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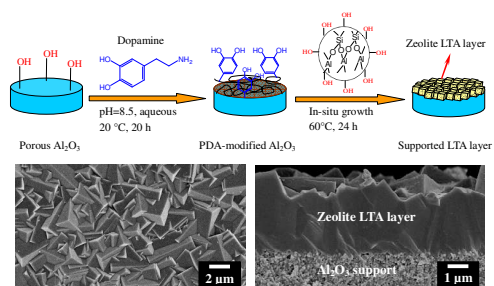
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A graphical Abstract

Inspired by bio-adhesive ability of marine mussel, a versatile and effective synthesis strategy was developed to prepare dense zeolite LTA membranes



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ARTICLE TYPE

Mussel-Inspired Polydopamine Modification of Supports for Facile Synthesis of Zeolite LTA Molecular Sieve Membranes

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Inspired by the bio-adhesive ability of the marine mussel, a simple, versatile, effective and green synthesis strategy was developed to prepare dense, phase-pure and reproducible zeolite molecular sieve membranes by using polydopamine (PDA) as a novel covalent linker. Through the formation of strong non-covalent and covalent chemical bonds, zeolite LTA nutrients can be attracted and bound to the support surface, thus promoting the nucleation and seeding-free growth of uniform, well-intergrown and phase-pure zeolite membranes. The zeolite LTA membranes prepared on PDA-modified Al_2O_3 disks were evaluated in single gas permeation and mixed gas separation. It is found that the zeolite LTA membranes prepared on PDA-modified support showed higher gas separation selectivities. At 373 K and 1 bar, the mixture separation factors of H_2/CO_2 , H_2/N_2 , H_2/CH_4 , and $\text{H}_2/\text{C}_3\text{H}_8$ are 7.8, 7.2, 6.6 and 18.3, which far exceed the corresponding Knudsen coefficients. Furthermore, in comparison with the previously proposed chemical modification methods, the modification procedure by PDA is done under a mild environment (simple immersion in buffered aqueous solution of DPA at room temperature), thus it is helpful to prepare zeolite membranes at a large-scale and reduce the costs of the membrane manufacturing.

Introduction

Separation and purification plays an important role in chemical industry. In comparison with conventional distillation and adsorption processes, membrane-based separations show many advantages such as energy saving and cost effectiveness.¹ With “molecular sieving” property, zeolite membranes is promising to discriminate the components of gaseous or liquid mixtures, i.e., allowing or excluding molecules to pass through the zeolite pore dependent on their molecular sizes. In the recent two decades, zeolite membranes have attracted much interest in many potential applications such as separation and reaction due to their uniform pore structure and high thermal stability.²⁻⁶ So far, various types of zeolite membranes, including MFI,⁷⁻¹⁰ LTA,¹¹⁻²² FAU,²³⁻²⁵ DDR,^{26, 27} CHA,^{28, 29} and AFI,^{30, 31} have been prepared on porous supports for gas/liquid separations. Among these molecular sieve membranes, zeolite LTA membranes are especially attractive. Zeolite LTA membrane with Si/Al ratio of 1 displays a strong hydrophilicity, and thus is promising for dehydration of water/organics solutions by pervaporation.¹¹⁻¹⁶ Indeed, zeolite LTA membranes have showed excellent separation performance in the dehydration of water/organics mixtures. In 2001, zeolite LTA membrane has been installed for the first time at an industrial scale for the de-watering of bio-ethanol by Mitsui Engineering and Shipping Co. Ltd.³² Until now, more than 100 pervaporation set-ups of zeolite LTA membrane have been built for the de-watering of bio-ethanol in

the world. Furthermore, zeolite LTA membrane for Na^+LTA (4A) with small pore size of about 0.4 nm (by ion exchange, the pore size of zeolite LTA can be engineered: (5A)) is expected to be used for the separation of small molecules such as hydrogen.¹⁷⁻²²

However, it has to admit that the gas separation performance of the zeolite LTA membrane is still far away from our expectation for the separation of small molecules. So far, there are only a few reports on successful shape-selective separations of gas mixtures through zeolite LTA membranes,²⁰⁻²² and most of the reported mixture separation factors were only close to Knudsen coefficients.^{33, 34} It is often found that zeolite LTA membranes contain inter-crystalline defects because the negatively charged silicate/aluminate building blocks are difficult to enter the narrow gaps between the zeolite LTA crystals.³⁵ Due to these inter-crystalline defects, gas transport through the membrane is mainly controlled by Knudsen diffusion rather than by a molecular sieve mechanism.^{17, 33} Therefore, it is difficult to synthesize zeolite LTA membrane with molecular sieving performances.

It is recognized that the formation of zeolite membranes on supports is a heterogeneous nucleation process.^{36, 37} As proposed by Myatt,³⁶ a homogeneous aluminosilicate gel was first formed on the support surface providing more favorable conditions for nucleation and growth in the vicinity of the surface, followed by crystal growth to form a continuous layer. Therefore, the promotion of nucleation on the substrate surface is crucial to the membrane formation. However, the heterogeneous nucleation of zeolite on the support surface is rather poor due to the weak interaction between molecular precursor species and the support

surface, which results in the difficulty to form a dense layer.^{38, 39} In order to promote nucleation and growth of the zeolite layers, seed coating^{39, 40} and chemical modification⁴¹⁻⁴³ of the support surface were usually applied to offer nucleation center.

Recently, we have developed a novel strategy for the seeding-free preparation of zeolite LTA membranes by using 3-aminopropyltriethoxysilane (APTES),^{41, 44} 1, 4-diisocyanate (DIC-4),⁴² and 3-chloropropyltrimethoxysilane (CPTMS)⁴³ as covalent linker between the zeolite layer and the porous α -Al₂O₃ support. Through the covalent linkers, the zeolite LTA nutrients were attached to the support surface and thus promoting the nucleation and growth of a continuous zeolite LTA layer. It should be noted these previous modification processes were usually done under harsh conditions (383 K in toluene), which

restricts the preparation 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 membranes. Inspired by the bio-adhesive ability of the marine mussel, Messersmith and co-workers have demonstrated that dopamine (DPA) can polymerize to form polydopamine (PDA), and stick on all kinds of organic and inorganic material surfaces.⁴⁵ The resultant PDA has emerged as a versatile platform for secondary reactions.⁴⁶⁻⁴⁸ Recently, based on the PDA reaction platform, we developed a simple, versatile and powerful synthesis strategy to prepare highly reproducible and selective zeolitic imidazolate frameworks ZIF-8 membranes.⁴⁹ Attributing to its adhesive ability through non-covalent adsorption and covalent reaction, PDA is very effective to attach precursor species onto supports for the facile synthesis of dense molecular sieve membranes. In the present work, we extend and develop this concept for in-situ growth of dense zeolite LTA molecular sieve membranes on PDA functionalized supports, as shown in Fig. 1. It can be expected that zeolite LTA membranes prepared on PDA functionalized supports will be more perfect and show higher gas separation performances.

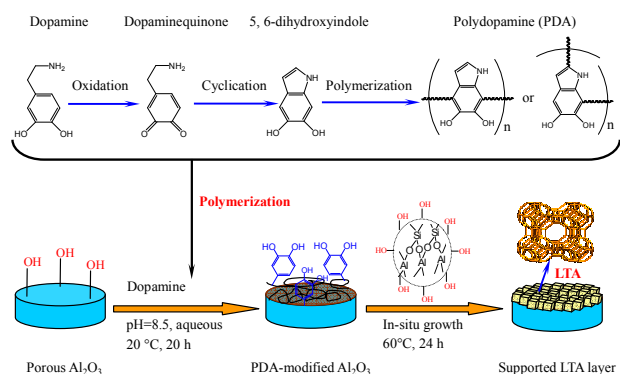


Fig. 1. Schematic diagram of the synthesis of zeolite LTA membranes on polydopamine modified alumina supports.

Experimental

Materials

Chemicals were used as received: LUDOX AS-40 colloidal silica

(40% SiO₂ in water, Aldrich); aluminum foil (99.99%, Aldrich); sodium hydroxide (>98%, Aladin); dopamine (DPA, 98%, Aldrich), tris(hydroxymethyl) aminomethane (Tris-HCl, 99%, Aladin); doubly distilled water. Porous α -Al₂O₃ (Fraunhofer Institute IKTS, former HITK/Inocermic, Hermsdorf, Germany: 18 mm in diameter, 1.0 mm in thickness, 70 nm particles in the top layer), 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), non-porous glass plates (home-made: 18 x 18 x 1 mm), and non-porous stainless steel disks (home-made: 18 mm diameter, 1.0 mm thickness) were used as supports.

Dopamine modification on the supports surface

Dopamine (2 mg/mL) was dissolved in 10 mM Tris-HCl (pH 8.5) in an open watch glass (diameter: 180 mm). And then the top surface of the porous α -Al₂O₃ disks were treated with dopamine at 293 K for 20 h, leading to polydopamine (PDA) layer with 50–200 nm thickness being deposited on the support surface.^{50, 51} After drying, PDA-modified α -Al₂O₃ supports show similar N₂ permeance with non-modified α -Al₂O₃ supports, indicating that PDA modification have no negative effect on the gas permeance of the support.³⁴

Preparation of zeolite LTA membranes

For synthesis of zeolite LTA membrane on the PDA-modified α -Al₂O₃ support surface, a clear synthesis solution with the molar ratio of 50 Na₂O : 1Al₂O₃ : 5SiO₂ : 1000H₂O, was prepared according to the procedure reported elsewhere.⁴¹⁻⁴³ The aluminate solution was prepared by dissolving 22.22 g sodium hydroxide in 50 g deionized water, then adding 0.3 g aluminum foil to the solution at room temperature. The silicate solution was prepared by mixing 4.17 g LUDOX AS-40 colloidal silica and 47.5 g deionized water at 333 K with vigorous stirring. The prepared aluminate solution was added into the silicate solution with stirring for 2 h to produce a clear, homogenous solution. The PDA-modified or non-modified α -Al₂O₃ disks were horizontally placed face down (Al₂O₃ tubes were placed vertically) in a Teflon-lined stainless steel autoclave, and then the synthesis solution was poured into the autoclave. After in-situ growth for 24 h at 333 K besides special instruction, the solution was decanted off and the zeolite LTA membrane was washed with deionized water several times, and then dried in air at 383 K over night for characterization and permeation measurement.

Characterization of zeolite LTA membranes

The morphology and thickness of the zeolite molecular sieve membranes were characterized 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. The phase purity and crystallinity of the zeolite membranes were confirmed by X-ray diffraction (XRD). The XRD patterns were recorded at room temperature under ambient conditions with Bruker D8 ADVANCE X-ray diffractometer with CuK α radiation at 40 kV and 40 mA. The surface chemical compositions of the PDA-modified α -Al₂O₃ disk were analyzed by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos) with a Mg K α line as an X-ray source. The FT-IR spectra was measured with a Tensor 27 instrument

(Bruker) through KBr pellets using the Ar/Xe laser line with $\lambda=633$ nm.

Single gas permeation and mixed gases separation

The zeolite LTA membranes supported on PDA-functionalized α -Al₂O₃ disks were evaluated by single gas permeation and mixed gas separation. For the permeation experiments, the supported zeolite LTA and FAU membranes were sealed in a permeation module with silicone O-rings. Before the measurements, the membranes were in situ activated at 383 K for 24 h under sweep gas to remove adsorbed water. The volumetric flow rates of the single gases H₂, CO₂, N₂, CH₄, C₃H₈ as well as of the equimolar binary mixtures of H₂ with CO₂, N₂, CH₄, C₃H₈ were measured using the Wicke-Kallenbach technique, as shown in detail elsewhere.⁴¹ The sweep gas N₂ (except for the N₂ permeation measurement, where CH₄ was used as sweep gas) was fed on the permeate side to keep the concentration of the permeating gas as low as possible thus providing a high driving force for permeation. On both sides of the membranes was atmospheric pressure. The fluxes of feed and sweep gases were determined with mass flow controllers. A calibrated gas chromatograph (Echrom A90) was used to determine the gas concentrations. 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.

$$\alpha_{i/j} = \frac{y_{i,Perm} / y_{j,Perm}}{y_{i,Ret} / y_{j,Ret}} \quad (1)$$

Dehydration of water/ethanol mixture by pervaporation

The properties of the as-synthesized zeolite LTA membranes prepared on PDA-functionalized α -Al₂O₃ tubes were also evaluated by pervaporation for dehydration of 95.0 wt% ethanol/water mixtures at 333~373 K. The apparatus used for the pervaporation experiments is illustrated schematically in Fig. S1. The 95.0 wt% ethanol/water mixtures, preheated to operating temperature, were fed to the out side of the zeolite LTA membrane in the permeation cell that was heated in a thermostatic water bath. The inside of the membrane was evacuated by a vacuum pump. The cold traps with liquid N₂ cooling were used to collect the permeate. The compositions of the feed and the permeate were analyzed by gas chromatogram (Jiedao GC-1690T).

The most important variables for pervaporation are the selectivity and the flux. The total flux (J), the component flux (J_i) and the separation factor (α) are defined as shown in Eq. 2.

$$J = \frac{W}{\Delta t \cdot A} \quad J_i = J \cdot x_{ip} \quad \alpha_{i/j} = \frac{x_{ip}}{x_{if}} \cdot \frac{x_{jf}}{x_{jp}} \quad (2)$$

Where W is total weight of the permeate (kg), Δt is collecting time (h), A is separation area of the membrane, x_{ip} is the weight fraction of species i in the permeate and x_{if} is the weight fraction of species i in the feed.

Results and discussion

By simple immersion of the Al₂O₃ supports in buffered aqueous solution of DPA (pH=8.5) at room temperature, DPA spontaneously polymerizes into PDA and readily deposits on the Al₂O₃ support.^{50, 51} As shown in Fig. 2, after PDA modification of Al₂O₃ support, the Al_{2p} peaks from the Al₂O₃ support were completely shielded. In good agreement with the previous reports,^{52, 53} the intensity of C_{1s} peaks enhances markedly, and a new N_{1s} peak emerges at binding energy of 399.5 eV. Further, the signal ratio of N/C of the PDA-modified Al₂O₃ support is 0.121, which is similar to that of the theoretical value for dopamine (N/C=0.125),⁴⁵ indicating a PDA layer was formed on the surface of Al₂O₃ support.

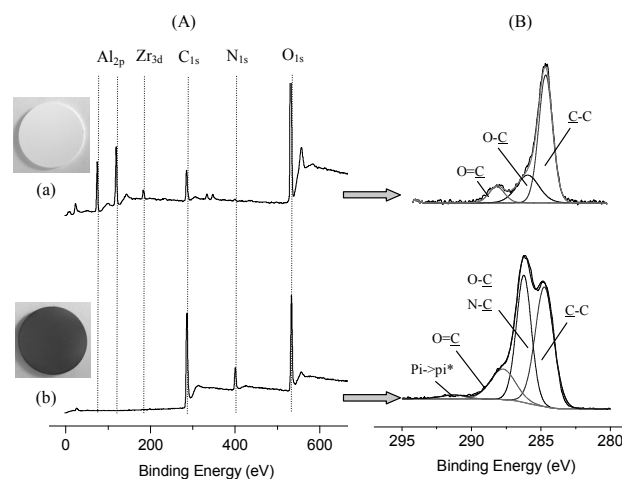


Fig. 2. X-ray photoelectron spectroscopy wide scan (A) and narrow scan for C1s peaks indicating the formation of PDA layer in the surface of Al₂O₃ support. (a) Bare Al₂O₃ support, and (b) PDA-modified Al₂O₃ support. The presence of C1s and Zr_{3d} in XPS of bare Al₂O₃ disk is due to the impurity.

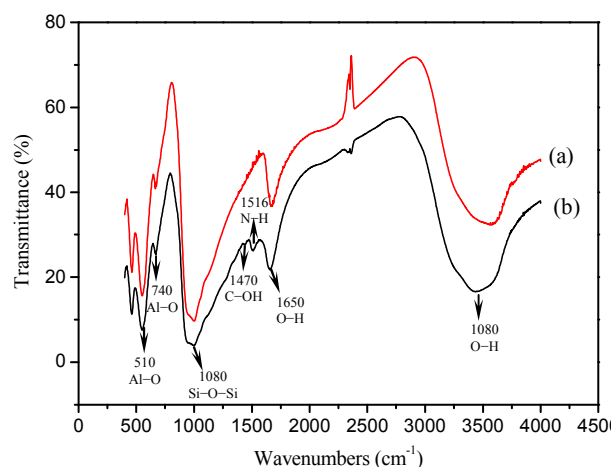


Fig. 3. FT-IR spectra of THE non-modified and PDA-modified zeolite LTA. (a) Non-modified LTA, (b) PDA-modified LTA.

Attributing to its excellent non-covalent adsorption and covalent reaction ability,^{45, 49} PDA can be used as highly

efficient molecular linker to attract and anchor the zeolite LTA nutrients onto the support surface to form of a homogeneous gel layer for nucleation, and thus promoting the growth of a dense zeolite LTA membrane layer. From the the FT-IR spectra shown in Fig. 3, the IR spectra of the PDA-modified zeolite LTA is similar to that of the zeolite LTA besides some new bands shown at 1470 cm^{-1} (C-OH), and 1516 cm^{-1} (N-H),⁵² indicating PDA can be grafted on the surface of zeolite LTA through the formation of covalent bonds, which is helpful for facile synthesis of a dense zeolite LTA membrane layer.

Fig. 4a and Fig. S2 show the top view FESEM images with different magnifications of the zeolite LTA membrane prepared on the PDA-modified $\alpha\text{-Al}_2\text{O}_3$ disk. It can be seen that the support surface is completely covered by uniform and compact LTA crystals, no visible cracks, pinholes or other defects can be found on the membrane layer. From the cross-section FESEM image, it can be seen that the zeolite LTA membrane is well intergrown, and has a thin thickness of about $3.0\text{ }\mu\text{m}$ (Figure 4b). The XRD patterns shows that the zeolite LTA membrane is phase-pure and there exist no preferential crystallographic orientation since all peaks match well with those of zeolite LTA powder besides Al_2O_3 signals from the support (Fig. S3). The PDA modification also promotes the growth of a dense zeolite LTA layer on $\alpha\text{-Al}_2\text{O}_3$ tubes. From the top view and cross-section of the zeolite LTA membrane on the tubular alumina supports (Fig. S4), it can be seen that a well intergrown zeolite LTA layer with a thickness of about $4.5\text{ }\mu\text{m}$ has consistently formed on the coarse surface of the alumina tube. Further, a dense zeolite LTA layer can be easily prepared on PDA-modified glass plate (Fig. S5a) and stainless steel disk (Fig. S5b), indicating that PDA modification is promising to eliminate the influence of surface chemistry. On the contrary, since the heterogeneous nucleation of zeolite on the support surface is restrained due to the weak interaction between the molecular precursor species and the support surface, no dense zeolite LTA layer could be formed on the non-modified support by direct in-situ growth, and the zeolite LTA layer was poor intergrown with observable pinholes and a rough surface.⁴¹

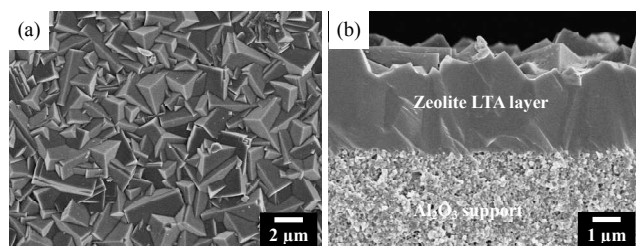


Fig. 4. Top view (a) and cross-section (b) FESEM images of the zeolite LTA membrane prepared on PDA-modified Al_2O_3 disks.

Indeed, even in a very short synthesis time of 12 h, a rather compact LTA layer with a thickness of about only $1.0\text{ }\mu\text{m}$ has been formed on the PDA-modified $\alpha\text{-Al}_2\text{O}_3$ disk (Figures 5a, b), indicating that the PDA functionality can promote the nucleation and growth of a dense zeolite LTA layer. With increasing crystallization time, the shape of the LTA particles in the membrane layer changes from hemispherical to cubic, and the thickness of the LTA layer continuously increases to $2.0\text{ }\mu\text{m}$ (16

h), $2.5\text{ }\mu\text{m}$ (20 h), and $3.5\text{ }\mu\text{m}$ (24 h) as revealed from the cross-sections (Figures 5d, f, h). The enhancement of nucleation and crystals growth on the PDA-modified $\alpha\text{-Al}_2\text{O}_3$ disk can also be deduced from membrane morphology. On the PDA-modified $\alpha\text{-Al}_2\text{O}_3$ disk, small and well intergrown crystals are formed as a compact and uniform zeolite layer (Figure 5g), while big and poorly intergrown crystals are formed as a loose zeolite layer on the non-modified $\alpha\text{-Al}_2\text{O}_3$ disk.⁴¹

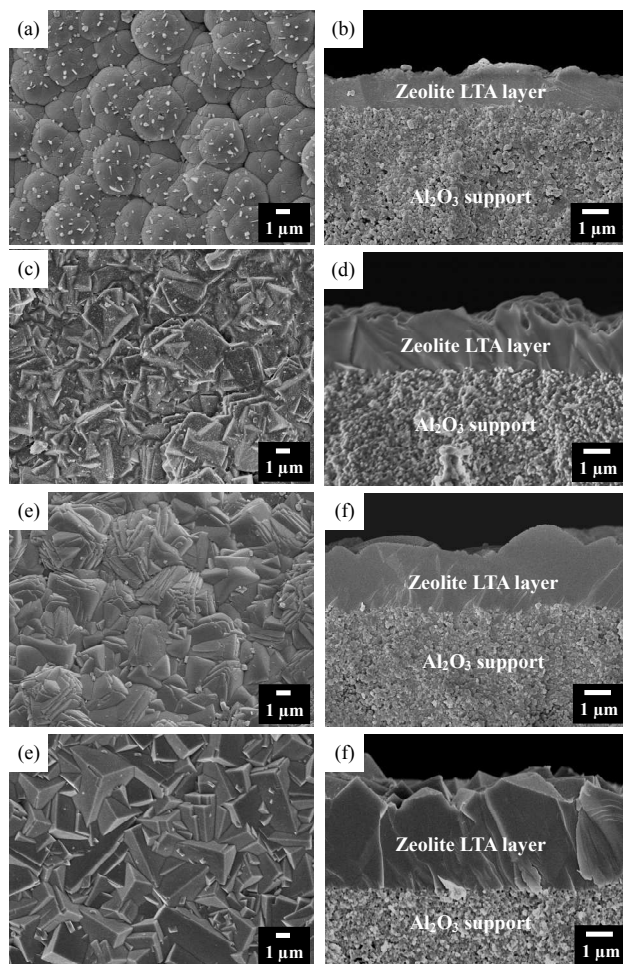


Fig. 5. FESEM images of the zeolite LTA membrane prepared on PDA-modified $\alpha\text{-Al}_2\text{O}_3$ disks for different synthesis time: 12 h (a, b), 16 h (c, d), 20 h (e, f) and 24 h (g, h). Top view (a, c, e), and cross-section (b, d, f).

As reported in our previous studies,^{21, 54} with DADMAC and APTES modification, the previously negative charge of the Al_2O_3 surface can change to positive or neutral, thus the relative positive surface charge of the support is helpful to avoid the electrostatic rejection between the negatively charged zeolite precursor species and the alumina support, thus promoting the nucleation and growth of the zeolite LTA membranes. It should be noted that PDA modification can not reverse or reduce the negative charge of the Al_2O_3 surface (Fig. S6). Therefore, the promotion of the nucleation and growth of the zeolite LTA membrane is mainly attributed to the excellent non-covalent adsorption and covalent reaction ability of PDA. In addition, the hydrophilicity of the support surface can significantly improved after PDA modification,⁵³ which can probably provide more

favorable conditions for nucleation and growth of hydrophilic zeolite LTA membrane.

Fig. 6 shows the permeances of the single gas through the zeolite LTA membrane as a function of the kinetic diameters of the permeating molecules at 373 K and 1 bar. As shown in Fig. 6, the H_2 permeance of $2.81 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ is much higher than the permeance of C_3H_8 ($1.37 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$), which is in accordance with the pore size of about 0.4 nm for zeolite Na⁺LTA (4A). For zeolite LTA with big cavities interconnected by small windows, the strongly adsorbed component CO_2 is immobilized in the cavities and thus permeation becomes diffusion-controlled in favor of the highly mobile component, leading to lower CO_2 permeance than that of N_2 or CH_4 . At 373 K, the ideal separation factors of H_2/CO_2 , H_2/N_2 , H_2/CH_4 and H_2/C_3H_8 , determined as the ratio of the single component permeance, are 8.2, 7.5, 6.8, 20.5, respectively, which by far exceed the corresponding Knudsen coefficients (4.7, 3.7, 2.8 and 4.7), suggesting that the zeolite LTA membrane prepared on the PDA-modified $\alpha\text{-Al}_2\text{O}_3$ disks displays high hydrogen selectivity.

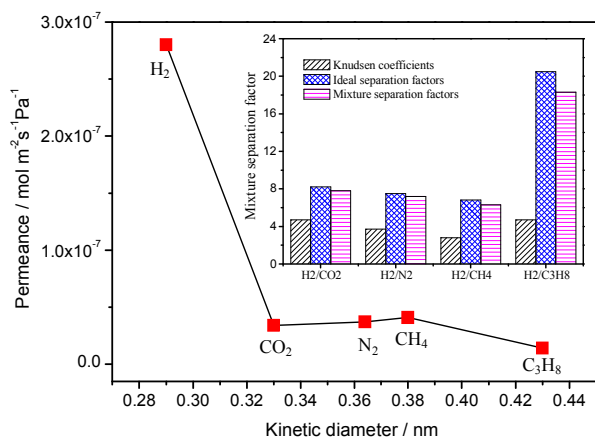


Fig. 6. Single gas permeance of different gases through zeolite LTA membrane prepared on PDA-modified Al_2O_3 disks as a function of the gas kinetic diameter at 373 K and 1 bar pressure difference. The inset shows the mixture separation factor of the zeolite LTA membrane prepared on PDA modified disks. For the corresponding SEM images of zeolite LTA see Fig. 4.

The molecular sieve performance of the zeolite LTA membrane prepared on the PDA-modified $\alpha\text{-Al}_2\text{O}_3$ disks was also confirmed by the separation of equimolar mixtures at 373 K and 1 bar. Comparing with the zeolite LTA membrane prepared on the non-modified $\alpha\text{-Al}_2\text{O}_3$ disks, the zeolite LTA membrane prepared on the PDA-modified $\alpha\text{-Al}_2\text{O}_3$ disks display higher separation selectivities. As shown in the inset of Fig. 6, for the 1:1 binary mixtures, the mixture separation factors of H_2/CO_2 , H_2/N_2 , H_2/CH_4 , and H_2/C_3H_8 are 7.8, 7.2, 6.3, and 18.3, which also exceed the corresponding Knudsen coefficients. Further, the zeolite LTA membrane prepared on PDA-modified $\alpha\text{-Al}_2\text{O}_3$ disk displays higher separation selectivities than those prepared on APTES-, DIC-4-, or CPTMS-modified $\alpha\text{-Al}_2\text{O}_3$ disks. The enhancement of the separation selectivities is attributed to the high adhesive ability of PDA through non-covalent adsorption and covalent reaction, thus strong binding strength between support and LTA layer in the case of the PDA modification. It is worth to note that the whole modification procedure by PDA

takes place under a mild environment (simple immersion at room temperature, non-toxic), which is simple and effective in comparison with the previously proposed seeds coating and chemical modification methods, thus it is helpful to reduce the costs of the membrane manufacturing and prepare zeolite LTA membranes at a large-scale for the industrial application in dewatering of bio-ethanol.

Zeolite LTA membranes with a strong hydrophilicity have displayed excellent performance in hydrophilic separations (Table S1). As shown in Table S1, the zeolite LTA membranes prepared on the PDA-modified $\alpha\text{-Al}_2\text{O}_3$ tube also show excellent pervaporation performances. At 333~373 K, all the separation factors (water/ethanol) are over 10000, and the water flux increases from 2.06 to 4.33 $\text{kg/m}^2\text{h}$ when the pervaporation temperature increases from 333 to 373 K. While pervaporation results from different groups were often difficult to compare because of the difference in supports and experimental conditions, it can be said that the zeolite LTA membranes in this work are among those with good separation performance. Furthermore, PDA modification is helpful to enhance the reproducibility of the membrane preparation, and over 80% zeolite LTA membranes (15 pieces of zeolite LTA membranes was prepared and tested) display similar separation performances with $\pm 5\%$ deviation.

It is found that PDA modification is also helpful to promote the facile preparation of other zeolite membranes like FAU and MFI membranes. Similar to the preparation of zeolite LTA membrane, dense zeolite FAU (2.0 μm Fig. S7) and MFI membranes (40.0 μm Fig. S8) can be formed easily without seeding on the PDA-modified $\alpha\text{-Al}_2\text{O}_3$ supports, while no continuous zeolite membranes can be prepared on non-modified supports. Further work is in progress to extend this synthesis approach to synthesis of other zeolite molecular sieve membranes.

Conclusions

In conclusion, inspired from the highly adhesive ability of the simulate mussel adhesive protein PDA, in the present work we have developed a simple, versatile, effective and seeding-free synthesis strategy to prepare dense zeolite molecular sieve membranes based on PDA reaction platform. Through the formation of strong non-covalent and covalent chemical bonds, zeolite nutrients are attracted and bound to the support surface, thus facilitating the nucleation and growth of uniform, well intergrown and phase-pure zeolite LTA molecular sieve membranes. For zeolite LTA membrane, at 373 K and 1 bar, the mixture separation factors of H_2/CO_2 , H_2/N_2 , H_2/CH_4 , and H_2/C_3H_8 are 7.8, 7.2, 6.6 and 18.3, with H_2 permeances higher than $2.2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. PDA modification also supports the facile seeding-free synthesis of other zeolite membranes like FAU and MFI membranes.

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