Hierarchical Control of MFI Zeolite Membrane towards Superior Butane Isomer Separation Performance

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Abstract: Microstructural optimization (such as thickness and preferred orientation) is a major concern for performance enhancement of zeolite membranes. In this study, we demonstrated that the introduction of hierarchy easily enabled concurrent thickness reduction and orientation control of zeolite membranes. Specifically, hierarchical MFI zeolite membranes comprising higher degree of (h0h) preferably oriented ultrathin (ca. 390 nm) selective top layers and porous intermediate layers on porous α-Al2O3 substrates were fabricated. The use of hollow-structured MFI nanoseeds and the employment of single-mode microwave heating during membrane processing were found indispensable for the preparation of MFI zeolite membranes with superior butane isomer separation performance, thereby surpassing the current n-/i-butane selectivity versus n-butane permeance trade-off limits of MFI zeolite membranes prepared via solution-based synthetic protocols.

Microstructure optimization is the driving force for the performance enhancement of molecular sieve membranes. Taking polycrystalline MFI zeolite membranes, which hold great promise for energy-efficient separation of several industrially important gas mixtures (such as an n-/i-butane isomer mixture), as an example, substantial studies have been conducted to elucidate the key factors influencing their separation performances. In general, b-oriented MFI zeolite membranes are deemed more suitable for accurate separation of p-iso-xylene mixture through the size-sieving mechanism (p-xylene: 5.6 Å; o-xylene: 6.8 Å), while fabrication of (h0h) preferably oriented MFI zeolite membrane is considered more advantageous for n-/i-butane isomer separation. Furthermore, thickness reduction of the functional layer provides an effective means for decreasing the diffusion resistance, and therefore overcoming the trade-off between gas permeance and selectivity of MFI zeolite membranes.

In recent decades, the use of ultra-thin (5–10 nm) zeolite nanosheets (NSs) as seeds for zeolite membrane fabrication represents an important landmark in this field due to the markedly decreased membrane thickness, thereby warranting ultra-high gas permeance. Nevertheless, the obstacle regarding to facile synthesis of uniform zeolite NSs still remained, which severely hindered its widespread application.

It has been well recognized that hollow-structured zeolites embracing large internal cavity and ultra-thin wall thickness (ca. 10 nm) commonly exhibited superior performance in catalytic cracking reactions or adsorption separation processes where intra-particle diffusion represented the rate-limiting step. Considering the structural similarity between zeolite NSs and hollow-structured zeolites, that is, ultra-thin layer thickness, it is expected that hollow-structured zeolites could serve as competent seeds for ultra-thin zeolite membrane fabrication; moreover, compared with zeolite NSs, hollow-structured zeolites can be prepared and processed more easily. Nevertheless, to date, very few studies have been conducted to explore the potential of hollow-structured zeolites in membrane-based separation processes.

Motivated by the above concerns, taking the MFI-type zeolite as an example, for the first time, hollow-structured zeolites were used as seeds for polycrystalline zeolite membrane fabrication in this study. The fabrication process was briefly described as follows: Initially, hollow-structured MFI nanoseeds were prepared via simple alkaline treatment of bulk MFI crystals under hydrothermal conditions. Subsequently, spin-coating technique was employed for deposition of uniform close-packed hollow-structured MFI seed layer on porous α-Al2O3 substrate. Finally, a MFI zeolite membrane with unique hierarchical structure, that is, an ultra-thin selective top layer with higher degree of (h0h) preferred orientation and a porous intermediate layer, was obtained after single-mode microwave-assisted secondary growth (shown in Figure 1). Among various factors, the use of hollow-structured MFI nanocrystals as seeds and the employment of single-mode microwave heating during secondary growth were found to be crucial in warranting the formation of hierarchical MFI zeolite membranes. By analogy with the high performance asymmetric hollow fiber membrane consisting of an ultrathin dense top layer and a porous intermediate layer filled with finger-or sponge-like internal cavities, we envisaged that the hierarchical structure in MFI zeolite membrane would greatly facilitate achieving a superior n-/i-butane separation performance.
The first step involved the preparation of hollow-structured MFI nanoseeds. Initially, uniform parent MFI nanocrystals with a mean grain size of 270 nm were synthesized via a facile hydrothermal method (Supporting Information, Figure S1)\cite{11}. Subsequent hydrothermal treatment of calcined parent MFI nanocrystals with TPAOH aqueous solution led to the formation of uniform hexaprismatic-shaped hollow nanoseeds with the wall thickness in the range of 10–20 nm (Figure 2a, b). Both XRD and ED patterns (Supporting Information, Figure S2) further confirmed the high purity and crystallinity of obtained hollow-structured MFI nanocrystals. As well documented previously, the formation process of hollow-structured MFI nanocrystals followed the dissolution-recrystallization mechanism.\cite{8b,12} Initially, cores of pristine MFI nanocrystals were dissolved because of a lower crystallinity. Subsequently, dissolved silica species were recrystallized on the surface of MFI nanocrystals in the presence of TPA\(^+\) template. Since TPA\(^+\) cations were too bulky to enter MFI zeolite pores, recrystallization mainly occurred on the outer surface, resulting in the maintenance of internal cavities and therefore, the formation of hollow-structured MFI nanoseeds with ultra-thin wall thickness. The \(\text{N}_2\) adsorption-desorption isotherm of hollow-structured MFI nanocrystals revealed a type IV isotherm with a remarkable H4-type hysteresis loop (Supporting Information, Figure S3a), indicating its hierarchical porous structure. The pore size distribution curve suggested the presence of additional mesopores apart from intrinsic micropores (0.55 nm) in the MFI framework (Supporting Information, Figure S3b, c), which could be ascribed to the alkaline etching during the dissolution-recrystallization process.\cite{13} Furthermore, the BET results suggested the presence of mesopores significantly contributed to the total surface area and pore volume of MFI nanoseeds (Supporting Information, Table S1).

Subsequently, spin-coating was employed for the seed layer deposition. As shown in Figure 2c,d and the Supporting Information, Figure S4, it was observed that after seeding, the surface of porous \(\alpha\)-Al\(_2\)O\(_3\) substrate had been fully covered with uniform closely-packed MFI seed layer with the thickness of about 650 nm, which was equivalent to 2–3 single layers of hollow-structured MFI nanoseeds.

In the next step, secondary growth was carried out to seal the gaps between MFI nanoseeds while simultaneously maintaining their internal cavities. Taking into consideration of the ultra-thin wall thickness of MFI nanoseeds, it was expected that an ultra-thin selective layer would be grown on top of the seed layer. Initially, conventional heating was employed. Nevertheless, hollow-structured MFI nanoseeds...
rarely grew up after 2 h hydrothermal reaction at 105°C (Supporting Information, Figure S5a). Further prolonging the reaction time to 12 h remained incapable of completely sealing intercrystalline defects (Supporting Information, Figure S5b). These defects could be eliminated upon concurrently increasing the reaction temperature and time to 140°C and 12 h, respectively (Figure 2e). However, simultaneously internal cavities of MFI nanoseeds were fully filled with the secondary growth portion, resulting in the loss of the hollow structure (Figure 2f). Furthermore, conventionally synthesized MFI zeolite (denoted as C-MFI) membranes did not show superiority in thickness (ca. 3.2 µm, shown in Figure 2f) compared with previous results. To preserve large internal cavities of MFI nanoseeds, ensuring completion of the reaction within a short period of time under mild reaction conditions has therefore become indispensable.

Previous research indicated that relying on the unique thermal and non-thermal effects of microwave irradiation, microwave-assisted synthesis of zeolite membranes enabled not only a significant reduction in reaction time but also a decrease of intercrystalline defect density in comparison with conventional heating, which was quite advantageous for the production of large membrane areas. Moreover, our recent study implied that single-mode microwave heating exhibited obvious superiority over common multi-mode microwave heating in terms of microwave field uniformity and intensity, resulting in concurrent reduction in the reaction temperature and time required for the formation of well-intergrown MFI zeolite membranes. Indeed, our experimental results indicated that well-intergrown MFI zeolite membrane (denoted as H-MFI) membrane could be obtained at 105°C within 2 h (Figure 2g). The cross-sectional SEM image (Figure 2h) clearly showed that prepared membrane was composed of an ultra-thin (ca. 390 nm) selective top layer and a porous intermediate layer with pore size up to 160 nm, implying that the hollow structure of MFI nanoseeds was well maintained during secondary growth. The ultrathin membrane thickness could be attributed to the absence of crystal core in hollow MFI nanoseeds which somehow prohibited the growth under the fast microwave heating, and the rapid formation of dense top layer under single-mode microwave heating may serve as a diffusion barrier for preventing further contact between the seed layer and the bulk solution so that the porous structure in the seed layer was well preserved. In addition, we envisaged that the interior hollow structure may survive the secondary growth in nature. To verify this hypothesis, given amount of hollow-structured MFI nanoseeds was subjected to single-mode microwave heating under identical reaction conditions. As shown in the Supporting Information, Figure S6, the grain size of the MFI nanoseeds slightly increased to about 450 nm while the hollow structure remained largely unchanged, thereby confirming the correctness of the above hypothesis.

It should be addressed that the MFI seeds exerted significant influence on final microstructure of MFI zeolite membranes. As a comparative experiment, MFI zeolite membrane was also prepared by using parent MFI nanocrystals as seeds (Figure 3a, b) while keeping other reaction conditions unchanged. After secondary growth, it was observed that a well-intergrown, 1.4 µm-thick uniform MFI zeolite (denoted as P-MFI) membrane had been formed (Figure 3c, d).

Simultaneously, the degree of (h00)-preferred orientation of MFI zeolite membrane was studied using XRD, considering their positive impact on the n- and -butane separation performance. The degree of (h00)-preferred orientation could quantitatively be evaluated by the integrated peak intensity ratio between the plane (101) and (020), that is, \( I_{101}/I_{020} \). As shown in Figure 4, the \( I_{101}/I_{020} \) value of H-MFI membrane was calculated to be 1.36 (taking into consideration the interference from randomly oriented porous intermediate layer, the actual \( I_{101}/I_{020} \) value derived from the ultra-thin selective top layer should be higher), which was higher than that of P-MFI membrane (0.46), thereby revealing the higher degree of (h00)-preferred orientation for H-MFI membrane. Furthermore, X-ray pole figure analysis...
was performed for further analyzing the membrane orientation. As shown in the Supporting Information, Figures S7 and S8, the calculated $S_{(101)}/S_{(020)}$ value (integrated peak area ratio between the area (101) and (020)) of H-MFI membrane (1.46) was higher than that of P-MFI membrane (0.8), which was in fair accordance with the XRD characterization results, thereby firmly confirming the higher degree of (h0h)-preferred orientation of H-MFI membrane. The above results are consistent with the conclusion drawn by Liu et al. who reported the positive effect of using hierarchical TS-1 zeolite seeds on preferred orientation control of TS-1 zeolite membranes.[13a] Anyway, our experimental results convincingly demonstrated the necessity of concurrent use of hollow-structured MFI nanoseeds and single-mode microwave heating for the preparation of ultra-thin MFI zeolite membrane with higher degree of (h0h)-preferred orientation.

In the next step, prepared MFI zeolite membrane was calcined to remove organic templates occluded within zeolite pores[17] and finally, gas permeation test was conducted to evaluate their n-i-butane isomer separation performance. As depicted in Figure 5, separation factor (SF) of equimolar n-i-butane mixture through the H-MFI membrane reached as high as 44.4 with a n-butane permeance of 3.3 × 10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1}, which not only well surpassed the upper bound limit for all MFI zeolite membranes synthesized via solution-based protocols, but also was superior to most MFI zeolite membranes prepared using MFI NSs as seeds except in rare cases where Tsapatsis and Yoon prepared high performance MFI zeolite membranes by gel-less secondary growth with MFI NSs as seeds.[15c,6a] Nevertheless, our method has obvious advantage in terms of process simplicity, since the use of MFI NS seeds which commonly required a complicated fabrication procedure and deliberately designed organic templates (like C_{22-6-6Br2} or dC_5) could be equivalently replaced by hollow nanoseeds obtained via simple alkaline treatment.

To better elucidate microstructural benefits of H-MFI membrane, n-i-butane separation performance of C-MFI and P-MFI membranes was also measured (shown in Figure 5). In comparison, H-MFI membrane exhibited the highest n-i-butane SF and n-butane permeance, which was attributed to the ultra-thin thickness, relatively higher degree of (h0h)-orientation of the selective top layer, and the porous nature of the intermediate layer, which mainly served as a buffer layer and therefore, exerted a negligible influence on the diffusion barrier property. Of particular note was that n-i-butane SF of H-MFI membrane was not only much higher than that of C-MFI membrane, but also superior to P-MFI membrane, which could be ascribed to the higher degree of (h0h)-preferred orientation.

To gain insight into the reproducibility of our synthesis protocol, three H-MFI membranes were prepared in parallel following the above-mentioned fabrication procedure (Supporting Information, Table S3). The relative standard deviations of the n-butane permeance and SF of n-i-butane isomer were 4.5% and 7.8%, respectively, which was indicative of sufficiently high process reliability and reproducibility.

To summarize, in this study, hierarchical zeolite membranes comprising ultra-thin selective top layers with higher degree of (h0h)-preferred orientation and porous intermediate layers were prepared through combining hollow-structured MFI nanoseeds with single-mode microwave heating during membrane processing. High uniformity and intensity of single-mode microwave heating led to the accelerated formation of hierarchical MFI zeolite membranes with desired microstructure under mild reaction conditions, thereby leading to superior n-i-butane separation performance. It is expected that introduction of hierarchy could bring new insights into the preparation of a wide range of high-performing molecular sieve membranes.

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**Conflict of interest**

The authors declare no conflict of interest.

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