

Precise hydrocarbon isomer separation with ultrathin vertically aligned nanochannel membranes

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**Precise hydrocarbon isomer separation with ultrathin vertically aligned
nanochannel membranes**

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Abstract

The separation of hydrocarbon isomers by thermally driven distillation remains highly energy intensive. Framework-based nanochannel membranes offer a highly energy efficient and low-carbon alternative; however, their conventional synthesis suffers from slow crystallization, poor orientation, and low separation performance. Here we introduce a nucleation-isolated superfast synthesis (NI-SFS) strategy that decouples nucleation from growth, producing ultrathin (~ 500 nm), nanosheet-based zeolite membranes with vertically aligned nanochannels. The NI-SFS route enables the superfast membrane formation within minutes by patching up the gaps among ultrathin fragile zeolite nanosheets without nanosheet damage using short-time secondary growth to avoid the conventional dissolution-recrystallization cycles. These nanochannel membranes achieve exceptional separation factors (25,000 for *n*-hexane/2,3-dimethylbutane, 57 for *n*-butane/isobutane, and 62 for *I*-butene/isobutene) with high permeances (up to 5.8×10^{-7} mol m⁻² s⁻¹ Pa⁻¹). The up-scaling membranes exhibited minimum performance loss, demonstrating the scalability of the NI-SFS membrane fabrication strategy. Techno-economic analysis shows >88% energy savings using membrane separation over distillation for the isomer separation. NI-SFS provides mechanistic insight into nanosheet assembly and establishes a scalable, energy-efficient platform for sustainable hydrocarbon separations.

Main text

Hydrocarbons are essential feedstocks to produce fuels and value-added chemicals^{1, 2}. However, the separation of their isomers, including hexanes, butanes, and butenes, remains a major challenge in the petrochemical industry due to their nearly identical boiling points (e.g., 0.43 K difference between *l*-butene and isobutene) and similar molecular dimensions. Currently, distillation, the dominant industrial method, is thermally driven and involves phase change, entailing high energy consumption, large-scale equipment, and substantial capital investment, thereby posing significant challenges for energy conservation, emission reduction, and process intensification³. Membrane technology could eliminate or partially eliminate phase change and thus improve energy efficiency². Although polymeric membranes have been widely studied, they suffer from an inherent trade-off between permeability and selectivity, as well as material aging and swelling in hydrocarbons⁴⁻⁶. Framework-based materials, including zeolites⁷⁻⁹, metal-organic frameworks (MOFs)¹⁰⁻¹², and covalent organic frameworks (COFs)¹³⁻¹⁵, possess well-defined microporous structures and tunable pore sizes. Membranes composed of these materials exhibit higher separation performance and stability in hydrocarbon separation, effectively addressing the limitations of polymeric membranes and emerging as promising candidates. Among them, zeolite membranes stand out for practical applications due to their exceptional hydrothermal and chemical stabilities¹⁶⁻¹⁸.

Nanosheets are ideal building blocks for constructing ultrathin vertically aligned nanochannel films/membranes through secondary growth for applications in molecular separation¹⁹, sensor²⁰ and catalysis²¹. However, these nanosheets are fragile and chemically active, making them susceptible to breakage or dissolution during the hydrothermal and solvothermal secondary growth. This results in prolonged synthesis and disordered nanochannel membranes with poor separation performance. Zeolite nanosheets with MFI¹⁹, MWW²², and SOD²³ frameworks were reported to synthesize ultrathin nanochannel membranes via secondary growth, mostly on the small-area disc supports, for efficient separation of hydrocarbon isomers and H₂/CO₂ mixtures. The synthesis of these nanosheet-based membranes requires dozens of hours, even though the gaps among nanosheets are generally small. This is contrary to the expectation of rapid and mild secondary synthesis, which should be sufficient to bridge the small gaps while minimizing damage to the fragile

nanosheets in the corrosive synthesis solutions. Furthermore, prolonged synthesis results in the uncontrollable deposition of randomly oriented crystals that disrupts the formation of oriented membranes. Although significant progress has been made on small-area disc supports, several key challenges must be addressed to prepare high-quality nanosheet-based nanochannel membranes: (1) synthesizing high-aspect-ratio nanosheets and maintaining their integrity in the membrane; (2) preserving the orientation of the nanosheet layers; and (3) enabling the rapid and scalable production of high-performance nanochannel membranes on commercial supports.

To address these challenges, we developed a nucleation-isolated superfast synthesis (NI-SFS) strategy, in which the nucleation of the precursor gel is decoupled from the crystallization of the nanochannel membrane. This approach enables minute-scale fabrication of ultrathin, highly *b*-oriented MFI zeolite membranes with high-density vertically aligned nanochannel (uniform $5.3 \text{ \AA} \times 5.6 \text{ \AA}$ nanochannel along the *b* axis) on commercial tubular alumina supports through the rational modification of synthesis conditions. The precursor gel is pre-nucleated to approach its nucleation peak before contacting the nanosheet seed layer, ensuring a uniform and sufficient supply of nuclei/precursors for secondary growth and the rapid formation of an ultrathin membrane without nanosheet dissolution. The synthesis efficiency is enhanced by 1-2 orders of magnitude compared with conventional synthesis, fulfilling the expectation of rapid and mild secondary growth for the fabrication of uniform nanosheet-based nanochannel membranes. These nanochannel membranes exhibit superior separation performance for hexane, butane, and butene isomer mixtures compared with most previously reported membranes.

NI-SFS mechanism for ultrathin, vertically aligned nanochannel membranes

Fig. 1 shows the proposed NI-SFS formation mechanism for preparing ultrathin, oriented and vertically aligned nanochannel membranes in minutes. The key synthesis modification was the nucleation-isolated synthesis strategy, in which the seeded support was suspended above the precursor gel and then brought into contact with the gel by overturning the autoclave after a 35-min preheating/gel-nucleation stage. During this initial nucleation period, the fragile nanosheet layer on the support above the gel remained intact (Supplementary Fig. 1). The abundant nuclei/nutrients in the gel were expected to induce

the growth of the nanosheet layers into a continuous membrane upon contact with the pre-nucleated gel. The rapid crystallization rate during the secondary-growth stage enabled the ultrafast formation of nanosheet-based membranes while preserving the *b*-axis orientation of the nanosheet layers. In addition, rational modifications to the NI-SFS synthesis included a balanced organic structural directing agent (OSDA) concentration and higher synthesis temperature. Membrane gels with suitable OSDA/H₂O ratios of 0.07%-0.13% that were still lower than the routine gel (OSDA/H₂O ratio of 0.20%)²⁴ enabled the formation of high-quality membranes due to the rapid nucleation. In contrast, OSDA/H₂O ratios that deviated from the optimal range yielded either poorly intergrown or randomly oriented zeolite membranes—a consequence of dissolution in OSDA-over gels and insufficient nucleation in OSDA-deficient gels, respectively (Supplementary Figs. 2 and 3). The OSDA-rich (active) gel (OSDA/H₂O ratio of 0.44%) in our previous studies²⁵ was used to reduce membrane synthesis time when regular seeds were coated. Obviously, the synthesis route using OSDA-rich gel was not appropriate to current preparation of nanosheet-based membranes. Increasing temperature from 413 K (the routine one) to 473 K was another key factor in dramatically accelerating uniform membrane formation. When the OSDA-compatible gel was subjected to elevated synthesis temperatures, sufficient nuclei and nutrients were generated in the gel, leading to the rapid and uniform formation of ultrathin, oriented nanosheet-based membranes.

High-quality MFI zeolite nanosheets with an aspect ratio (AR) greater than 1,000 and a thickness of about 5 nm (Figs. 2a and Supplementary Fig. 4) were directly synthesized through the rational modification of a previously reported procedure and subsequently used for seed-layer assembly⁸. These nanosheets were uniformly dispersed in deionized water and seeded onto the unmodified inner surface of commercial alumina tubes by program-controlled dip coating. The thickness of the seed layer was about 100 nm (Figs. 2b, 2c). The nanosheet morphology enabled the formation of an ultrathin seed layer with complete surface coverage, facilitating the subsequent growth of high-quality, ultrathin zeolite membranes through mild/short-time secondary growth. Once the pre-nucleated gel contacted the nanosheet seed layer by overturning the autoclave, the seed layer rapidly merged into an ultrathin and uniform membrane within minutes, with minimal nanosheet dissolution.

In conventional hydrothermal synthesis (CHS, Fig. 1), the nanosheets contacted the gel prior to synthesis and were dissolved in the corrosive gel after heating, since there were not sufficient nuclei to support the expanding of nanosheets at that time (Supplementary Fig. 5). Consequently, the continuity of nanosheet layer was disrupted, and several hours were required for multicycles of dissolution-recrystallization to repair the boundary defects. The CHS procedure suffered from a poor balance between membrane growth and nanosheet preservation, leading to the formation of thick, randomly oriented, low-quality zeolite membranes despite prolonged synthesis times.

The continuous nanosheet-based nanochannel membranes were obtained by NI-SFS for only 15 min. Scanning Electron Microscope (SEM) images of the membrane (Figs. 2d and 2e) showed that the nanosheets remained flat on the support, preserving the morphology of the seed layer while exhibiting increased intergrowth. The membrane thickness was ~500 nm, only 5 times that of the seed layer. This thickness remains among the thinnest reported for membranes fabricated on tubular supports, despite being slightly thicker than that of previously reported nanosheet-based zeolite membranes (~200 nm) prepared on disc supports with well-defined surface modification^{17, 26-29}. To gain insight into the microstructure and crystallinity of the nanochannel membranes, cross-sectional transmission electron microscopy (TEM) was performed on thin sections prepared by focused ion beam (FIB) milling and mounted onto a copper grid using platinum adhesive (Supplementary Fig. 6). The TEM image (Fig. 2f) shows a highly ordered microstructure of the thin membrane, consisting of tightly packed, intergrown, and well-oriented nanosheet layers. SEM characterization of the MFI membrane grown on a glass support under the same NI-SFS conditions further supports this rapid intergrowth behavior (Supplementary Fig. 7). The surface and cross-sectional SEM images show that the glass substrate was fully covered by intergrown plate-like MFI crystals, forming a continuous and relatively thin film layer, indicating that the pre-nucleated gel rapidly promoted lateral intergrowth of the nanosheet seed layer to generate a compact *b*-oriented MFI film within 15 min. The high-resolution TEM image and the corresponding selected area electron diffraction (SAED) maps confirmed the *b*-orientation of the lattice planes, in agreement with the SEM and XRD results (Fig. 2g). In contrast, nanochannel membranes prepared by

CHS for 6 h were randomly oriented and exhibited a thickness of approximately 4 μm (Supplementary Figs. 8 and 9).

Single-gas permeation and permoporosimetry analysis were used to verify the quality of the vertically aligned nanochannel membranes prepared by NI-SFS, in comparison with the routine disordered membrane prepared by CHS. In single-gas permeation tests, the NI-SFS membrane exhibited significantly higher permeance compared with the CHS one. The single-gas permeances of smaller (faster) gases, from H_2 to *n*-butane, through the NI-SFS membrane were 1.5-2.5 times higher than those through the CHS one (Fig. 2h), owing to its thinner structure and well-oriented and vertically aligned nanochannels. The ideal selectivities, defined as the permeance ratios of fast over slow gases (herein, hydrogen or nitrogen over sulfur hexafluoride, H_2/SF_6 or N_2/SF_6), are well-established metrics for assessing the quality of zeolite membranes. The ideal H_2/SF_6 and N_2/SF_6 selectivities of the NI-SFS membrane were 799 and 606, respectively, which were 75.9% and 89.3% higher than those of the CHS membrane, indicating the former membrane has higher quality. Permoporosimetry analysis showed that only 2.3% of the N_2 permeance through the NI-SFS membrane originated from intrinsic non-zeolitic pores, accounting for 10.4% of defect contribution observed in the CHS membrane (Fig. 2i). Collectively, these results confirm that NI-SFS membrane shows higher quality and higher permeances than the CHS one³⁰.

To gain insight into the mechanism underlying the ultrafast preparation of vertically aligned nanochannel membranes via the NI-SFS strategy, we investigated the nucleation and crystallization evolution of MFI zeolites and membranes. As shown in Fig. 3a and Supplementary Fig. 10, increasing synthesis temperature from 413 K (the routine one) to 473 K markedly accelerated both nucleation and crystallization, reducing the nucleation period (0-15% relative crystallinity) from 90 to 35 min. Solid-state ^{29}Si Nuclear Magnetic Resonance (NMR) spectroscopy further confirmed the enhanced degree of framework development at elevated temperatures (Fig. 3b). After crystallization, the fraction of fully condensed Q^4 species reached 84.35% at 473 K which was higher than that (80.21%) observed at 413 K, indicating a more extensively polymerized silicate network. This higher degree of condensation directly correlated with the nucleation efficiency and the nuclei readiness of the gel to support epitaxial membrane growth.

Therefore, increasing synthesis temperature is essential for shortening the nucleation period of the gel and increasing crystallization rate and crystallinity of MFI zeolites and membranes. XRD patterns reveal the gradual emergence of characteristic MFI reflections, indicating the formation of ordered structural building units from 15 to 55 min of synthesis time at 473 K for the modified membrane gel, consistent with observation from the high-resolution transmission electron microscopy (HRTEM) (Fig. 3c and Supplementary Fig. 11)³¹. Dynamic Light Scattering (DLS) results showed a monotonic increase in particle size, consistent with minimal aggregation of nuclei (Fig. 3d). Concurrently, the zeta potential became increasingly negative with nucleation time, suggesting that the nuclei exhibit high dispersion stability in the gel (Fig. 3e). The HRTEM image further verified that the gel contained uniformly dispersed nanoclusters with clear lattice fringes after 35 min of nucleation during the temperature-ramping period, confirming the presence of semi-crystalline nuclei at this stage (Fig. 3f).

All membranes prepared for 10-20 min (starting from the gel-support contact) displayed a high degree of *b*-orientation, with the crystallographic orientation index ($CPO_{020/501}$) approaching unity, as shown in the XRD patterns (Supplementary Fig. 12). The formation evolution of the NI-SFS membranes prepared for 10-20 min at 473 K was investigated by XRD and SEM (Figs. 3g-i and Supplementary Fig. 13). These results indicated that the orientation of seed layer remained well preserved for different synthesis times. The support surface was fully covered by a continuous zeolite layer with thickness of ~400 nm after only 10 min of hydrothermal synthesis (Supplementary Fig. 14). The membrane showed medium ideal *n*-butane/isobutane selectivity of ~11, indicating that the membrane is continuous but has only a few boundary defects. As the synthesis time increased from 10 to 20 min, membrane intergrowth and membrane thickness increased, while permeance decreased (Supplementary Table 1). The increase in membrane selectivity (82.1%) was obviously lower than the decrease in permeance (204%) when the synthesis time was extended from 15 to 20 min. Therefore, 15 min was identified as the optimal synthesis time. For comparison, CHS membranes were prepared under different synthesis temperatures and times, namely 473 K for 6 h and 413 K for 12 h (Supplementary Table 2). The membrane synthesized at 473 K for 6 h showed an *n*-butane permeance of 2.1×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ (627 gas permeance units (GPU); 1 GPU = 3.348×10^{-10} mol m⁻² s⁻¹ Pa⁻¹) and

a separation factor of 33, while the membrane synthesized at 413 K for 12 h exhibited a lower *n*-butane permeance of $1.3 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ (388 GPU) but a higher separation factor of 45. These results indicate that CHS can improve membrane selectivity under milder and longer crystallization conditions, but this is accompanied by reduced permeance due to increased transport resistance. In contrast, NI-SFS achieved superior performance within only 15 min, highlighting its advantage in rapidly forming thin and low-defect *b*-oriented MFI membranes.

Decreasing synthesis temperature to 453 K resulted in discontinuous membrane with ideal *n*-butane/isobutane selectivity of only 8, even though no obvious defects were observed in the SEM images (Supplementary Fig. 15), suggesting insufficient driving force at a relatively low temperature for nanosheet merging. Moreover, excessively high synthesis temperature of 493 K also increased the risk of uncontrolled overgrowth to form a thicker membrane (~800 nm), resulting in 60.5% reduction in *n*-butane permeance and 40% reduction in ideal *n*-butane/isobutane selectivity compared to the optimal membrane prepared at 473 K. The timing of contact between the nanosheet layer and the nucleated gel is critical. When contacting the seeded support with the gel was delayed by 1.5 h at 473 K, the resulting zeolite membrane exhibited defects observable by SEM along with poor crystallographic orientation (Supplementary Fig. 16). The decline in membrane quality could be attributed to the formation of enlarged and non-uniform nuclei/crystallites during the crystal-growth phase (0.5-2 h of heating), which become unsuitable for repairing defects in the nanosheet layer and thereby hinder the formation of a uniform, defect-few membranes. These results indicate that nucleated gel containing abundant and finely dispersed nuclei is well-suited for fabricating continuous nanosheet-based membranes via the NI-SFS route. Moreover, when the seeded support was brought into contact with the gel before being suspended above it, the resulting membrane exhibited even poorer compactness than the NI-SFS membrane (Supplementary Fig. 17), suggesting that the nanosheets are readily damaged upon contact with the synthesis gel and highlighting the importance of preserving their integrity.

Superior performance of oriented nanochannel membranes

The separation performance of the ultrathin, vertically aligned nanochannel membranes prepared by NI-SFS was evaluated in several binary hexane, butane and butene mixtures.

For *n*-hexane/2,2-dimethylbutane and *n*-hexane/2,3-dimethylbutane separations, the membranes exhibited consistently high *n*-hexane permeance with increasing *n*-hexane partial pressure (Figs. 4a, 4b). Under equimolar binary feed conditions consisting of linear and a di-branched hexane component, the *n*-hexane permeance remained stable at 2.4×10^{-7} and 2.2×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ (~750 and 660 GPU, respectively), with increasing *n*-hexane partial pressure, **while the *SF*s for *n*-hexane/2,2-dimethylbutane and *n*-hexane/2,3-dimethylbutane both exceeded 25,000.** Test temperature had little effect on the separation performance of the membranes for the three binary hexane isomer mixtures (Supplementary Fig 18). This combination of high permeance and extremely high *SF* indicates that the *b*-oriented straight MFI nanochannels provide highly efficient transport pathways for linear hexane while effectively excluding di-branched hexane isomers. As shown in Fig. 4c and Supplementary Fig. 19, the membrane exhibited an *n*-hexane permeance of 1.8×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ (540 GPU) with an *n*-hexane/2-methylpentane *SF* of 210 and *n*-hexane/3-methylpentane *SF* of 280, further confirming the excellent separation performance and structural integrity of the *b*-oriented MFI membrane.

Comparable robustness was also observed for C4 isomer separations (Supplementary Tables 3-4). For an *n*-butane/isobutane mixture (90/10) at 303 K and 126 kPa, the membranes delivered a *SF* of 57 with a high *n*-butane permeance of 5.8×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ (1,732 GPU), confirming the formation of high-quality NI-SFS membranes (Fig. 4d). The *n*-butane permeance decreased more rapidly than that of isobutane as *n*-butane partial pressure increased, leading to a gradual decline in *SF*, consistent with literature reports³²⁻³⁶. Similar trends were observed for the same membrane for separating a 50/50 *n*-butane/isobutane mixture (Supplementary Fig. 20). Temperature-dependent measurements showed that the permeance of *n*-butane increased but the *SF* decreased slightly with temperature (Supplementary Fig. 21). At 303 K and 151 kPa for a 90/10 *I*-butene/isobutene feed, the membrane achieved a *SF* of 62 with a *I*-butene permeance of 2.6×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ (750 GPU). Increasing the pressure drop from 111 to 151 kPa caused only a slight variation in *I*-butene permeance, whereas the *SF* increased gradually, indicating enhanced suppression of isobutene transport in the oriented MFI channels (Fig. 4e). During a 48-h continuous separation test, both permeance and *SF* remained stable, confirming the excellent durability and molecular-sieving stability of the NI-SFS membrane for butene

isomer separation (Fig. 4f). Feed-composition-dependent measurements further highlighted membrane quality: for both *n*-butane/isobutane and *I*-butene/isobutene mixtures, the *SF* increased with increasing fraction of the linear isomer in the feed (Supplementary Figs. 22 and 23), indicating a crowding-enhanced molecular sieving effect within the oriented nanochannels³⁷. Adsorption measurements further supported these results, showing consistently higher uptake of linear butane and butene isomers than their branched counterparts, particularly at low pressures (Supplementary Figs. 24 and 25).

To further evaluate the scalability and reproducibility of the NI-SFS strategy, six 20-cm-long *b*-oriented MFI membranes (~3.3 times of the length of the short ones) were fabricated and evaluated in separating butane isomer mixtures (Fig. 4g). The 20-cm-long membranes maintained high *n*-hexane/2,2-dimethylbutane separation performance with *SF*s above 20,000, comparable to those of the 6-cm-long membranes (Fig. 4h and Supplementary Table 4). Reproducible *n*-butane/isobutane separation performance for 6-cm- and 20-cm-long membranes is shown in Supplementary Fig. 26 and Supplementary Tables 1 and 3. In the separation of 50/50 *n*-hexane/2,2-dimethylbutane mixture using 20-cm-long NI-SFS membrane, the *n*-hexane permeance and *SF* changed little with increasing *n*-hexane partial pressure and remained as high as $2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ (597 GPU) and 20,000 (Fig. 4i). In the separation of a 50/50 *n*-butane/isobutane mixture, the long membrane delivered a stable *SF* of 71 and *n*-butane permeance of $3.0 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ (896 GPU) for the continuous 48-h test (Fig. 4j). The slightly lower permeance of the 20-cm-long membranes (~25% lower than that of the short ones) is likely associated with stronger feed-side concentration polarization³⁸⁻⁴⁰. The temperature-, pressure- and flowrate-dependent measurements of the long membranes in butane isomer and hexane isomer mixtures were consistent with those for the short ones (Supplementary Figs. 27-30)

Breakthrough performance of NI-SFS membranes and techno-economic analysis

Membrane fabrication is often restricted by a trade-off between separation performance and synthesis efficiency. Synthesis efficiency, which affects membrane cost, is defined as the reciprocal of the synthesis time⁴¹. The NI-SFS strategy improved synthesis efficiency by 1-2 orders of magnitude relative to the CHS one for zeolite membrane synthesis, placing the present membranes in a previously inaccessible region of the performance-efficiency plot in butane isomer separation (Fig. 5a and Supplementary Tables 6). For C6 isomer

separation, the up-scaling oriented NI-SFS membranes (membrane area: $\sim 40 \text{ cm}^2$) showed extremely high SFs (higher than 20,000) which was higher than all the reported membranes, and occupied the upper-performance region in the plot of n -hexane permeance versus n -hexane/2,2-dimethylbutane SF compared with the reported small-area membranes (membrane area: $< 10 \text{ cm}^2$) (Fig. 5b and Supplementary Table 8). For butane isomer separation, the large-area NI-SFS membranes also outperformed most previously reported membranes that had small membrane areas (Fig. 5c). It established a new benchmark for high-performance zeolitic nanochannel membranes.

To assess the industrial relevance of the NI-SFS-derived nanochannel membranes, techno-economic analysis was performed using Aspen Plus to benchmark membrane-based separation against conventional distillation and reactive distillation for butene and butane isomer separations (Supplementary Figs. 31-33 and Tables 7-14)⁴². For *I*-butene/isobutene feed compositions of 10/90 and 30/70 targeting 99% isobutene purity, conventional distillation required energy duties of 80.41 and 14.78 MW, respectively, while reactive distillation required 4.52 and 8.50 MW, respectively. In contrast, the membrane-based process enabled by the high-performance NI-SFS nanochannel membranes required only 0.31 and 0.59 MW for the two feed compositions, respectively (Fig. 5d). These values correspond to energy savings of approximately 99% and 93% for the 10/90 feed, and 96% and 93% for the 30/70 feed, relative to conventional and reactive distillations, respectively. The specific separation costs for the membrane process were only 2.03 and 5.93 $\text{\$ t}^{-1}$ for the 10/90 and 30/70 *I*-butene/isobutene feeds, respectively, which are substantially lower than those of the distillation-based processes (Fig. 5e).

Conventional distillation was modeled using *n*-butane/isobutane feeds of 10/90 and 30/70 at a feed rate of $5,000 \text{ kg h}^{-1}$, targeting 99% isobutane purity. The corresponding energy duties were 3.35 and 4.04 MW, respectively, whereas the membrane-based process reduced them to 0.23 and 0.49 MW, corresponding to savings of 93% and 88%, respectively (Supplementary Fig. 34). The specific separation costs of membrane separation were only 1.62 and 4.83 $\text{\$ t}^{-1}$ for the 10/90 and 30/70 *n*-butane/isobutane feeds, respectively (Fig. 5f). Overall, the large reductions in energy duty and separation cost arise from the elimination of reboilers, condensers and associated heat duties, together with the high permeance and SF of the NI-SFS nanochannel membranes. These results demonstrate that the NI-SFS

342 nanochannel membrane process is a highly competitive and energy-efficient alternative to
343 conventional separation technologies for hydrocarbon isomer separation.
344

Conclusions

We report a NI-SFS strategy that enables the ultrafast fabrication of high-quality, *b*-oriented MFI zeolite membranes with well-aligned straight nanochannels and minimal non-zeolitic defects. By decoupling gel nucleation and crystallization, the precursor gel reached a highly active nucleation state before contacting with the nanosheet-seeded support, thereby preserving nanosheet integrity and meanwhile ensuring sufficient nutrient supply for epitaxial growth of membrane. As a result, continuous ultrathin (~ 500 nm) *b*-oriented MFI membranes were obtained within only 15 min, representing less than 5% of the synthesis time required by conventional hydrothermal methods.

The resulting membranes exhibited outstanding molecular-sieving performance for multiple challenging hydrocarbon isomer separations. For hexane isomer mixtures, the membranes showed exceptional discrimination between linear and branched isomers, with *SFs* exceeding 25,000 for *n*-hexane/2,2-dimethylbutane (50/50) and *n*-hexane/2,3-dimethylbutane (50/50) while maintaining high *n*-hexane permeances of $(2.2\text{--}2.5) \times 10^{-7}$ mol m⁻² s⁻¹ Pa⁻¹ (660-750 GPU). The membranes also exhibited excellent butane/butene isomer separation performance, achieving a *n*-butane/isobutane *SF* of 57 with an *n*-butane permeance of 5.8×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ (1,732 GPU) in a 90/10 *n*-butane/isobutane mixture and a *I*-butene/isobutene *SF* of 62 with a *I*-butene permeance of 2.6×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ (750 GPU) in a 90/10 *I*-butene/isobutene separation at 303 K. Six up-scaling 20-cm-long NI-SFS membranes maintained high *n*-hexane/2,2-dimethylbutane separation performance, delivering *SFs* of >20,000 with an *n*-hexane permeances of $1.7\text{--}2 \times 10^{-7}$ mol m⁻² s⁻¹ Pa⁻¹ (507-597 GPU), which was comparable to the short ones. It indicates the NI-SFS strategy is scalable for zeolite membranes. Both short and up-scaling membranes displayed stable separation performance in the continuous 48-h test. Techno-economic analysis further shows that membrane-based processes enabled by NI-SFS membranes can reduce energy consumption by 88-93% compared with conventional distillation and reactive distillation for butane and butene isomer separation. In summary, this work establishes the NI-SFS strategy as a scalable and energy-efficient platform for producing ultrathin, vertically aligned nanochannel membranes, offering a promising route for high-efficiency separation of hydrocarbon isomers.

Methods

MFI membrane fabrication by NI-SFS

MFI membranes were fabricated by the nucleation-isolated superfast synthesis (NI-SFS) strategy using MFI nanosheets as shown in Supplementary Fig. 35. **Nanosheets preparation:** the MFI nanosheets were synthesized by a modified bottom-up method in the previous report⁸ Briefly, bis-1,5-(tripropyl ammonium) pentamethylene diiodide (dC5) was used as the organic structure-directing agent, and the nanosheet synthesis gel had a molar composition of 80 TEOS: 3.75 dC5: 20 KOH: 9500 H₂O. The gel was hydrolyzed under an air purge at room temperature to reduce ethanol content, filtered through a 0.45 μm syringe filter, and then mixed with pre-synthesized MFI seed nanoparticles at a silica mass ratio of 1:200. Detailed preparation procedures for dC5 and MFI nanoparticles are provided in the Supplementary Information. The resulting precursor was transferred into a Teflon-lined stainless-steel autoclave and crystallized at 413 K for 4 d. The obtained MFI nanosheets were collected by centrifugation, washed with deionized water until the pH reached 7-8, freeze-dried, and calcined in air at 753 K for 4 h to remove the OSDA.

Nanosheet coating: commercial $\alpha\text{-Al}_2\text{O}_3$ tubular supports were cut into 6-cm-long segments for regular synthesis or 20-cm-long segments for scale-up synthesis. Both ends of the supports were sealed with Duncan ceramic glaze and fired at 1223 K, after which the outer surface was wrapped with a heat-shrunk PTFE tube to prevent seed deposition on the exterior surface. The dried supports were immersed in a 0.1 wt% MFI nanosheet suspension for 60 s and withdrawn at a rate of 0.2 cm s^{-1} , followed by drying at 333 K for 12 h to form a *b*-oriented nanosheet seed layer on the inner surface of the tubular support.

Membrane synthesis: For NI-SFS membrane growth, the nanosheet-coated tubular support was suspended above the synthesis gel in a stainless-steel autoclave during the initial heating stage. The membrane synthesis gel had a molar composition of 1 TEOS: (0.12-0.24) TPAOH: 180 H₂O. After heating for 35 min, the gel reached a highly active nucleation state, and the autoclave was overturned to bring the pre-nucleated gel into contact with the seeded inner surface of the tubular support. Membrane crystallization was then conducted at 473 K for 10-20 min, followed by rapid water quenching to below 333 K within 5 min. The membranes were washed with deionized water and dried at 333 K overnight. **OSDA removal:** the OSDA was removed by ozone calcination at 473 K for 48

h at a flow rate of 200 SMLPM. The calcined membranes were stored at 473 K prior to separation testing.

Membrane quality assessment

Single-gas permeation tests were performed using gases with different kinetic diameters, including small probe molecules and larger molecules such as SF₆, to evaluate the gas transport behavior, membrane continuity and ideal selectivity. The ideal selectivities, such as H₂/SF₆ and N₂/SF₆, were used as quantitative indicators of membrane compactness and defect level. The single-gas permeance (P_i , mol m⁻² s⁻¹ Pa⁻¹) was calculated from the pressure drop across the membrane (ΔP_i , kPa) and normalized flux (N_i , mol m⁻² s⁻¹), as shown in Equation 1. Ideal selectivity was defined as the ratio of the permeances of components i and j, as described in Equation 2.

$$P_i = \frac{N_i}{\Delta P_i} \quad (1)$$

$$\alpha_{ideal} = \frac{P_i}{P_j} \quad (2)$$

Permporosimetry analysis was further carried out to distinguish transport through intrinsic MFI micropores from that through non-zeolitic defects. By monitoring the change in gas permeance during progressive pore blocking, the contribution of non-zeolitic pores to the total permeance was quantified. Together, these measurements were used to evaluate the structural quality, defect minimization and effective molecular-sieving ability of the NI-SFS-derived membranes. The pore size was calculated according to Kelvin's equation 3:

$$d_k = \frac{-4V_m\gamma}{RT \ln\left(\frac{P}{P_s}\right)} \quad (3)$$

Detailed experimental conditions, analytical methods and calculation equations for permporosimetry analysis are provided in the Supplementary Information.

Mixture separation performance evaluation

The separation performance of the MFI membranes was evaluated using representative C4 and C6 hydrocarbon isomer mixtures. For C4 isomers, including *n*-butane/isobutane and *l*-butene/isobutene, gas-phase mixture separation was conducted using a **permeate-vacuum method**. Because these C4 isomers are gaseous under the testing conditions, the

feed composition, flow rate and pressure were directly controlled using gas-flow regulation systems, while the permeate side was evacuated to provide the driving force for permeation. This method enabled accurate evaluation of C4 alkane and alkene isomer separation under controlled pressure and temperature conditions. For C6 isomer separation, including *n*-hexane/2,2-dimethylbutane, *n*-hexane/2,3-dimethylbutane and *n*-hexane/methylpentane mixtures, **Wicke-Kallenbach measurements** were used. Unlike C4 isomers, C6 hydrocarbons are liquid at room temperature and have relatively low vapor pressures; therefore, nitrogen was used to generate, dilute and carry saturated hydrocarbon vapors from temperature-controlled reservoirs. The feed partial pressures were controlled by adjusting the reservoir temperature, while nitrogen sweep gas was used on the permeate side to collect permeated species for gas chromatographic analysis. Membrane performance was evaluated using permeance, separation factor and separation performance index. Detailed experimental conditions, analytical methods and calculation equations are provided in the Supplementary Information.

The membrane performance was quantified by permeance and separation factor (*SF*). Permeance was calculated from the component flux normalized by the transmembrane partial-pressure difference as described in equation 1. The *SF* was defined as the molar composition ratio of the preferentially permeating component to the less-permeating component in the permeate divided by the corresponding ratio in the feed, as described in equation 4.

$$SF = \frac{(y_i/y_j)_p}{(x_i/x_j)_f} \quad (4)$$

where x_i and x_j are the molar fractions of components i and j in the feed, and y_i and y_j are their molar fractions in the permeate. Component i represents the preferentially permeating linear isomer, such as *n*-butane, *l*-butene or *n*-hexane, while component j represents the corresponding branched isomer, such as isobutane, isobutene, 2,2-dimethylbutane, 2,3-dimethylbutane or methylpentane.

Separation performance index (*SPI*, GPU) is defined as the product of the permeance of fast gas and (*SF*-1), which is a performance parameter as described in equation 5.

$$SPI = P_i \times \alpha_{i,j} \quad (5)$$

Data availability

The data that support the findings of this study are available in the main text and Supplementary Information.

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Author Contributions Statement

J.W. and R.Z. conceived the project. J.W. performed the nanosheet synthesis, membrane fabrication, separation experiments and data analysis. H.L. performed the process simulation and techno-economic analysis. H.W. contributed to electron microscopy, X-ray diffraction and structural analysis. K.Y. and B.W. assisted with experiments and characterization. W.X. contributed resources and discussion on membrane scale-up. M.Y. and R.Z. supervised the work and revised the manuscript. J.W. wrote the manuscript with input from all authors. All authors discussed the results and approved the final manuscript.

Competing Interests Statement

The authors declare that they have no competing interests.

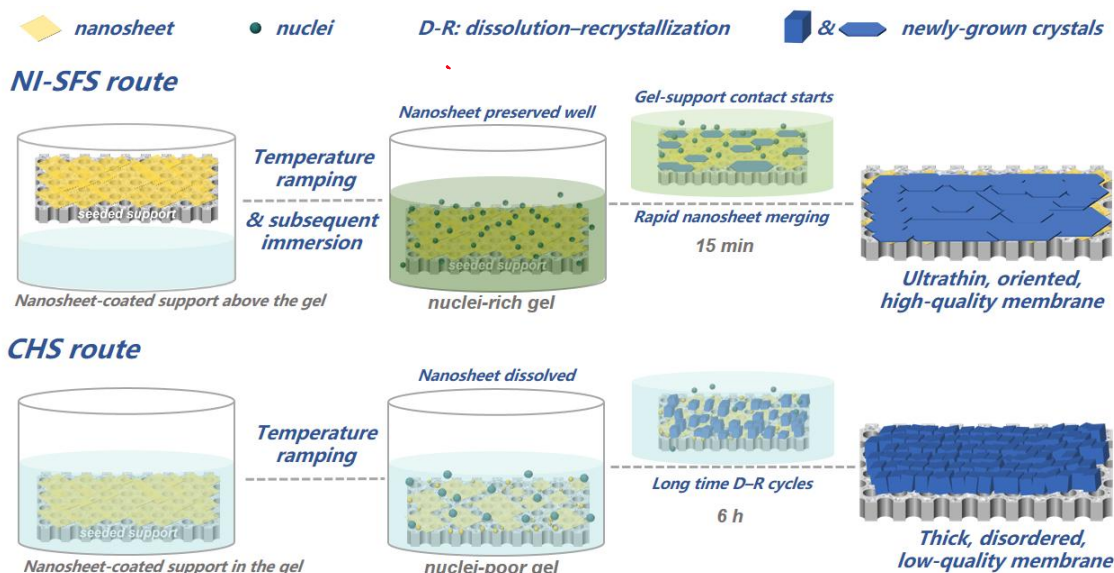


Fig. 1. Schematic of NI-SFS and CHS strategies for preparing zeolitic nanochannel membranes. NI-SFS: nucleation-isolated superfast synthesis; this strategy results in minute-scale superfast synthesis of ultrathin, oriented nanosheet-based membranes with minimum nanosheet destruction. CHS: conventional hydrothermal synthesis; this strategy results in hour-scale synthesis of randomly oriented membranes with repeated seeds' dissolution-crystallization cycles.

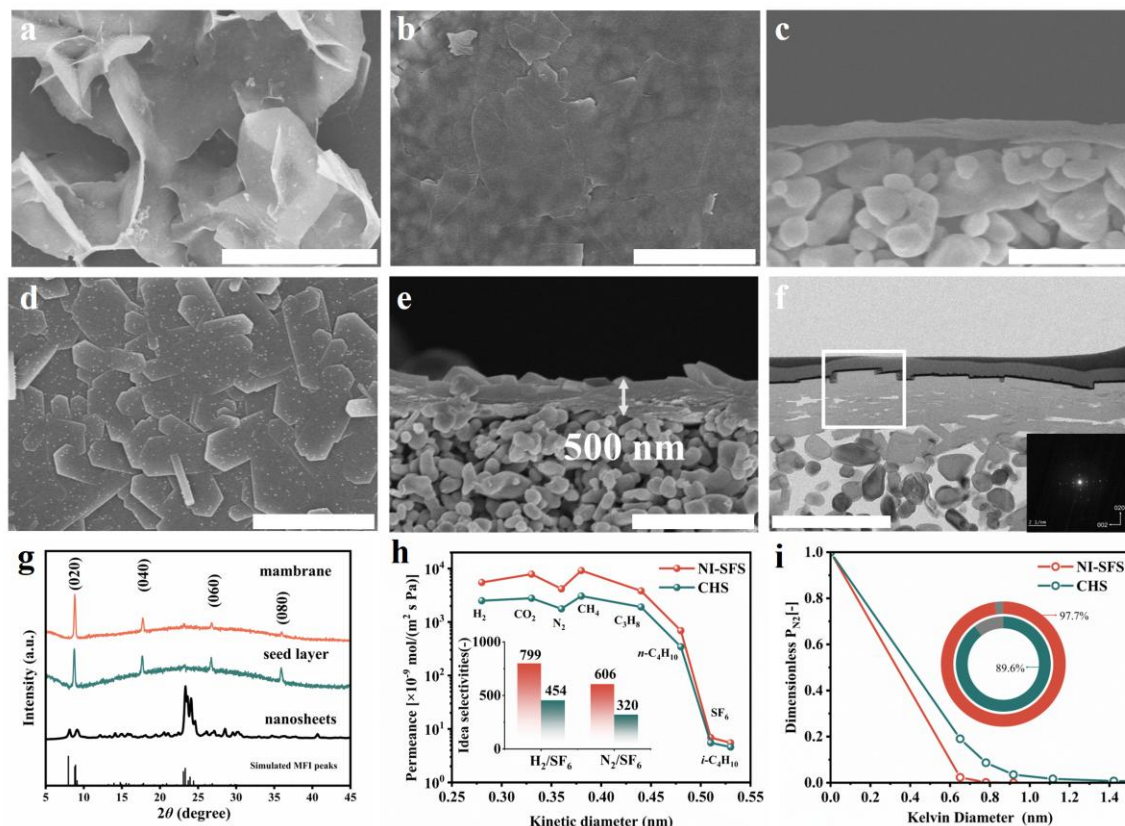


Fig. 2. Characterization of MFI nanosheets and ultrathin, *b*-oriented MFI membranes prepared by nanosheet-induced growth. **a**, SEM image of the MFI nanosheets. **b**, **c**, Surface and cross-sectional SEM images of the *b*-oriented MFI nanosheet seed layer deposited on the inner surface of the α -Al₂O₃ tubular support. **d**, **e**, Surface and cross-sectional SEM images of the *b*-oriented MFI membrane prepared by NI-SFS at 473 K for 15 min, showing a continuous membrane layer with a thickness of approximately 500 nm. **f**, Cross-sectional TEM image of the NI-SFS-derived membrane, with the corresponding FFT pattern shown in the inset; membrane surface was sputtered with Pt. **g**, XRD patterns of the MFI nanosheets, nanosheet seed layer, and NI-SFS-derived membrane on a glass substrate, confirming the preservation of *b*-orientation after membrane growth. **h**, Single-gas permeance comparison of *b*-oriented MFI membranes prepared via NI-SFS and randomly oriented membranes synthesized via CHS using nanosheets, measured at 303 K and 200 kPa feed pressure. **i**, Normalized N₂ permeance of NI-SFS and CHS membranes as a function of the Kelvin diameter obtained from permoporosimetry analysis; inset pie charts show the relative contributions of zeolitic and non-zeolitic pores to N₂ permeance in the NI-SFS and CHS membranes. **Scale bars:** **a-c**, 1 μ m; **d, e**, 2 μ m; **f**, 1 μ m; **inset in f**, 2 nm⁻¹.

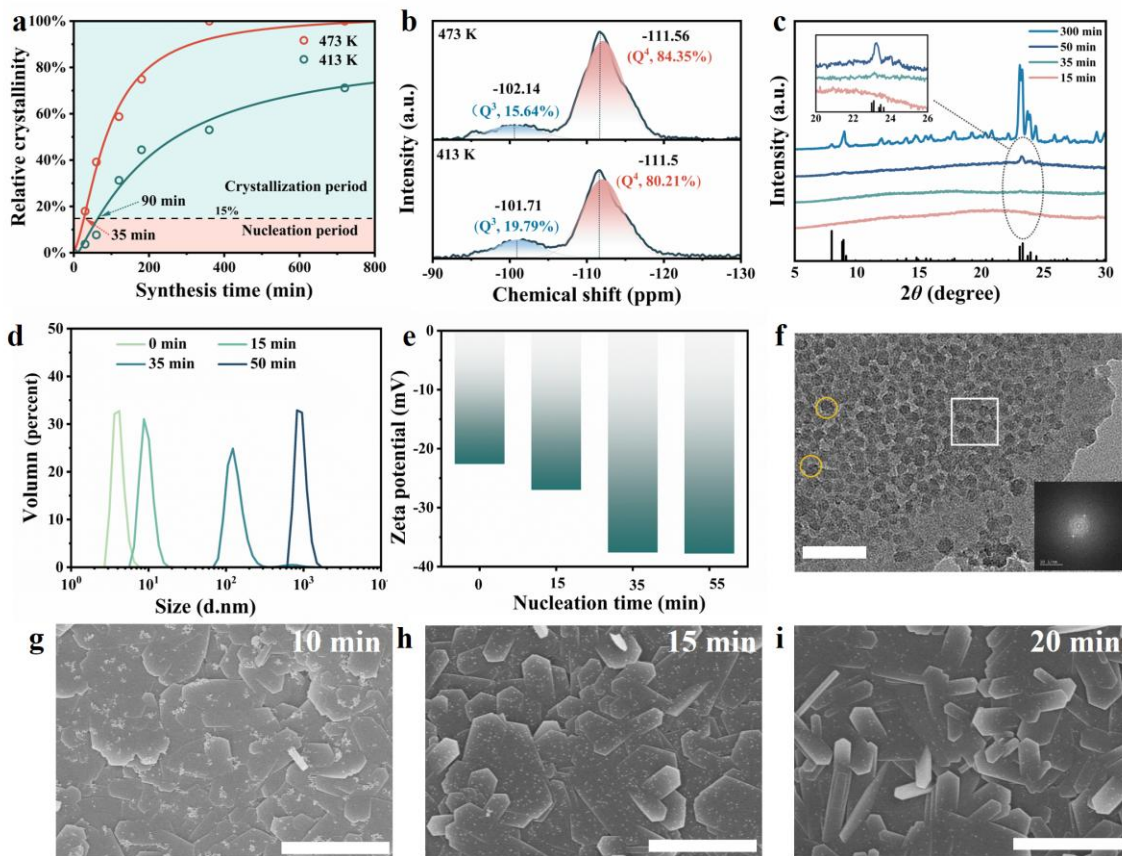


Fig. 3. Mechanism of NI-SFS growth of ultrathin, *b*-oriented MFI membranes. **a**, Relative crystallinities of the dried solids separated from the gel (molar ratio of the gel: 1 TEOS: 0.18 TPAOH: 180 H₂O; same below) at 413 K (green) and 473 K (red). Synthesis times corresponding to <15% relative crystallinity are identified as the nucleation period. **b**, ^{29}Si MAS NMR spectra of the dried solids separated from the gel after 12 h of crystallization at 473 K and 413 K. **c**, XRD patterns of the dried solids separated from the gel after different nucleation times during heating. **d**, Particle size distributions measured by DLS at different nucleation times. **e**, Zeta potential of gels as a function of nucleation time. 0-35 min is the temperature-rise stage (RT to synthesis temperature of 473 K) and the rest is the temperature-stable stage. **f**, High-resolution TEM image of the dried solids separated from the gel after nucleation for 35 min during heating and FFT pattern transferred from the white-boxed region in the image. Surface SEM images of *b*-oriented MFI membranes prepared by NI-SFS in 10 min (**g**), 15 min (**h**), and 20 min (**i**) at 473 K. Scale bars: **f**: 50 nm; **g-i**, 2 μm .

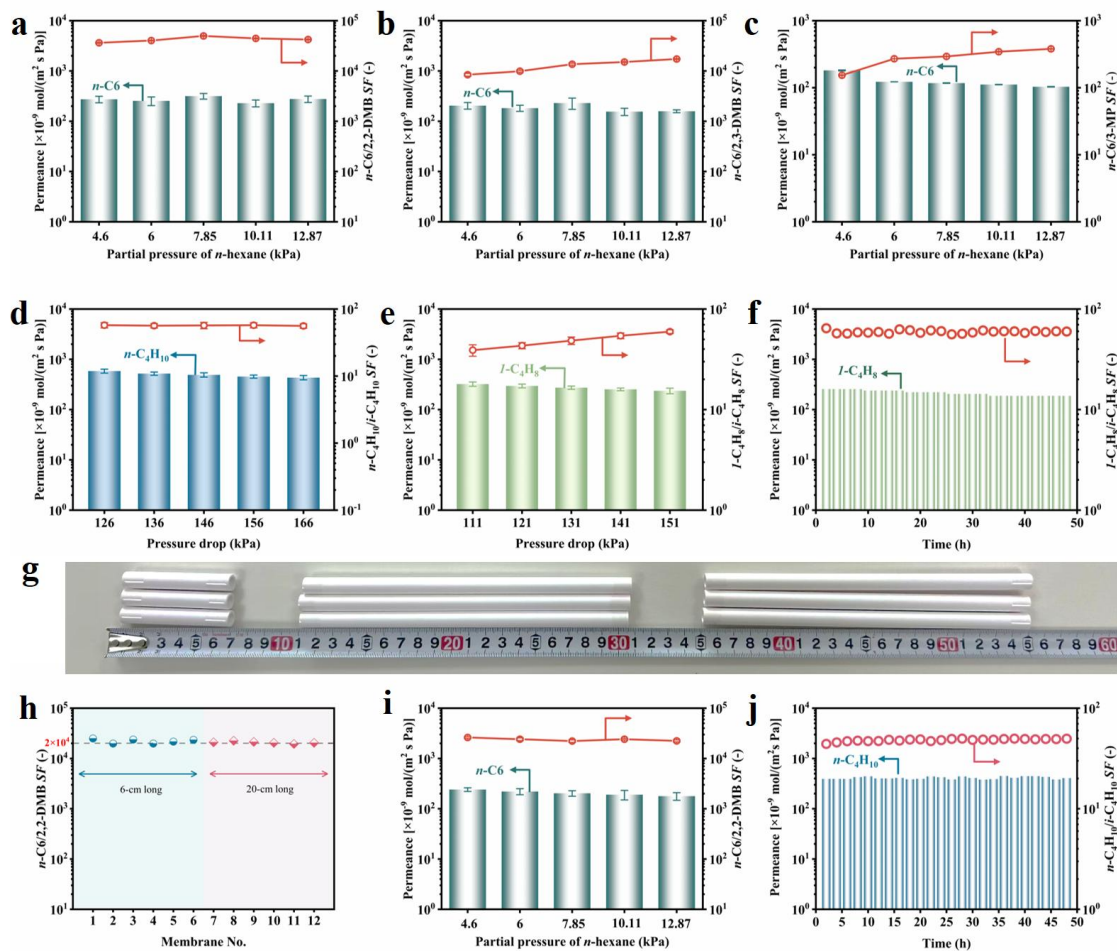


Fig. 4. Separation performance of MFI membranes prepared by NI-SFS at 473 K. Effect of *n*-hexane partial pressure on permeance and *SF* at 373 K in a 50/50 *n*-hexane/2,2-dimethylbutane mixture (a), a 50/50 *n*-hexane/2,3-dimethylbutane mixture (b), and a 50/50 *n*-hexane/3-methylpentane mixture (c). d, Effect of pressure drop across membrane on permeance and *SF* in a 90/10 *n*-butane/isobutane mixture at 303 K and feed flow rate of 400 SCCM (standard cubic centimeter per minute). e, Effect of pressure drop across membrane on permeance and *SF* in a 90/10 *I*-butene/isobutene mixture at 303 K and feed flow rate of 200 SCCM. f, Long-term stability test of the 6-cm-long membrane in a 90/10 *I*-butene/isobutene mixture at 303 K and 151 kPa pressure drop. g, Photo of 6-cm-long and 20-cm-long tubular MFI membranes prepared by NI-SFS. h, Comparison of *n*-C₆/2,2-DMB separation factors of 6-cm- and 20-cm-long MFI membranes by NI-SFS. Detailed separation data are summarized in Supplementary Table 4. i, Effect of *n*-hexane partial pressure on permeances and *SF* for *n*-hexane/2,2-dimethylbutane separation through a 20-cm-long membrane in a 50/50 mixture at 373 K. j, Long-term stability test of the 20-cm-long membrane in a 50/50 *n*-butane/isobutane mixture at 303 K and a pressure drop of 126 kPa.

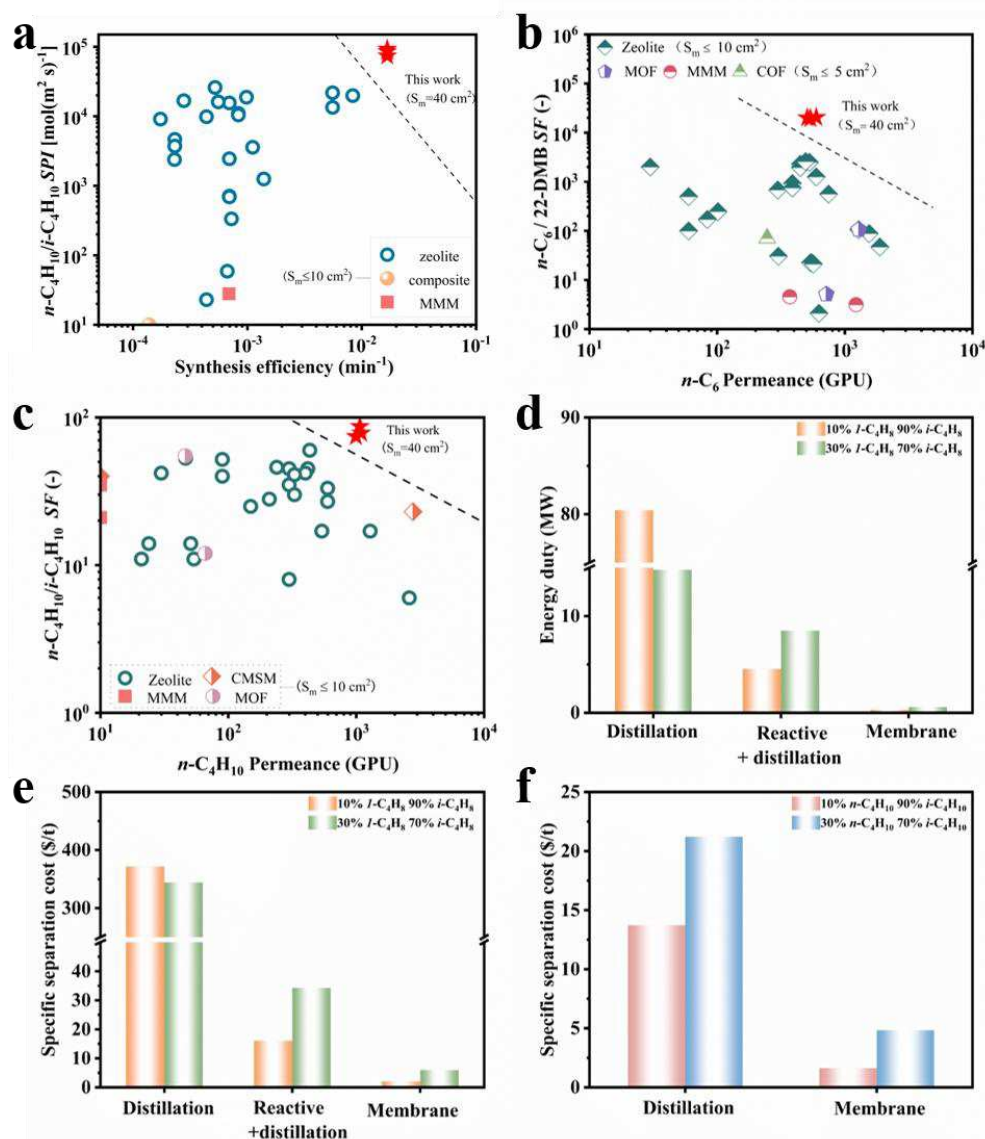


Fig. 5. Performance benchmarking and process-level advantages of NI-SFS-derived MFI membranes. **a**, Comparison of NI-SFS method with the reported conventional methods for the synthesis of MFI membranes in the plot of SPI versus synthesis efficiency. It demonstrates that the NI-SFS strategy simultaneously improves membrane separation performance and synthesis efficiency. Detailed data are listed in Supplementary Tables 6. Comparison of $n\text{-C}_6/2,2\text{-DMB}$ separation performance (**b**) and $n\text{-butane/isobutane}$ (**c**) between the 20-cm-long b -oriented NI-SFS-derived MFI membranes in this work and reported membranes including MOFs, zeolites and polymers in the permeance versus SF plot. Detailed performance data are listed in the Supplementary Tables 6 and 8. The red stars indicate the scaled-up 20-cm-long membranes in this work (membrane area: $\sim 40\text{ cm}^2$); others: small-area membranes with area less than 10 cm^2 . Comparison of simulated energy duty (**d**) and specific separation cost (**e**) for $i\text{-butene/isobutene}$ separation using distillation, reactive distillation combined with distillation, and membrane separation at feed compositions of 10%/90% and 30%/70%.

643 f, Comparison of specific separation cost for *n*-butane/isobutane separation by distillation and
644 membrane separation at feed compositions of 10%/90% and 30%/70%.

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