in this study with other zeolite FAU membranes from literature.

Membrane	Seeding	Thickness (μm)	T (°C)	H_2 permeances (mol m^{-2} s^{-1} Pa^{-1})	Separation factor			Reference
					H_2/CO_2	H_2/CH_4	H_2/C_3H_8	
FAU[a]	No	2.7	50	2.84×10^{-7}	–	14.7[b]	177.5[b]	This study
				1.87×10^{-7}		9.9	127.7	
FAU	No	5.0	25	5.5×10^{-7}	5.4[b]	–	–	[26]
FAU	No	2.5	100	5.0×10^{-7}	8.0[b]	5.6[b]	18.6[b]	[29]
				4.0×10^{-7}	6.5	4.0	11.1	
FAU[c]	Yes	3.5	23	1.9×10^{-7}	4.5	2.7	–	[28]
FAU[d]	Yes	6.0		0.1×10^{-7}	4.9	2.9	–	
FAU	Yes	25	37	35×10^{-7}	3.8	–	–	[23]
FAU	Yes	–	16	8.8×10^{-7}	4.9	–	–	[50]
LTA	No	3.5	20	3.0×10^{-7}	5.3	3.6	–	[38]
LTA	No	3.5	20	2.3×10^{-7}	6.7	4.9	15.8	[40]
MFI	Yes	2	25	7.9×10^{-6}	1.8	–	–	[51]
CHA	No	–	27	3.0×10^{-8}	1.3	25	–	[52]
CHA[e]	No	100	20	7.02×10^{-7}	4.8[b]	–	21[b]	[53]

[a] Prepared on PDA-modified support.
[b] Ideal separation factor.
[c] Conventional heating.
[d] Microwave heating.
[e] Ionothermal synthesis.
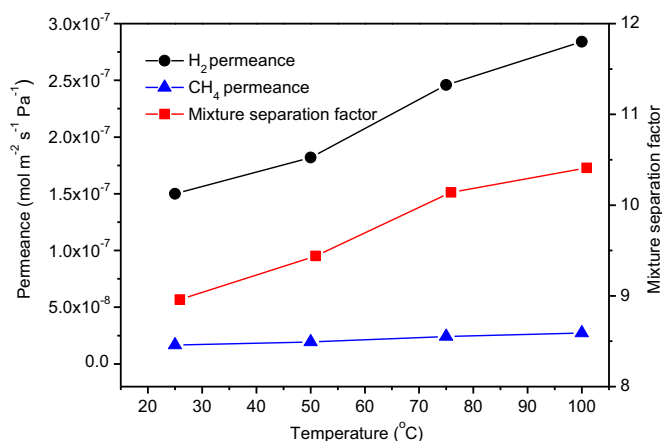
Fig. 8. Mixed gas permeances and H_2/CH_4 selectivity of the zeolite FAU membrane prepared on PDA-modified α-Al$_2$O$_3$ tube at 75 °C for 24 h as a function of temperature at 1 bar.
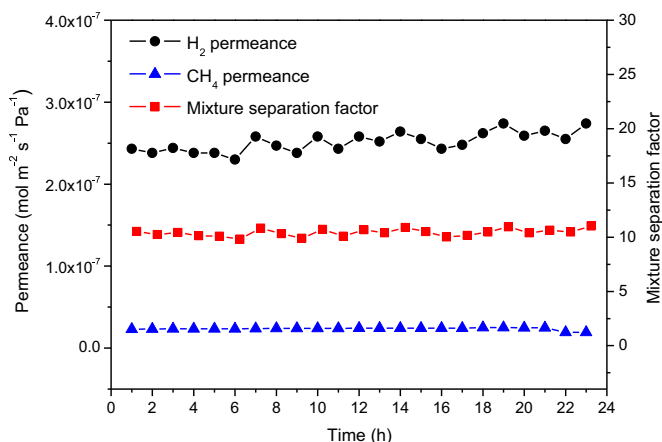
Fig. 9. Thermal stability evaluation of the zeolite FAU membrane prepared on PDA-modified α-Al$_2$O$_3$ tube for the separation of an equimolar H_2/CH_4 mixture at 100 °C and 1 bar.

respectively, which by far exceeded the corresponding Knudsen constants. Moreover, relative high H_2 permeances of approximately 1.9×10^{-7} mol m^{-2} s^{-1} Pa^{-1} had been obtained on account of the

thin membrane layer of 2.3 μm. Note that CO_2 is undesirable in many applications and its separation and removal from natural gas is emergent considering of energy effectiveness, thus in future work, we will focus on the separation of CO_2 by using the zeolite FAU membrane prepared on PDA-modified support and enhance the separation performance due to its large pore size by pore engineering.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at 10.1016/j.memsci.2015.07.045

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