

Mild Fabrication of Highly (*h0 h*)-Oriented MFI Zeolite Membrane from Self-Pillared Nanosheets Toward Superior Butane Isomer and Ammonia Separation

Yi Liu, Shengyan Meng, Xiao Fan, Kaishi Ding, Jiahui Yan, Mingming Wu, Shijie Yang, Jinming Lu, and Yi Liu*

Mild fabrication of (*h0 h*) preferentially oriented MFI zeolite membrane, which has been proven advantageous for high-efficiency *n*-/*i*-butane isomer separation, remains a grand challenge. In this study, the preparation of highly (*h0 h*)-oriented MFI zeolite membrane is achieved through combining self-pillared pentasil (SPP) nanosheet seeds with single-mode microwave heating. Benefiting from the unique geometry and hierarchical structure, both preferred orientation and grain boundary structure of MFI zeolite membranes can be deliberately controlled under mild reaction conditions. Gas permeation results imply that obtained membrane exhibit *n*-/*i*-C₄H₁₀ separation factor of 55.2 with *n*-C₄H₁₀ permeance of $2.55 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, surpassing the performance of state-of-the-art MFI zeolite membranes produced via solution-based synthetic protocol; simultaneously, its NH₃/H₂ and NH₃/N₂ separation factor reaches as high as 353.8 and 1362.2 with NH₃ permeance of $\approx 1.2 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, showing great promise for energy-efficient NH₃ separation during Haber-Bosch process.

(N₂/H₂/NH₃ mixtures), where NH₃ serves as a cornerstone for global fertilizer production and an emerging hydrogen storage medium.^[2] So far, energy- and cost-demanding cryogenic distillation technique remains commonly used in these separations, leading to high energy consumption and operation costs due to their close boiling points.^[3] In contrast, membrane technique, with its potential for energy-efficient operation and reduced pollutant emissions, offers a promising alternative to distillation technique.^[4]

MFI-type zeolites feature a uniform 3D channel system, wherein straight channels and sinusoidal channels are aligned along the *b*-axis (5.3 Å × 5.6 Å) and *a*-axis (5.1 Å × 5.5 Å), respectively.^[5] These uniform pores, specifically those aligned along the *a*-axis, enable precise discrimination between *n*-C₄H₁₀ (4.7 Å) and

i-C₄H₁₀ (5.3 Å) based on size-based sieving effect, making it an ideal candidate for high-efficiency butane isomer separation.^[6] Previous studies elucidated that *n*-/*i*-C₄H₁₀ separation factor (SF) of MFI zeolite membranes was dependent on their preferred orientation roughly following the order of (*h0 h*)-orientation > *a*-orientation > *b*-orientation.^[7] Therefore, the fabrication of MFI zeolite membranes exhibiting a high degree of (*h0 h*)-preferred orientation represents the favorable configuration for achieving superior *n*-/*i*-C₄H₁₀ separation.

Diverse protocols, including tertiary growth,^[5c] cooperative templating,^[8] and microwave heating,^[9] have been developed for the fabrication of highly (*h0 h*)-oriented MFI zeolite membranes. Nonetheless, in most cases, the synthesis of zeolite membranes must be carried out at elevated temperatures (>140 °C), potentially leading to increased membrane thickness and grain boundary defect density, and therefore, inferior *n*-/*i*-C₄H₁₀ separation performance.^[10]

Seed morphology has been proven to significantly influence the preferred orientation of zeolite membranes.^[11] However, a more in-depth elucidation of the interplay between seed morphology and (*h0 h*)-orientation degree in MFI zeolite membranes remains rarely explored yet. Self-pillared pentasil (SPP) zeolites, featured with orthogonally connected single-unit-cell nanosheets (NSs) that resemble a house-of-cards configuration, has attracted considerable attention in catalysis and adsorption due to their

1. Introduction

In spite of significant progress made in petroleum industry, energy-efficient separation of butane isomers remains a grand challenge in meeting the demands of downstream industries in which *iso*-butane (*i*-C₄H₁₀) is used as the blending stock for high-octane gasoline production and normal butane (*n*-C₄H₁₀) is employed in alkylation reactions.^[1] Such challenges mirror those encountered in other separation systems, such as ammonia (NH₃) recovery from Haber-Bosch tail gas

Y. Liu, S. Meng, X. Fan, K. Ding, J. Yan, M. Wu, S. Yang, J. Lu, Y. Liu
State Key Laboratory of Fine Chemicals
Frontiers Science Center for Smart Materials
School of Chemical Engineering
Dalian University of Technology
Linggong Road 2, Ganjingzi District, Dalian 116024, China
E-mail: diligenliu@dlut.edu.cn

Y. Liu
Dalian Key Laboratory of Membrane Materials and Membrane Processes
Dalian University of Technology
Linggong Road 2, Ganjingzi District, Dalian 116024, China

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adfm.202506949>

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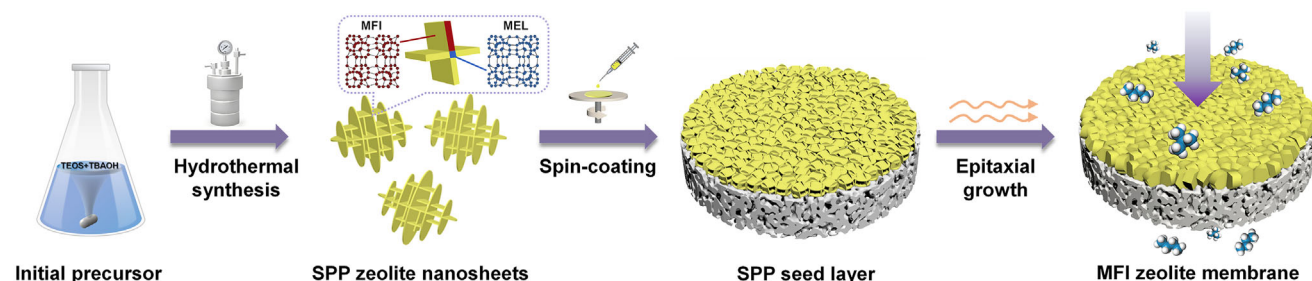


Figure 1. Schematic representation for the fabrication of MFI zeolite membrane with SPP zeolite NSs as seeds.

large surface areas, reduced diffusion path length, and sufficient active sites.^[12] Nevertheless, its potential use as building units of selective zeolite membranes remains largely unexplored to date. Benefiting from the architecture of exposed *a*-/*c*-axis crystal plane in all directions, it is expected that the unique geometry can enhance the degree of (*h*0*h*)-preferred orientation, leading to the remarkable improvement in *n*-/*i*-C₄H₁₀ separation performance; simultaneously, the above reaction is expected to be conducted under mild conditions, offering additional advantages in terms of thickness and grain boundary defect reduction.^[10,13]

Motivated by the aforementioned concerns, in this work, we pioneered the mild fabrication of highly (*h*0*h*)-oriented MFI zeolite membranes through adopting SPP zeolite NSs as seeds. The experimental process was briefly outlined as follow (**Figure 1**): Initially, SPP NS seeds were prepared through in situ hydrothermal growth. Subsequently, uniform close-packed SPP seed layer was deposited on porous α -Al₂O₃ substrate via spin-coating. Finally, MFI zeolite membrane with desired microstructure was mildly

synthesized through single-mode microwave heating during epitaxial growth process.

2. Results and Discussion

2.1. Preparation of SPP Zeolite NSs

The first step involved the preparation of SPP zeolite NSs using tetrabutylammonium (TBA)-silica sols.^[12a] As shown in **Figures 2a** and **S1** (Supporting Information), uniform spindle-shaped nanocrystals with an average size of 180 nm and rough surface morphology were readily synthesized under optimized reaction conditions. TEM images (**Figure 2b,c**) revealed that obtained products were formed through orthogonal rotational intergrowth of MFI zeolite NSs with an average thickness of $\approx$ 4 nm, consistent with previously reported SPP zeolite materials in the literature.^[12a,c] Relevant XRD pattern (**Figure 2d**) confirmed that all diffraction peaks of above samples fitted well with results

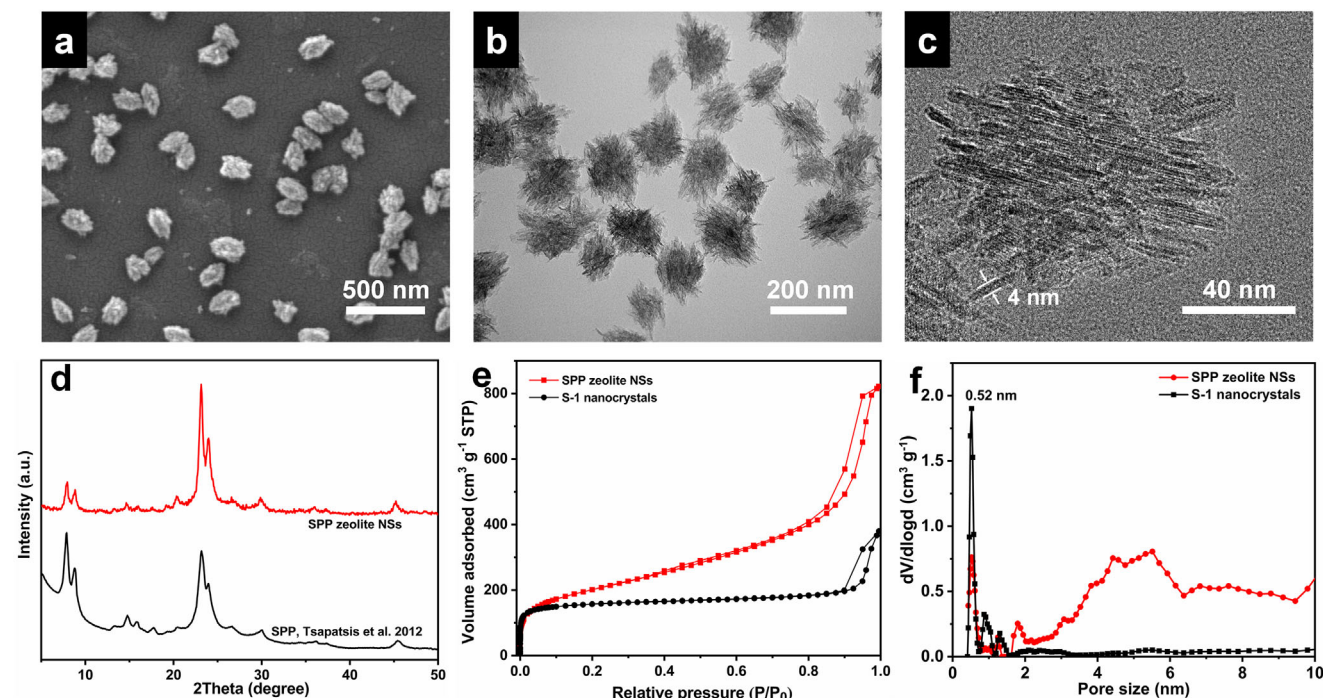


Figure 2. a) SEM image, b,c) TEM images and d) XRD patterns of SPP zeolite NSs and previously published data from Tsapatsis et al. e) Ar adsorption-desorption isotherms and f) pore size distribution curves of SPP zeolite NSs and S-1 nanocrystals.

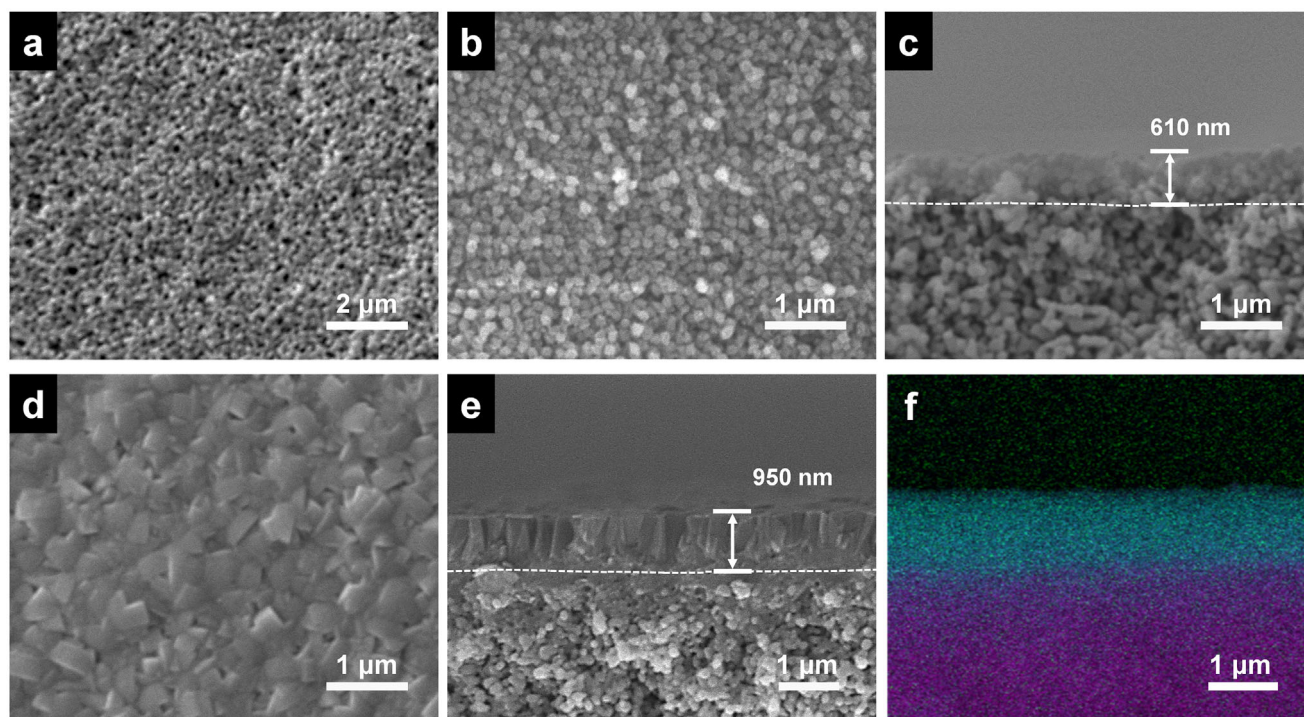


Figure 3. SEM images of the a) porous α - Al_2O_3 substrate, b,c) SPP seed layer and, d,e) SPP-MFI membrane. f) Cross-sectional EDXS mapping of SPP-MFI membrane (color code: Si = green; Al = purple).

reported in the literature.^[12a,14] Textural properties of obtained SPP zeolite NSs were further investigated. For comparison, conventional Silicalite-1 (pure-silica MFI, referred to as S-1) nanocrystals with an average grain size of 160 nm were synthesized (shown in Figure S2, Supporting Information).

The Ar adsorption-desorption isotherm of SPP zeolite NSs revealed steep type-IV isotherm with distinct hysteresis loop at relative pressures between 0.4 and 1.0, suggesting the presence of abundant mesopores;^[14b] while S-1 nanocrystals exhibited type-I isotherm with additional hysteresis loop caused by crystal stacking, implying their intrinsic microporous structure (Figure 2e).^[9b] Pore size distribution calculated from the nonlocal density functional theory (NLDFT) method (Figure 2f) indicated that S-1 nanocrystals were dominantly microporous, while SPP zeolite NSs showed broad distribution of additional mesopores ranging between 2 and 8 nm. Furthermore, the BET surface area and total pore volume of SPP zeolite NSs exceeded those of S-1 nanocrystals, primarily owing to the presence of abundant mesopores (Table S1, Supporting Information).^[12a] The ^{29}Si MAS NMR spectra of both SPP zeolite NSs and S-1 nanocrystals displayed two isotropic resonances at -105 and -114 ppm, which correspond to Q^3 ($(\text{SiO})_3\text{SiOH}$) and Q^4 ($(\text{SiO})_4\text{Si}$) species, respectively (Figure S3, Supporting Information).^[15] Integration of ^{29}Si MAS NMR signals allowed us to calculate the Q^4/Q^3 ratio, providing quantitative insights into the density of silanol groups stemming from the extraction of silicon atoms from MFI zeolite framework.^[16] Compared with S-1 nanocrystals, our SPP zeolite NSs showed lower Q^4/Q^3 ratio, revealing increased silanol group density within SPP zeolite NSs. Given the importance of maintaining structural integrity of SPP seeds during membrane pro-

cessing, mechanical robustness of obtained SPP zeolite NSs was evaluated further. As shown in Figure S4 (Supporting Information), SPP zeolite NSs maintained their structural integrity despite being subjected to vigorous stirring (500 rpm) for 2 weeks, which was advantageous for obtaining a homogeneous seed suspension and ensuring deposition of uniform seed layer.

2.2. Deposition of SPP Seed Layer

Subsequently, spin-coating was employed for depositing SPP NS seeds on porous α - Al_2O_3 substrates (Figure 3a). As shown in Figure 3b,c, a uniform and closely packed SPP seed layer with thickness of ≈ 600 nm was readily obtained under optimized deposition conditions. Corresponding XRD pattern revealed that prepared SPP seed layer was randomly oriented (Figure S5, Supporting Information).

2.3. Epitaxial Growth of MFI Membrane

In the following step, epitaxial growth was performed to seal the inter-crystalline gaps between adjacent seeds. Herein, single-mode microwave heating was employed for epitaxial growth of the SPP seed layer in view of its capability in providing better control over the microstructure of zeolite membranes, relying on a higher microwave field intensity and uniformity.^[9b,11a,17] Our results demonstrated that extending the reaction duration resulted in the gradual sealing of intercrystalline defects (Figure S6, Supporting Information). After reacting at 100°C for 2 h, a well-intergrown MFI zeolite (denoted as SPP-MFI) membrane with

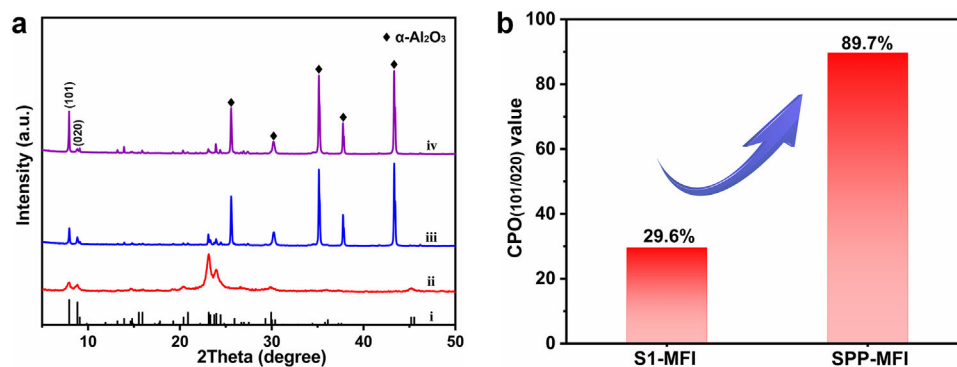


Figure 4. a) XRD patterns of (i) simulated MFI peaks, (ii) SPP zeolite NSs, (iii) S1-MFI membrane and (iv) SPP-MFI membrane. b) Variation in $\text{CPO}_{(101/020)}$ values of S1-MFI and SPP-MFI membranes.

the thickness of 950 nm and grain size of 440 nm (Figure 3d,e) could be readily formed; moreover, relevant XRD pattern confirmed that resulting membrane was indeed composed of pure MFI zeolite phase with remarkable (*h*0*h*)-orientation (Figure 4a). As far as we know, this marked the lowest reaction temperature in terms of highly (*h*0*h*)-oriented MFI zeolite membrane fabrication; moreover, its thickness was the thinnest among (*h*0*h*)-oriented MFI zeolite membrane (Table S2, Supporting Information). Relevant EDXS mapping further showed an obvious interface between the top layer and underlying substrate (Figure 3f), indicating that there was no conspicuous penetration in substrate pores.

It should be addressed that the morphology of zeolite seeds was found to have a profound influence on the microstructure of MFI zeolite membranes. For comparison, S-1 nanocrystals were used as seeds while keeping other reaction conditions unchanged. After seeding, we observed that the surface of porous α -Al₂O₃ substrate had been fully covered with uniform closely-packed S-1 seed layer with an average thickness of 640 nm (Figure S7, Supporting Information). After epitaxial growth, a uniform 1.2 μm -thick MFI zeolite (denoted as S1-MFI) membrane was readily obtained (Figure S8, Supporting Information); moreover, relevant XRD pattern revealed that all above membranes belonged to pure MFI zeolite phase (Figure 4a).^[18]

Simultaneously, we quantified the degree of (*h*0*h*)-preferred orientation of aforementioned membranes through calculating the crystallographic preferred orientation (CPO) index, considering its close relationship with the *n*-/*i*-C₄H₁₀ separation performance.^[9a,19] The CPO values of SPP-MFI membrane derived from diffraction intensities at (101) and (020) reflections (abbreviated as $\text{CPO}_{(101/020)}$) achieved 89.7%, which was remarkably higher than that of S1-MFI membrane (29.6%), demonstrating much higher degree of (*h*0*h*)-preferred orientation for SPP-MFI membrane (Figure 4b). This may be attributed to the unique geometry of SPP zeolite NSs, in which the orthogonally connected zeolite lamellae within SPP seeds predominantly exposed *a*-/*c*-axis crystal planes in all directions during seed layer deposition (Figure S9, Supporting Information), thus minimizing the presence of *b*-axis planes. Obviously, the avoidance of *b*-axis exposure in seed layer minimized the possibility of *b*-oriented crystal facet generation in the membrane, resulting in higher degree of (*h*0*h*)-preferred orientation of obtained membrane.

2.4. Gas permeation Properties of MFI Membrane

Finally, Wicke-Kallenbach technique was employed to evaluate the gas permeation behavior of both SPP-MFI and S1-MFI membranes (Figure S10, Supporting Information). As shown in Figure 5a, single gas permeation results revealed that the gas permeance through SPP-MFI and S1-MFI membranes generally decreased with increasing kinetic diameter of guest molecules. In terms of SPP-MFI membrane, SF of equimolar *n*-/*i*-C₄H₁₀ isomer mixture reached 55.2 with *n*-C₄H₁₀ permeance of $2.55 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, implying that *n*-C₄H₁₀ with purity >98% could be processed using a single-stage membrane process, meeting the requirements for oxidative production of maleic anhydride. Superior *n*-/*i*-C₄H₁₀ SF compared with its ideal selectivity (~43.7) could be attributed to competitive transportation and crowding-out effect through the membrane.^[1a,9a] It should be noted that both *n*-/*i*-C₄H₁₀ SF and *n*-C₄H₁₀ permeance of obtained SPP-MFI membrane were superior to those of S1-MFI membrane (Figure 5b). Obviously, increased *n*-C₄H₁₀ permeance could be ascribed to reduced thickness of the former. To gain insights into enhanced *n*-/*i*-C₄H₁₀ SF, the ideal selectivity of H₂/SF₆ gas pair, widely used to evaluate grain boundary defect density in MFI zeolite membranes, was calculated.^[18] The ideal H₂/SF₆ selectivity for SPP-MFI membrane achieved 479.2, which was much higher than that observed for S1-MFI membrane (225.5), indicating that fewer grain boundary defects existed within SPP-MFI membrane. Remarkable reduction in grain boundary defect density could be associated with the hierarchical structure and abundant surface silanol groups of SPP NS seeds, which facilitated firm attachment of the gel precursor over zeolite seeds, and therefore, more pronounced epitaxial growth compared with S-1 nanocrystals.^[16] Obviously, reduced grain boundary defect density and higher degree of (*h*0*h*)-preferred orientation concurrently contributed to superior *n*-/*i*-C₄H₁₀ separation performance.

The effect of feed composition on *n*-/*i*-C₄H₁₀ permeation properties was further studied (Figure 5c). We found that the *n*-C₄H₁₀ permeance increased with increasing *n*-C₄H₁₀ feed composition; while the *n*-/*i*-C₄H₁₀ SF first increased, reached the maximum value of 61.1 at *n*-C₄H₁₀ feed composition of 70%, and then slightly decreased. The impact of operating pressure on separation performance of equimolar *n*-/*i*-C₄H₁₀ isomer mixture was

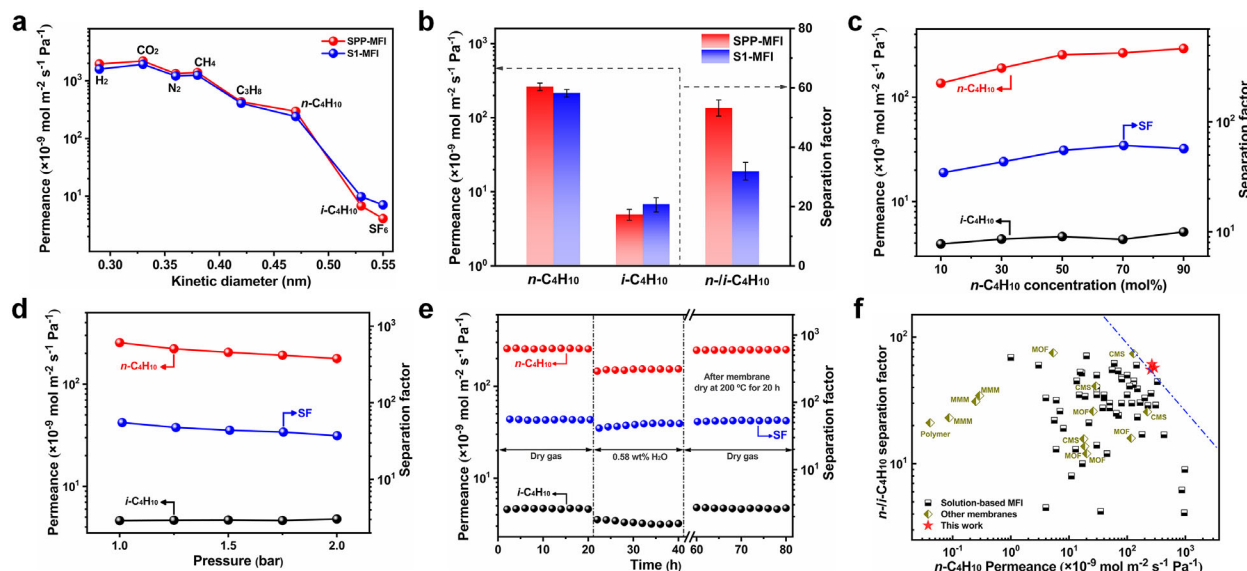


Figure 5. a) Single-gas permeation behavior of SPP-MFI and S1-MFI membranes measured at ambient conditions. b) Separation performance of equimolar *n*-/*i*-C₄H₁₀ gas pairs through SPP-MFI and S1-MFI membranes. The dependence of *n*-/*i*-C₄H₁₀ gas mixture separation performance of SPP-MFI membrane on (c) *n*-C₄H₁₀ feed concentration and (d) feed pressure. e) Long-term operating stability of SPP-MFI membrane toward equimolar *n*-/*i*-C₄H₁₀ gas pair under dry and humid environments, respectively. f) Comparison of *n*-/*i*-C₄H₁₀ separation performance of SPP-MFI membranes with *n*-C₄H₁₀ feed concentrations of 50, 70, and 90 in this study with other pristine pure MFI zeolite membranes synthesized through solution-based methods, and other types of membranes reported in the literature. Detailed performance data are listed in Tables S4 and S5 (Supporting Information).

also investigated. In line with previous reports, both *n*-C₄H₁₀ permeance and *n*-/*i*-C₄H₁₀ SF were found to decrease with increasing feed pressure from 1.0 to 2.0 bar (Figure 5d), indicating that preferential intrusion of bulky *i*-C₄H₁₀ hindered the fast permeation of *n*-C₄H₁₀ through zeolite pores.^[1a,7a,10a] With increasing the feed pressure, the *n*-C₄H₁₀ flux gradually increased, and the membrane demonstrated a *n*-C₄H₁₀ flux of 35.6 mmol m⁻² s⁻¹ at a feed pressure of 2.0 bar (Figure S11, Supporting Information).

Aiming at practical applications, long-term separation performance of the SPP-MFI membrane was evaluated further (Figure 5e). It was observed that both *n*-C₄H₁₀ permeance and SF of equimolar *n*-/*i*-C₄H₁₀ isomer mixture remained unchanged after continuous operation for 20 h. Considering the presence of water vapors in butane isomer mixture under practical conditions, saturated water vapors (0.58 wt%) were further introduced and their impact on *n*-/*i*-C₄H₁₀ separation performance was studied. As depicted in Figure 5e, our membrane exhibited slightly decreased *n*-C₄H₁₀ permeance in the presence of water vapors, owing to competitive adsorption between *n*-C₄H₁₀ and H₂O in zeolite pores;^[20] simultaneously, *n*-/*i*-C₄H₁₀ SF remained largely unchanged. After drying at 200 °C overnight, its *n*-/*i*-C₄H₁₀ separation performance could be fully recovered. Compared to previous literature, the butane isomer separation performance of our membrane easily exceeded that of MFI zeolite membranes synthesized through solution-based methods (Figure 5f; Tables S3 and S4, Supporting Information).

It is worth mentioning that the use of single-mode microwave heating during epitaxial growth was essential for the structural tailoring of MFI zeolite membranes. For comparison, we also prepared the MFI zeolite membrane through hydrothermal reaction at 100 °C while keeping other synthetic parameters unchanged. Our results showed that the SPP seed layer scarcely

grew up after 2 h (Figure S12a, Supporting Information). Although further extending the reaction time to 18 h enabled complete sealing of grain boundary defects (Figure S12b–d, Supporting Information), the CPO index of obtained membrane was only 21.7% (Figure S13, Supporting Information). Gas permeation results demonstrated that its *n*-/*i*-C₄H₁₀ SF was only 23.8 with *n*-C₄H₁₀ permeance of 1.98 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹. We inferred that the unique non-thermal effect of single-mode microwave heating, such as high field uniformity, strong field intensity and hot-spot effect resulted in the reinforced intergrowth and van der Drift's evolutionary selection,^[21] and therefore superior *n*-/*i*-C₄H₁₀ separation.

It should be noted that in addition to *n*-/*i*-C₄H₁₀ separation, our SPP-MFI membrane further exhibited remarkable separation capabilities for ammonia (NH₃) systems. Specifically, for equimolar NH₃/H₂ mixtures, the membrane achieved a remarkable SF of 353.8 with NH₃ permeance of 1.23 × 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹. Moreover, in equimolar NH₃/N₂ separation, the SF of 1362.2 with NH₃ permeance of 1.17 × 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ was obtained under ambient conditions. We inferred that preferential adsorption of NH₃ within the zeolite pores, hindering permeation of H₂ or N₂, represents the main cause for the observed high NH₃ selectivity over H₂ and N₂.^[22] These results underscore the potential of MFI zeolite membranes for energy-efficient separation of NH₃/N₂/H₂ mixtures, which is commonly encountered in ammonia synthesis and utilization.

3. Conclusion

To summarize, in this study, MFI zeolite membranes with highly (*h0 h*)-preferred orientation were successfully prepared by integrating SPP NS seeds with single-mode microwave heating

during membrane processing. The unique geometry and hierarchical structure provided by SPP NS seeds allowed for an optimized membrane structure under milder reaction conditions. Prepared MFI zeolite membranes exhibited an n/i -C₄H₁₀ SF of 55.2 with n -C₄H₁₀ permeance of 2.55×10^{-7} mol m⁻² s⁻¹ Pa⁻¹, which ranked the highest among the pristine MFI zeolite membranes prepared through solution-based synthetic protocols; moreover, this also represented the lowest reaction temperature for the synthesis of (*h0 h*)-oriented MFI zeolite membranes. Additionally, the membranes also exhibited exceptional NH₃/H₂ and NH₃/N₂ separation performance, thus demonstrating great promise for energy-efficient NH₃ separation during Haber-Bosch process.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

gas separation, membrane, nanosheets, orientation, zeolites

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