

--*Supplementary Materials for

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

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Materials

Tetrapropylammonium hydroxide (TPAOH, 25 wt% aqueous solution, TCI Co.), tetraethylorthosilicate (TEOS, 98%, Sigma-Aldrich), 1-iodopropane ($\text{C}_3\text{H}_7\text{I}$, 99%, Macklin), 1,5-diaminopentane ($\text{C}_5\text{H}_{14}\text{N}_2$, 98%, Adamas-beta), potassium carbonate (K_2CO_3 , 99%, Sinopharm Chemical Reagent Co., Ltd.), potassium hydroxide (KOH, 98%), ethyl acetate (Sinopharm Chemical Reagent Co., Ltd.), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%, Wuxi Yasheng Chemical CO. Ltd), *n*-hexane (99%, Aladdin Reagent (Shanghai) Co., Ltd), 2-methylpentane (2MP, 99%, Aladdin Reagent (Shanghai) Co., Ltd), 3-methylpentane (3MP, 99%, Aladdin Reagent (Shanghai) Co., Ltd), 2,2-dimethylbutane (2,2-DMB, 99%, Aladdin Reagent (Shanghai) Co., Ltd), 2,3-dimethylbutane (2,3-DMB, 99%, Aladdin Reagent (Shanghai) Co., Ltd), deionized (DI) water was homemade. The gases of hydrogen (H_2 , 99.999%), carbon dioxide (CO_2 , 99.999%), nitrogen (N_2 , 99.999%), methane (CH_4 , 99.999%), propane (C_3H_8 , 99.99%), *n*-butane (*n*- C_4H_{10} , 99.99%), isobutane (*i*- C_4H_{10} , 99.99%), *l*-butene (*l*- C_4H_8 , 99.99%), isobutene (*i*- C_4H_8 , 99.99%), sulfur hexafluoride (SF_6 , 99.99%) were purchased from Nanjing Changyuan Industrial Gases CO., Ltd of China. Commercial tubular alumina supports (Inopor®, outer diameter: 10 mm, inner diameter: 7 mm, active inside α -alumina layer: 200 nm) were purchased from Rauschert Distribution GmbH Co. and used as received without further modification. Glass slides were purchased from sail brand.

Characterization

The morphologies of zeolite crystals, nanosheet seed layers and MFI membranes were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800). The accelerating voltage was typically set in the range of 5-10 kV depending on the sample conductivity and imaging requirement. The tubular membranes were carefully fractured using diagonal cutting pliers to expose a fresh surface and cross-section samples, while direct contact with fingers was avoided to minimize surface contamination. Prior to SEM imaging, all samples were sputter-coated with a thin Au/Pt

conductive layer for 40 s at 40 mA.

Energy-dispersive X-ray spectroscopy (EDX, EMAX x-act, Horiba) equipped on the FE-SEM system was used to analyze elemental distributions across the membrane cross-sections. EDX elemental mapping was performed to distinguish the zeolite membrane layer from the α -Al₂O₃ support, and the membrane thickness was determined from the cross-sectional SEM images and corresponding elemental mapping results.

High-resolution transmission electron microscopy (HRTEM, Talos F200X G2) was performed at an accelerating voltage of 200 kV to examine the crystalline structure and channel orientation of the MFI nanosheets and membranes. For TEM characterization of the MFI membranes, electron-transparent cross-sectional lamellae were prepared by focused ion beam milling (FIB, Helios G4 UX). A trench was milled using concentrated Ga⁺ ions at 30 kV and 0.75 nA, followed by thinning to obtain a suitable specimen for TEM analysis. The crystal orientation was further analyzed using fast Fourier transform (FFT) patterns and selected-area electron diffraction (SAED) when applicable.

Powder and membrane X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV diffractometer using Cu K α radiation. The diffraction data were recorded over a 2 θ range of 5–45° with a step size of 0.05°. XRD was used to identify the crystalline phase of the MFI seeds and membranes and to evaluate the preferential orientation of the membrane layers. The curved surface of tubular membranes weakens the XRD peaks of zeolite layer and influenced the judgement of orientation of the membrane¹. NI-SFS membranes were prepared on disc silicon support under the same optimized condition for the clear orientation judgement of MFI membranes as shown in Figure 2g.

Solid-state ²⁹Si magic-angle spinning nuclear magnetic resonance (²⁹Si MAS NMR) spectra were recorded on a Bruker AVANCE III HD 400 MHz spectrometer equipped with a 3.2 mm magic-angle spinning probe. The spectra were used to analyze the local silicon coordination environments in the MFI zeolite framework.

Dynamic light scattering (DLS) and zeta potential measurements were carried out on a

Malvern Zetasizer Nano ZS90 instrument. The zeolite particle or nanosheet suspensions were diluted with deionized water before measurement to avoid multiple scattering. DLS was used to estimate the hydrodynamic particle size distribution, while zeta potential measurements were used to evaluate the colloidal stability of the seed suspensions.

Preparation of MFI nanosheets

The MFI nanosheets were synthesized using a bottom-up approach modified from previously report. Specifically, bis-1,5-(tripropyl ammonium) pentamethylene diiodide (dC5) and MFI seed crystals were synthesized following the procedure of Jeon et al ². The purity of OSDA-dC5 prepared according to Jeon's method was confirmed by ¹³C NMR (Supplementary Fig 36). The precursor gel for MFI nanosheet growth had a molar composition of 80 TEOS: 3.75 dC5: 20 KOH: 9500 H₂O. To reduce ethanol content and promote crystallization, the gel was hydrolyzed under an air purge (50 mL min⁻¹) at room temperature for 16 h, followed by filtration using a 0.45 μ m syringe filter. The purified gel was then mixed with pre-synthesized MFI seed nanoparticles at a silica mass ratio of 1:200 (seed suspension to gel). The nanoparticles have a size of 30 nm and were confirmed by XRD to be phase-pure MFI (Supplementary Fig 37). The well-mixed precursor was transferred into a Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 413 K for 4 d. The obtained nanosheets were collected by centrifugation at 10,000 rpm, washed three times until the pH of the suspension reached 7-8, and subsequently collected by freeze-drying (Supplementary Fig 38). The OSDA was removed from the crystal in air at 753 K for 4 h with heating and cooling rates of 3 K min⁻¹.

Preparation of MFI nanosheets coating on α -Al₂O₃ tubes

The α -Al₂O₃ tubular supports were cut into 6-cm-long or 20-cm-long (for up-scaling investigation) segments, and approximately 1 cm of Duncan ceramic glaze was applied to each end of the supports, followed by firing at 1223 K with a heating and cooling rate of 3 K min⁻¹. Before coating, the outer surface of the dried supports was wrapped

with a PTFE tube and heat-shrunk at 413 K for 10 min to tightly enclose the support and prevent seed deposition on the exterior. The dried supports were then immersed in the MFI nanosheet seed suspension for 60 s and withdrawn at a linear speed of 0.2 cm s⁻¹ followed by drying at 333 K for 12 h to form a *b*-oriented nanosheet seed layer. Schematic diagram of the dip-coating method is shown as Supplementary Fig 39. According to previous studies, the coating thickness can be precisely controlled by adjusting the mass fraction of the zeolite nanosheet suspension. In this study, the optimized mass fraction of the MFI nanosheet suspension was 0.1 wt%.

Preparation of *b*-oriented MFI membrane by NI-SFS

The *b*-oriented MFI membranes were prepared by nucleation-isolated superfast synthesis (NI-SFS) using MFI nanosheet-coated α -Al₂O₃ tubular supports. The membrane synthesis gel had a molar composition of 1 TEOS: (0.12–0.24) TPAOH: 180 H₂O. Typically, TEOS and TPAOH were sequentially added into deionized water under stirring to form a homogeneous synthesis gel. 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 to avoid premature contact between the seed layer and the gel. After heating for 35 min, the gel reached a highly active nucleation state. The autoclave was then overturned to bring the pre-nucleated gel into contact with the seeded inner surface of the tubular support, initiating rapid membrane crystallization. The crystallization was conducted at 473 K for 10–20 min, followed by rapid water quenching to below 333 K within 5 min. The obtained membranes were washed thoroughly with deionized water and dried at 333 K overnight. The organic structure-directing agent (OSDA) was removed by low-temperature ozone calcination. The dried membranes were first treated under an ozone-containing atmosphere at 473 K for 48 h under an ozone flow rate of 200 SCCM. The calcined membranes were stored at 473 K prior to separation testing.

The *b*-oriented MFI films were prepared on MFI nanosheet-coated glass slides by the NI-SFS method. The synthesis gel was prepared with a molar composition of 1 TEOS:

(0.12–0.24) TPAOH: 180 H₂O. Briefly, TEOS and TPAOH were sequentially added into deionized water under stirring to form a homogeneous synthesis gel. The MFI nanosheet-coated glass slide was suspended above the gel in a stainless-steel autoclave during the initial heating stage to prevent direct contact between the seed layer and the gel. After heating at 473 K for 35 min, the autoclave was inverted to allow the pre-nucleated gel to contact the nanosheet-coated surface, initiating rapid crystallization of the b-oriented MFI film. The crystallization was performed at 473 K for 10–20 min, followed by rapid water quenching to below 333 K within 5 min. The obtained MFI films were washed thoroughly with deionized water and dried at 333 K overnight.

Preparation of MFI membrane by CHS

For comparison, MFI membranes were also prepared by conventional hydrothermal synthesis (CHS) using MFI nanosheet-coated α -Al₂O₃ tubular supports. The membrane synthesis gel had a molar composition of 1.0 SiO₂: 0.18 TPAOH: 180 H₂O, which was the same as the optimized gel in the above NI-SFS route. Typically, TEOS and TPAOH were sequentially added into deionized water under continuous stirring, and the mixture was further stirred at room temperature for 4 h to obtain a homogeneous synthesis gel. The nanosheet-coated tubular support was then directly placed into a stainless-steel autoclave containing the synthesis gel, allowing the seeded surface to remain in contact with the gel throughout the heating and crystallization process. After 35 min, the temperature reached the synthesis temperature of 473 K. The reaction was carried out for 6 h. When synthesis temperature was set to the widely reported 413 K, synthesis time was up to 12 h. This direct gel–seed contact during temperature ramping induced the dissolution of nanosheet seed layer and repeated dissolution–recrystallization processes, leading to thick and poor-oriented membranes. After crystallization, the membrane was removed from the autoclave, washed thoroughly with deionized water to remove residual gel species and loosely attached crystals, and dried at 333 K overnight. The organic structure-directing agent (OSDA) was removed by low-temperature ozone calcination. The dried membranes were first treated under an ozone-

containing atmosphere at 473 K for 48 h under an ozone flow rate of 200 SCCM. The calcined membranes were stored at 473 K prior to separation testing.

Investigating crystallization behavior of MFI zeolite under different synthesis conditions

To clarify the role of synthesis temperature and OSDA concentration in the NI-SFS process, the crystallization behavior of MFI zeolite was investigated by zeolite synthesis experiments. The synthesis conditions were designed to be consistent with those used for membrane growth, except that no seeded tubular support was introduced into the synthesis gel. This design allowed the intrinsic nucleation and crystallization behavior of the synthesis gel to be evaluated without the influence of secondary growth on the nanosheet seed layer.

MFI zeolite powders were synthesized under different conditions, including the optimized NI-SFS condition, lower-temperature crystallization, lower-OSDA-concentration crystallization and the CHS reference condition. At selected crystallization times, the solid products were collected, washed with deionized water, dried and characterized by X-ray diffraction (XRD). The relative crystallinity of each sample was estimated by integrating the characteristic MFI diffraction peaks at $2\theta = 7.9^\circ$, 8.9° and 23.2° . The sample with the highest crystallinity after sufficient crystallization was used as the reference sample with 100% relative crystallinity.

The initial crystallization rate was evaluated from the early-stage crystallization curves. The effective crystallization-rate constant, k , was defined as the reciprocal of the time required to reach 15% relative crystallinity^{1,3}:

$$k = \frac{1}{t_{15\%}} \quad (1)$$

where $t_{15\%}$ is the crystallization time at which the relative crystallinity reaches 15%.

The initial crystallization rate, r_0 , was then estimated according to:

$$r_0 = k \times g_0 \quad (2)$$

where g_0 represents the initial nutrient concentration in the synthesis gel, expressed as the SiO_2 concentration. This simplified treatment provides a useful comparison of the

early crystallization kinetics under different synthesis conditions.

Crystallographic Preferred Orientation

The preferred orientation of MFI crystals in the membrane was evaluated by the crystallographic preferred orientation index ($CPO_{(020)/(501)}$), derived from the relative intensities of the (020) and (501) reflections in the PXRD patterns of the membrane and randomly oriented MFI powder. The CPO value was calculated according to the following equation:

$$CPO_{(020)/(501)} = \frac{\frac{I_{(020)}^{membrane}}{I_{(501)}^{membrane}} - \frac{I_{(020)}^{powder}}{I_{(501)}^{powder}}}{\frac{I_{(020)}^{membrane}}{I_{(501)}^{membrane}}} \quad (3)$$

where $I_{(020)}$ and $I_{(501)}$ denote the intensities of the corresponding diffraction peaks⁴.

Single gas permeation test

For the single-gas permeation test, the membranes were degassed at 433 K with flowing helium on both feed and permeate sides for at least 12 h to remove adsorbed water. Pure gas was then introduced into the membrane module at a feed pressure of 200 kPa and 303 K. Single-gas permeation was conducted using the dead-end method, as described in previous studies (Supplementary Fig. 40)⁵. 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 4. Ideal selectivity was defined as the ratio of the permeances of components i and j , as described in Equation 5.

$$P_i = \frac{N_i}{\Delta P_i} \quad (4)$$

$$\alpha_{ideal} = \frac{P_i}{P_j} \quad (5)$$

Permoporosimetry analysis

Permoporosimetry analysis was used to evaluate the quality of the MFI membranes and to quantify the relative contributions of zeolitic and non-zeolitic pores to N₂ permeance (Supplementary Fig. 41). In this test, nitrogen was used as the non-condensable probing gas, while *n*-hexane vapor was used as the condensable adsorbate because of its strong

adsorption in MFI channels. As the relative pressure of *n*-hexane vapor increased, zeolitic micropores and small non-zeolitic defects were progressively blocked by adsorption or capillary condensation. The remaining N₂ permeance therefore reflected the contribution from larger open defects.

Before the permoporosimetry measurement, the membrane was mounted in a stainless-steel permeation module and activated under dry nitrogen flow to remove adsorbed moisture. The N₂ permeance of the fresh membrane was first measured in the absence of *n*-hexane vapor and defined as the initial permeance, P_0 . Subsequently, a controlled amount of *n*-hexane vapor was introduced into the nitrogen feed stream by passing part of the nitrogen flow through a temperature-controlled *n*-hexane saturator. The *n*-hexane relative pressure, P/P_s , was adjusted by mixing the saturated and dry nitrogen streams. At each P/P_s value, the system was allowed to reach a steady state before recording the N₂ permeance.

The corresponding Kelvin diameter, d_k , was calculated using the Kelvin equation:

$$d_k = \frac{-4V_m\gamma}{RT \ln\left(\frac{P}{P_s}\right)} \quad (6)$$

where γ is the surface tension of *n*-hexane, V_m is the molar volume of *n*-hexane, R is the universal gas constant, T is the measurement temperature, P is the vapor pressure of *n*-hexane and P_s is the saturated vapor pressure of *n*-hexane^{6, 7}. Although the Kelvin equation is not strictly applicable to sub-nanometer zeolitic micropores, the calculated Kelvin diameter provides a convenient operational parameter for comparing the pore-blocking behavior of different membranes under identical testing conditions.

The normalized N₂ permeance was calculated as:

$$P_{norm} = \frac{P}{P_0} \quad (7)$$

where P is the N₂ permeance measured at a given *n*-hexane relative pressure and P_0 is the initial N₂ permeance without *n*-hexane vapor. For MFI membranes, the N₂ permeance decrease at very low *n*-hexane relative pressure is mainly associated with the blocking of intrinsic zeolitic channels. Therefore, the permeance loss after

introducing *n*-hexane vapor can be assigned to the contribution from zeolitic pores, whereas the residual N₂ permeance after zeolitic-pore blocking is attributed to non-zeolitic pores.

The contribution of non-zeolitic pores to N₂ permeance was estimated as:

$$\text{Contribution of non – zeolitic pores} = \frac{P_{\text{defect}}}{P_0} \times 100\% \quad (8)$$

and the contribution of zeolitic pores was calculated as:

$$\text{Contribution of zeolitic pores} = \left(1 - \frac{P_{\text{defect}}}{P_0}\right) \times 100\% \quad (9)$$

where P_{defect} is the N₂ permeance after the zeolitic channels are blocked by *n*-hexane vapor.

Gas mixture separation experiments

Different separation modes were used for C4 and C6 isomer mixtures because of their different boiling points and vapor pressures. C4 isomers, including *n*-butane/isobutane and *I*-butene/isobutene, are gases under the testing conditions and can therefore be directly supplied as gas mixtures with controlled flow rate and pressure; their separation was evaluated by the permeate-vacuum method without carrier gas in the feed. In contrast, C6 isomers are liquids at room temperature and have relatively low vapor pressures, making direct gas feeding difficult due to the condensation of gases. Therefore, *n*-hexane isomer separations were performed in Wicke-Kallenbach mode, where nitrogen was used as carrier gas in the feed and sweep gas in the permeate to generate stable vapor feeds and accurately control hydrocarbon partial pressures.

The separation performance of MFI membranes was evaluated using a 50/50 *n*-butane/isobutane (*I*-butene/isobutene) mixture via the permeate-vacuum method (Supplementary Fig. 42), where the permeate side was maintained at an absolute pressure of 5 kPa. No carrier gas was used on either the feed or permeate sides in this case. Testing was conducted on the same homemade setup. The flow rate and composition of the *n*-butane/isobutane (*I*-butene/isobutene) feed mixture were precisely controlled with mass flow controllers, and the feed pressure was regulated using a back-pressure regulator. The membrane module was placed in an air-forced

oven to control the test temperature. In the permeate-vacuum method, the permeate side was evacuated by an oil-free vacuum pump (KNF, N840), with the volumetric flow rate of the permeating gas monitored using a soap bubble flow meter at the pump outlet. The feed flow rate was typically maintained at 400 SCCM. The feed and permeate compositions were analyzed using a gas chromatograph (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and a 30-m-long SH-Rt-Q-BOND PLOT column (outer diameter: 0.53 mm, membrane thickness: 20 μm). The detector and column temperatures were set to 473 K and 323 K, respectively. The separation performance of MFI membrane was evaluated by the parameters of permeance (P_i , $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ or gas permeation unit (GPU), 1 GPU = $3.348 \times 10^{-10} \text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$), separation factor (SF , dimensionless parameters) and separation performance index (SPI , $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ or GPU). **GPU was used as the unit of permeance for easy comparison with the literature data.**

The permeance (P_i) is the partial pressure drop (ΔP_i , kPa) normalized permeation flux of the composition i (N_i , $\text{mol m}^{-2} \text{s}^{-1}$) as described in equation 2. The concentration difference of feed (permeate) gas between the starting point and the ending point is always negligible since the fluxes of butane and butene of the short MFI membranes are relatively low, and thus ΔP_i is simply defined as the arithmetical partial pressure drop (kPa) across the membrane.

The SF is the molar concentration ratio (y_i/y_j) in the permeate divided by that (x_i/x_j) in the feed for compositions of i (n -butane or l -butene) and j (isobutane or isobutene) as described in equation 10.

$$SF = \frac{(y_i/y_j)_p}{(x_i/x_j)_f} \quad (10)$$

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 11.

$$SPI = P_i \times (SF - 1) \quad (11)$$

The separation performance of n -hexane isomer mixtures were evaluated using the

Wicke-Kallenbach (W-K) mode, as illustrated in Supplementary Fig. 43. Nitrogen was used as the carrier gas and introduced into each pure-component feed reservoir to generate saturated vapor streams via bubbling, which were then combined into a single feed line. The feed partial pressure was controlled by adjusting the temperature of the reservoirs. The mixed vapor stream was fed into a stainless-steel membrane module, while nitrogen was simultaneously used as the sweep gas on the permeate side at a total flow rate of 100 SCCM (200 SCCM while testing 20-cm-long tube membrane). The total pressure on both sides was maintained at atmospheric pressure.

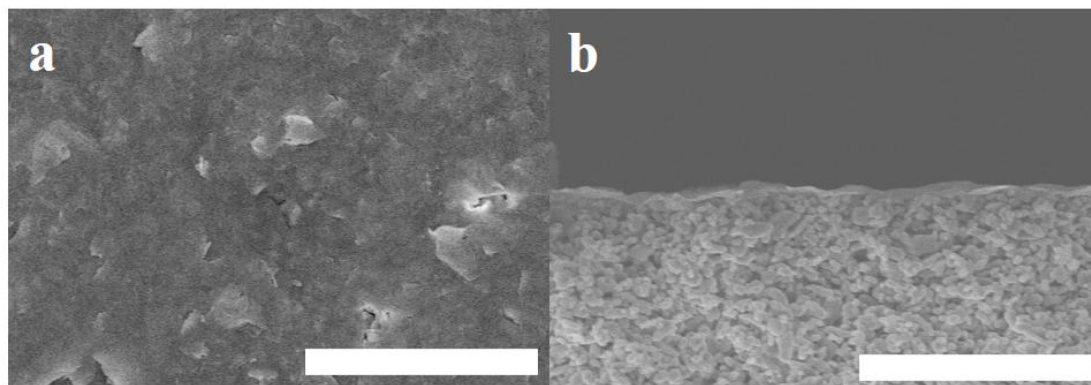
For separation tests, the membrane tube was mounted in a stainless-steel module and sealed at both ends using high-temperature- and corrosion-resistant *O*-rings. The module was placed in an oven, and the operating temperature was controlled in the range of 303-393 K. The feed reservoirs were immersed in a thermostatic bath, and the feed partial pressures were adjusted by varying the bath temperature. When the bath temperature is 268, 273, 278, 283, and 288 K, the partial pressures of *n*-hexane are 4.6, 6.0, 7.85, 10.11, and 12.87 kPa, respectively.

The concentrations of each component in the permeate stream were analyzed using a gas chromatograph equipped with a flame ionization detector (FID) (Shimadzu GC-2014). Methane was used as an internal standard for quantitative analysis. The membrane separation performance was evaluated using two parameters: permeance (P_i), and SF which was described above.

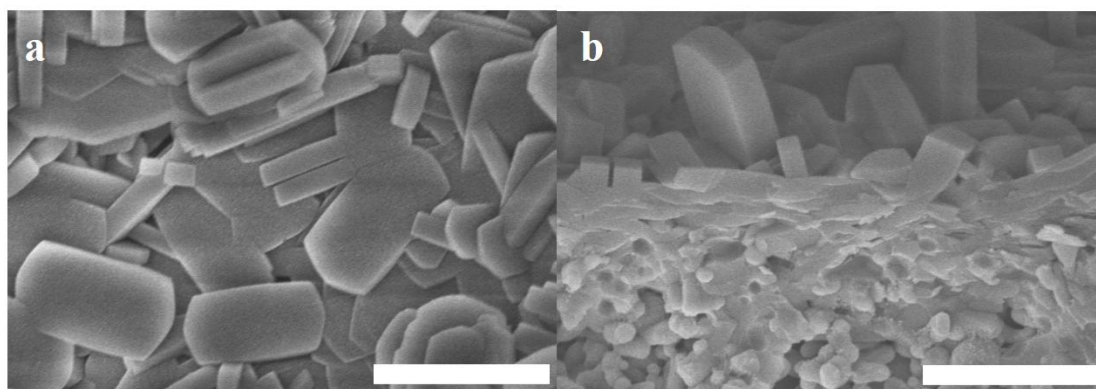
Process Simulation and Calculation

Process simulations were carried out using Aspen Plus V12.1 to evaluate the separation performance and energy efficiency of the NI-SFS-derived *b*-oriented MFI membranes for hydrocarbon isomer separations. Two representative feed systems were considered, including *n*-butane/isobutane and *I*-butene/isobutene mixtures with industrially relevant compositions. Membrane properties, including permeance and selectivity, were obtained from experimental measurements. Four industrially relevant feed conditions were employed, with *n*-butane and *I*-butene concentrations of 10 mol% and

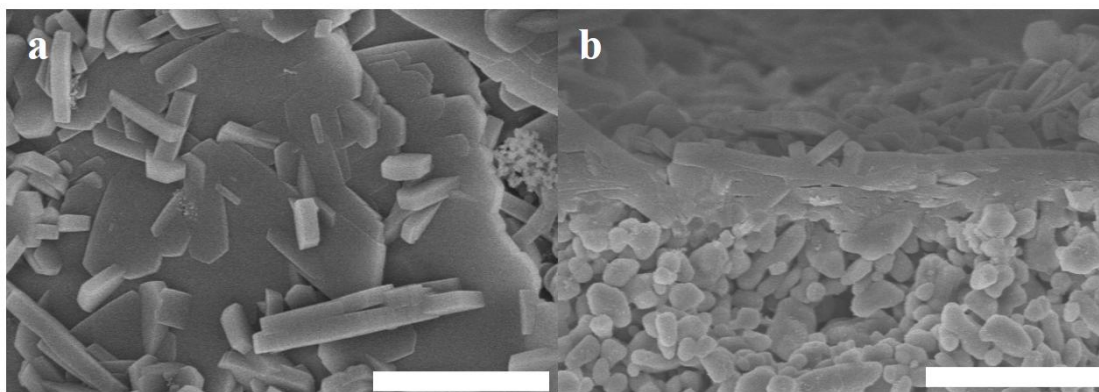
30 mol%, respectively. The membrane process was modeled using the first- or secondary-stage configuration with a pressure-driven operation. Conventional separation processes, including distillation and reactive distillation, were also simulated for comparison under identical feed conditions. Key performance metrics, including energy consumption, membrane area, separation efficiency, and capital cost, were calculated for each process. Energy consumption was obtained from Aspen utility modules, while equipment sizing and economic evaluation were conducted using Aspen's built-in costing tools.



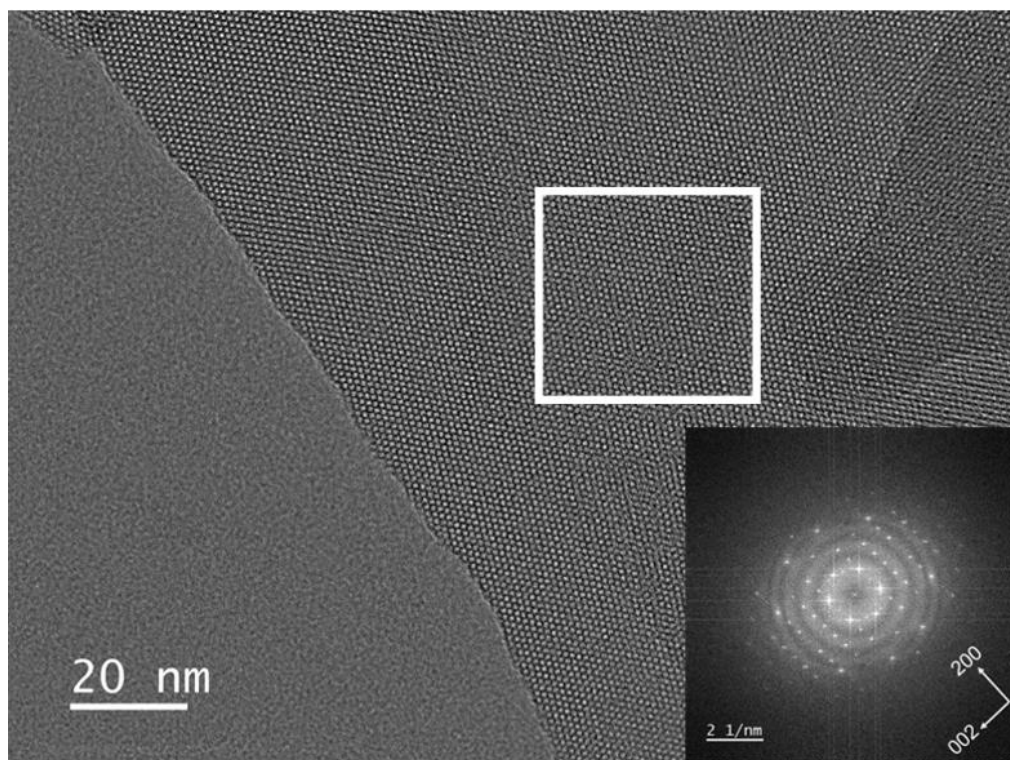
Supplementary Fig. 1. Surface (a) and cross-sectional (b) SEM images of the MFI nanosheet-coated support after heating above the synthesis gel at 473 K for 35 min before gel contact. Scale bars: 2 μm .



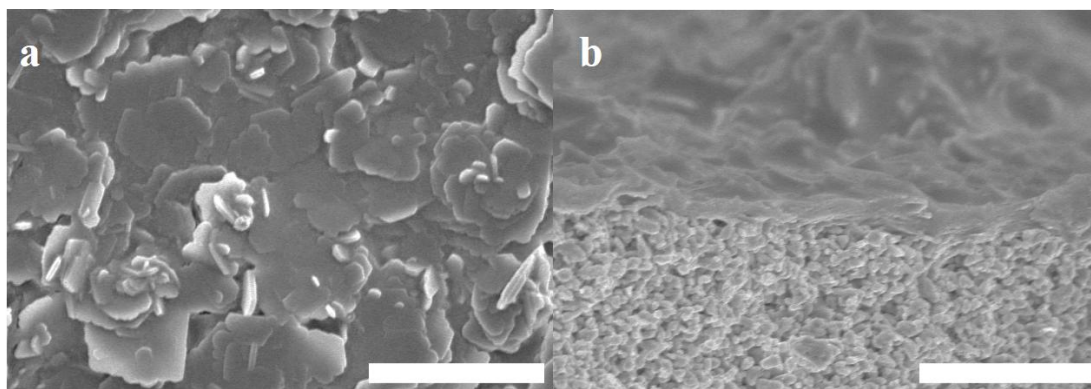
Supplementary Fig. 2. (a) Surface and (b) cross-sectional SEM images of MFI membranes using an MFI nanosheet seed layer prepared by NI-SFS at 473 K for 15 min, with a high OSDA/H₂O ratio of 0.3% (molar ratio of 1 TEOS: 0.18 TPAOH: 60 H₂O). Scale bars: 2 μ m.



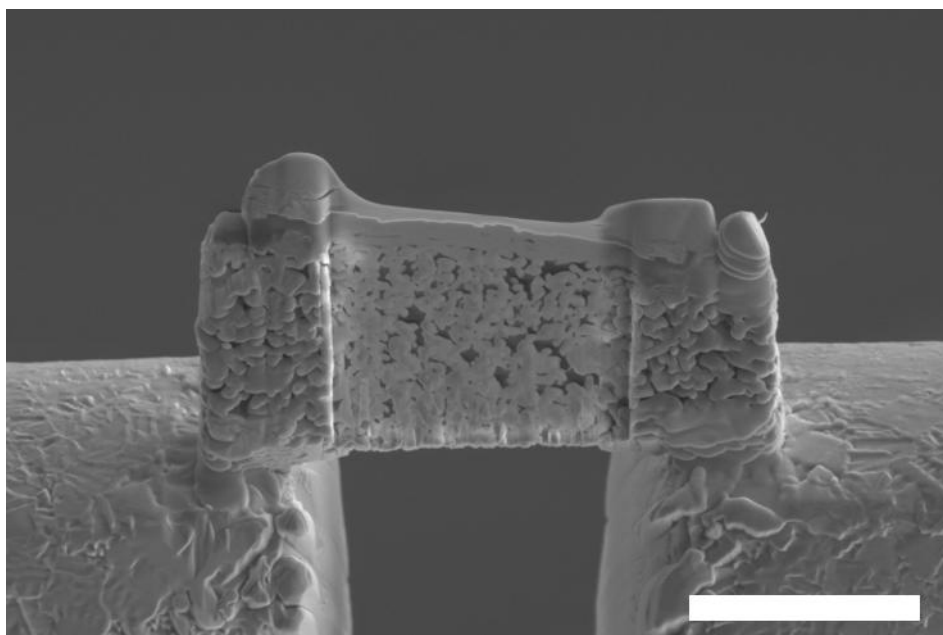
Supplementary Fig. 3. (a) Surface and (b) cross-sectional SEM images of MFI membranes using an MFI nanosheet seed layer prepared by NI-SFS at 473 K for 15 min, with a low OSDA/H₂O ratio of 0.06% (molar ratio of 1 TEOS: 0.18 TPAOH: 300 H₂O). Scale bars: 2 μ m.



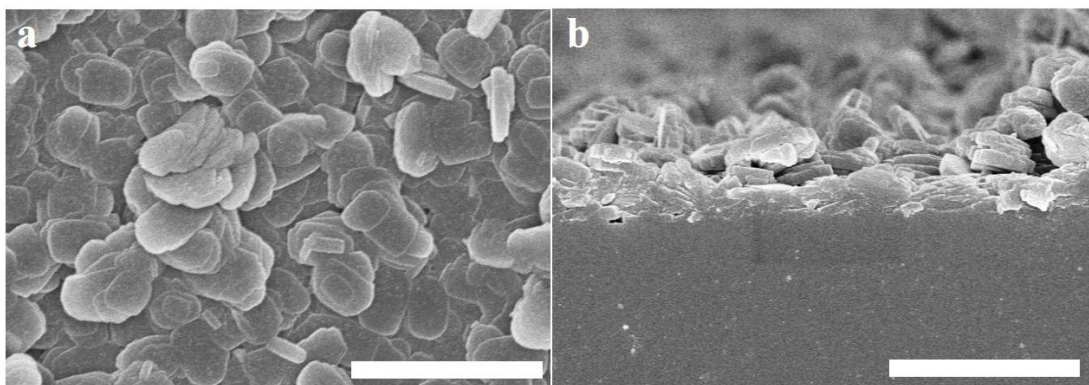
Supplementary Fig. 4. HRTEM image of an MFI nanosheet showing *b*-direction pore channels, with the corresponding fast Fourier transform pattern shown in the inset.



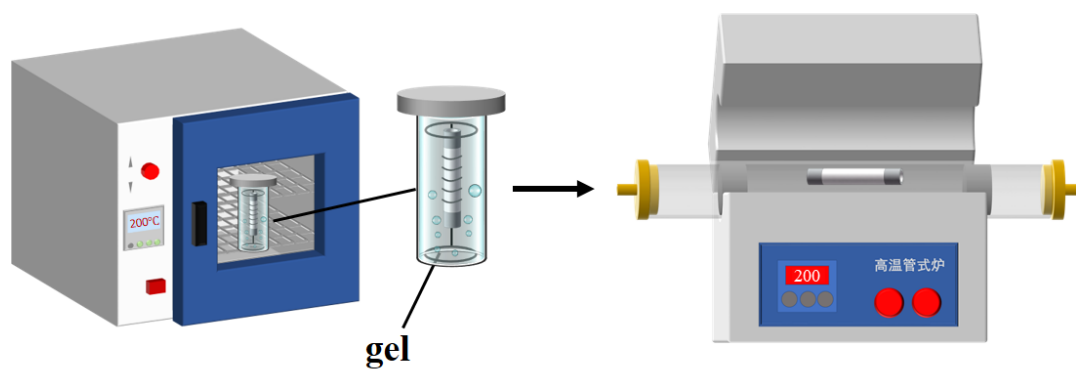
Supplementary Fig. 5. (a) Surface and (b) cross-sectional SEM images of MFI membranes using an MFI nanosheets seed layer prepared by CHS at 473 K for 1 h. Scale bars: 5 μm .



Supplementary Fig. 6. SEM image of FIB milled section for *b*-oriented MFI membrane prepared by NI-SFS at 473 K for 15 min. Scale bar: 5 μm .



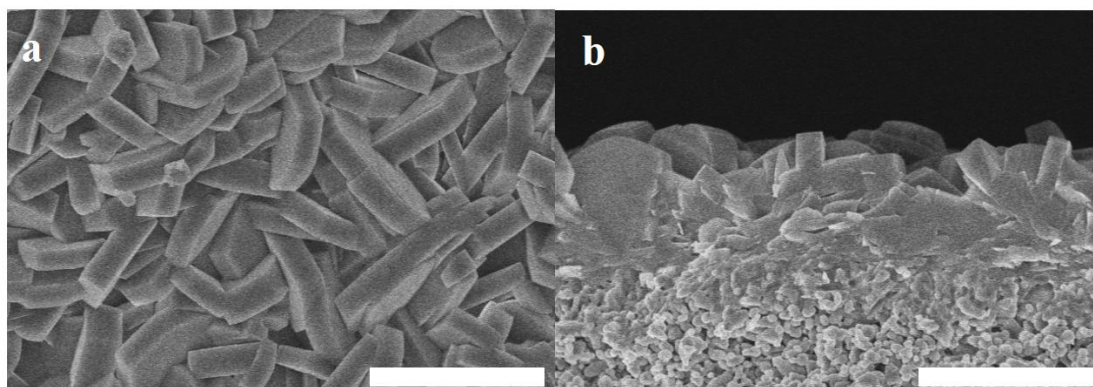
Supplementary Fig. 7. (a) Surface and (b) cross-sectional SEM images of MFI membranes using an MFI nanosheets seed layer prepared by NI-SFS on glass support at 473 K for 15 min. Scale bars: 2 μm .



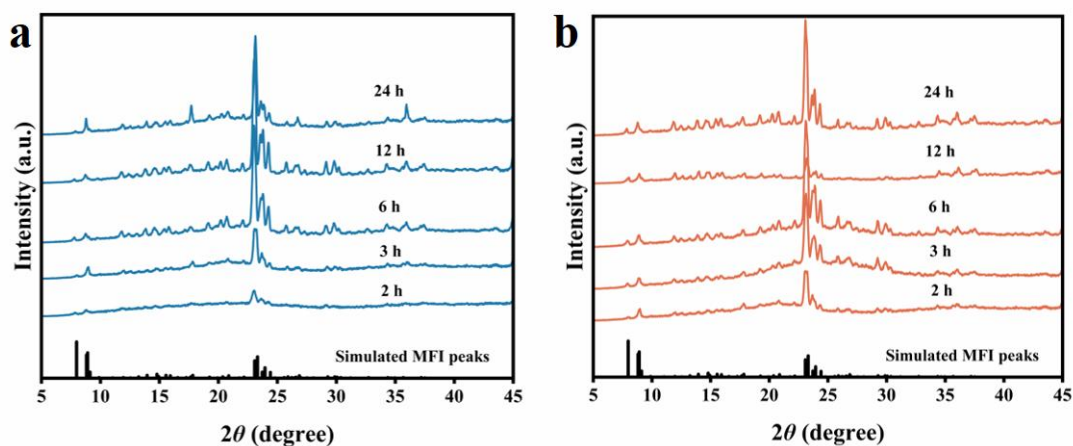
Step 1:hydrothermal synthesis

Step 2: remove the template agent

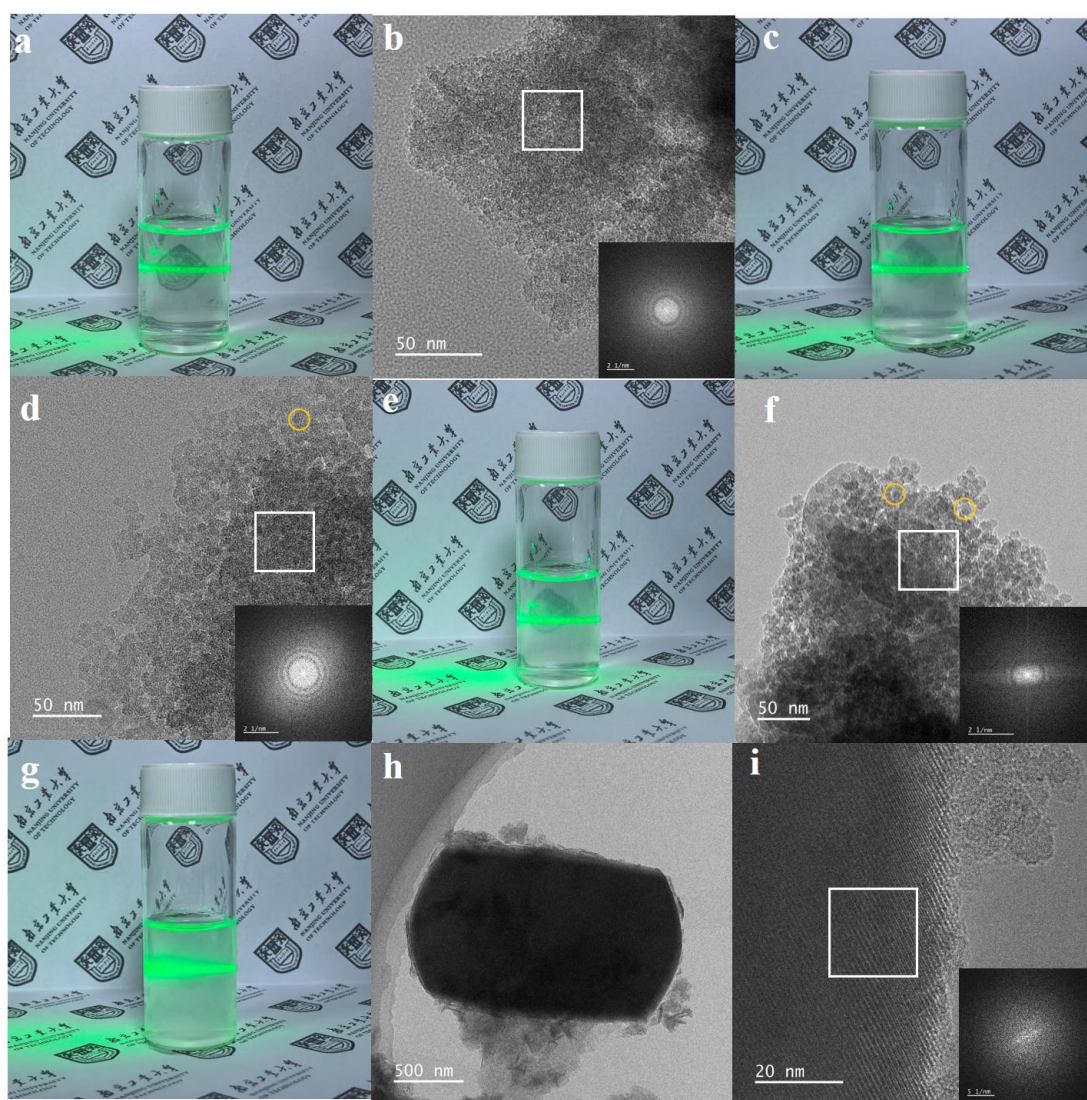
Supplementary Fig. 8 Schematic illustration of conventional synthesis.



Supplementary Fig. 9. (a) surface and (b) cross-sectional SEM images of the MFI membranes prepared using nanosheets by CHS for 6 h at 473 K (gel molar ratio: 1: 0.18: 180). Scale bars: 5 μm .



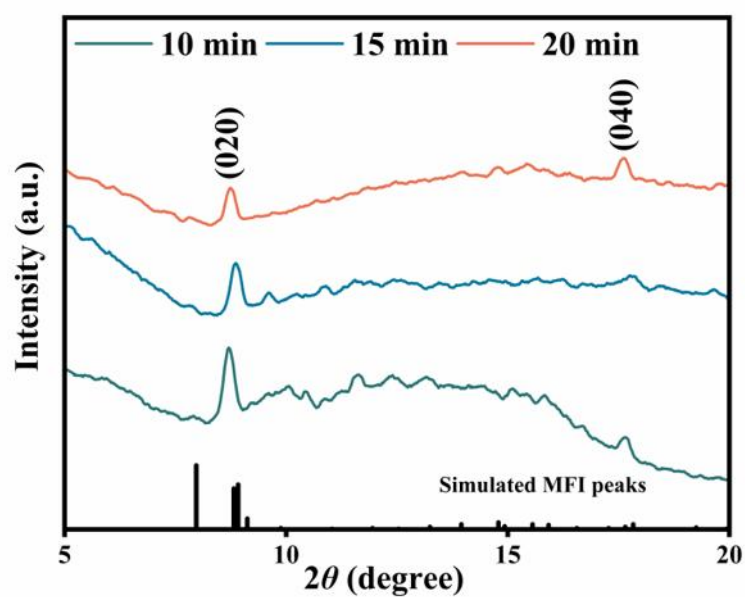
Supplementary Fig. 10. XRD patterns of synthesis gels (1 TEOS: 0.18TPAOH: 180 H₂O) collected at (a) 413 K and (b) 473 K as a function of synthesis time, showing the progressive development of MFI crystallinity and the better crystallinity at higher temperature. It shows that increasing the synthesis temperature significantly shortens the induction period of MFI crystallization.



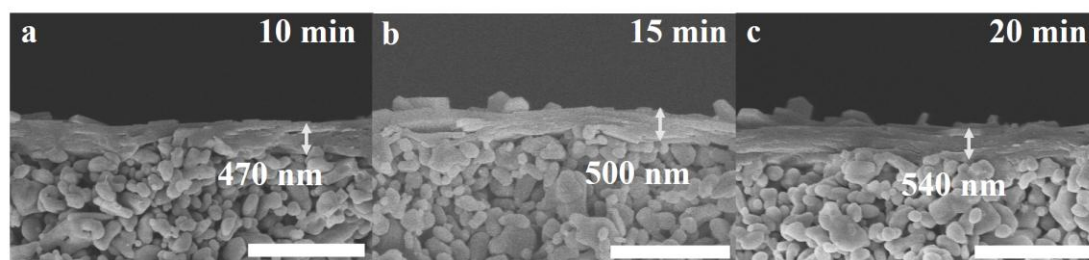
Supplementary Fig. 11. Photographs showing the Tyndall effect and corresponding HRTEM images with fast Fourier transform (FFT) patterns (insets) of gels nucleated for (a-b) 5 min, (c-d) 15 min, (e-f) 25 min, and (g-i) 55 min during the gel nucleation process. The timing starts from the beginning of heating: 0-35 min is the temperature-rise stage (RT to synthesis temperature of 473 K) and the rest is the temperature-stable stage. No support was used to simulate the gel nucleation only.

During the temperature-ramping stage, the synthesis gel rapidly evolves into a nucleation-rich state before contacting the nanosheet-coated support. Once the pre-nucleated gel contacts the seeded inner surface of the tubular support, abundant active nuclei and soluble silicate species are immediately available for epitaxial intergrowth

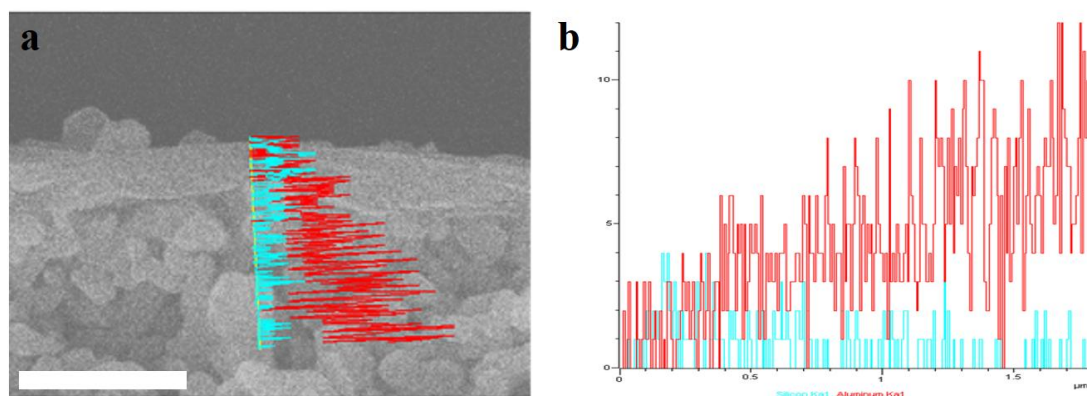
of the MFI nanosheets. This accelerated crystallization process enables the formation of a continuous *b*-oriented MFI membrane within 10–20 min.



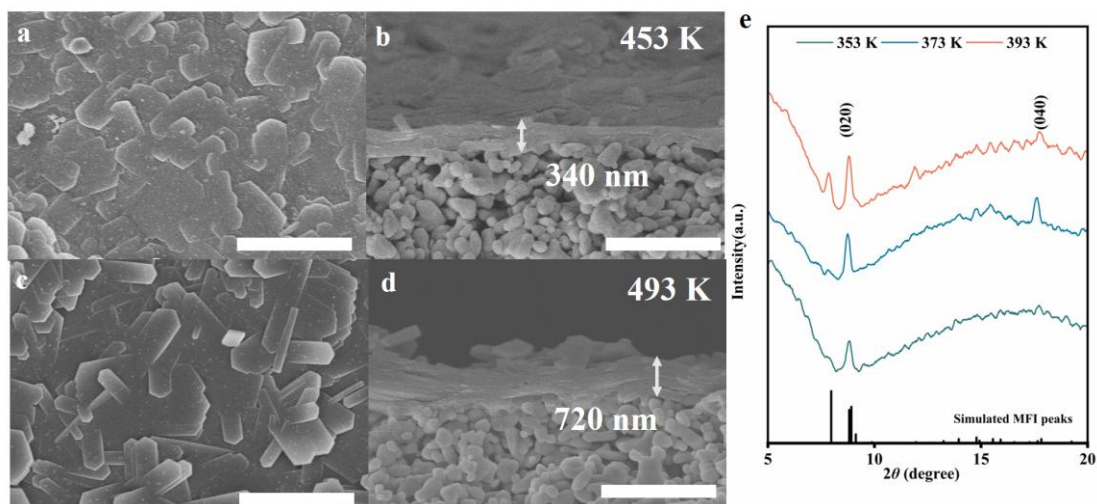
Supplementary Fig. 12. XRD patterns of the corresponding membranes prepared for 10, 15 and 20 min by NI-SFS (nucleation-isolated superfast synthesis) at 473 K, showing the evolution of crystallinity and orientation with synthesis time.



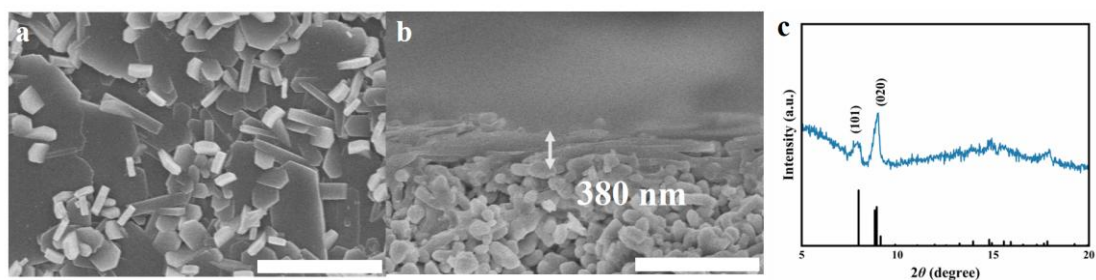
Supplementary Fig. 13. Cross-sectional SEM images of *b*-oriented MFI membrane prepared by NI-SFS for (a) 10 min, (b) 15 min and (c) 20 min at 473 K. Scale bars: 2 μm .



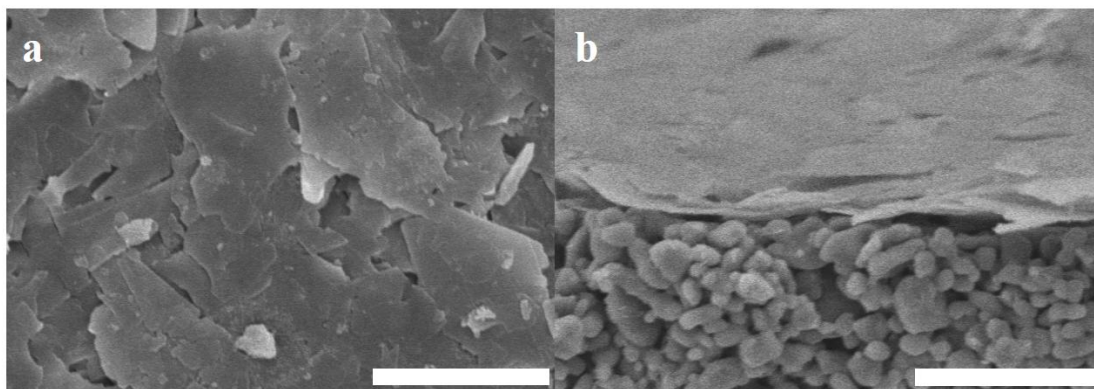
Supplementary Fig. 14. (a) Cross-sectional SEM image and (b) EDX of *b*-oriented MFI membrane prepared by NI-SFS at 473 K for 10 min using MFI nanosheets on the tubular support. (scale bar: 2 μm). Aluminum content increased fast (across the interface to alumina support) but silicon content decreased after the detection depth of about 430 nm, indicating that the effective MFI membrane thickness was about 430 nm.



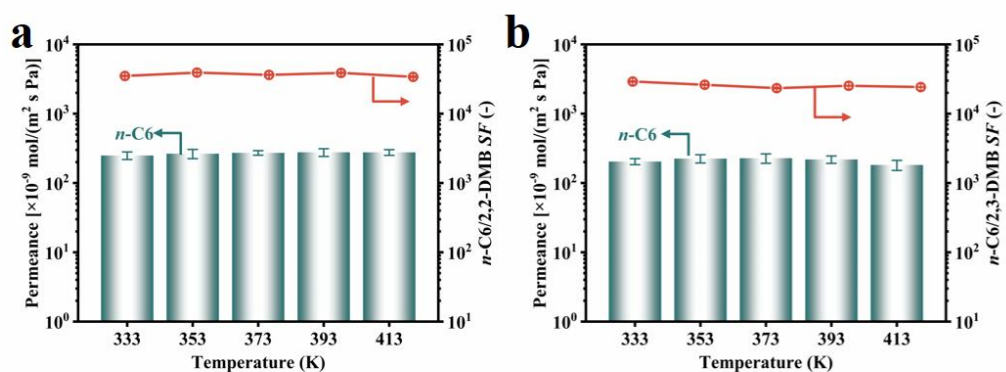
Supplementary Fig. 15. SEM images of *b*-oriented MFI membrane surface and cross-section prepared by NI-SFS (nucleation-isolated superfast synthesis) at (a, b) 453 K and (c, d) 493 K for 15 min, and (e) XRD patterns of the corresponding membranes showing the evolution of crystallinity and orientation with increasing synthesis temperature (Peaks marked with asterisks (*) originate from the α -Al₂O₃ support). Scale bars: 2 μ m.



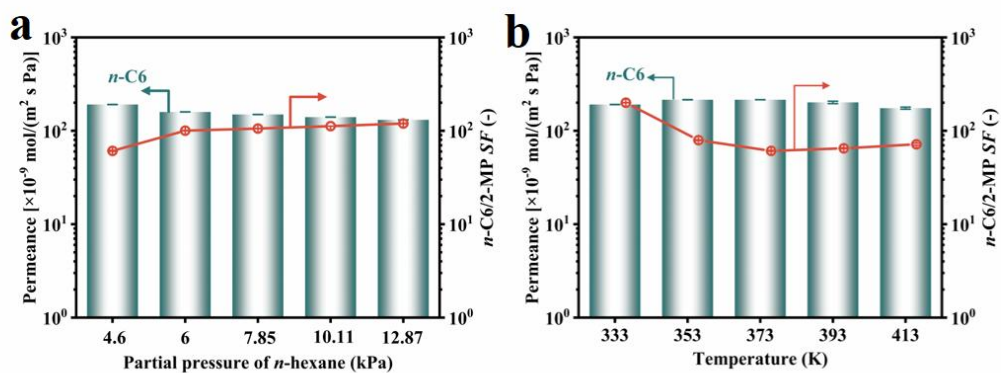
Supplementary Fig. 16. (a) Surface and (b) cross-sectional SEM images of MFI membrane on α -Al₂O₃ tubular support synthesized in 15 min by NI-SFS with a pre-heating time before the support-gel contact of 1.5 h. (c) XRD patterns of the corresponding membranes (Peaks marked with asterisks (*) originate from the α -Al₂O₃ support). Scale bars: 2 μ m.



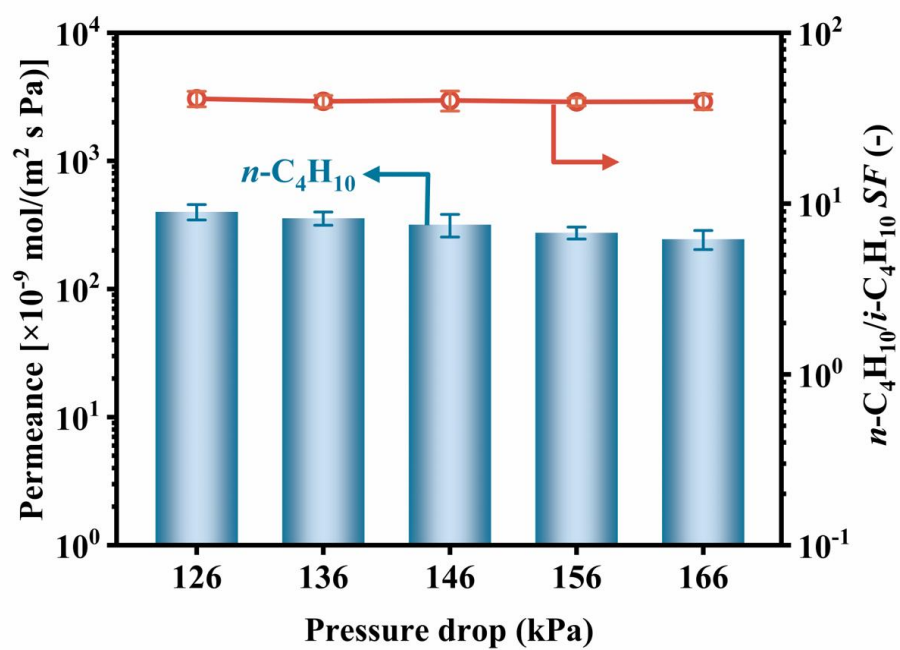
Supplementary Fig. 17. (a) surface and (b) cross-sectional SEM images of the MFI membranes prepared using nanosheets by NI-SFS for 20 min at 473 K (gel molar ratio: 1: 0.18: 180). Scale bars: 2 μm .



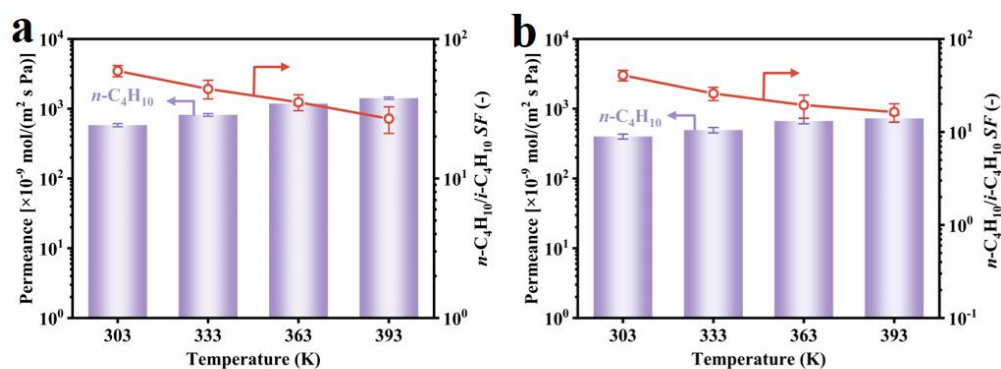
Supplementary Fig. 18. Effect of temperature on (a) n -hexane permeance and n -hexane/2,2-dimethylbutane separation factor in a 50/50 n -hexane/2,2-dimethylbutane mixture, and (b) n -hexane permeance and n -hexane/2-methylpentane separation factor in a 50/50 n -hexane/2-methylpentane mixture for the NI-SFS-derived MFI membrane with 100 SCCM N₂ sweep gas.



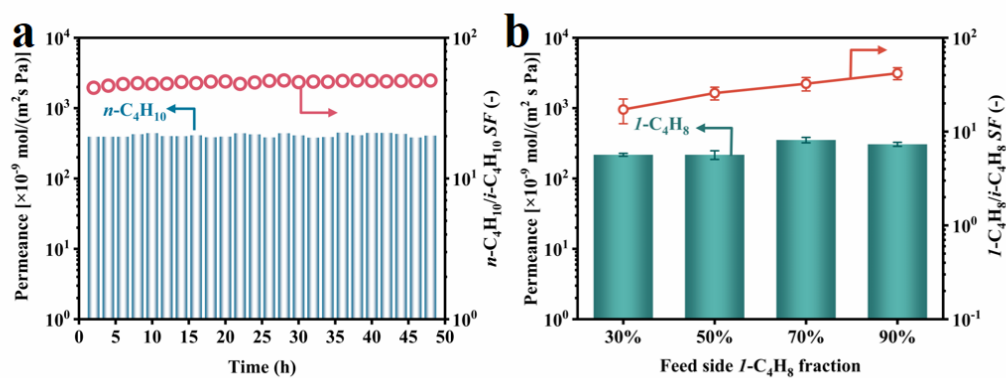
Supplementary Fig. 19. Effect of (a) *n*-hexane partial pressure and (b) temperature on *n*-hexane permeance and *n*-hexane/2-methylpentane separation factor for a 50/50 *n*-hexane/2-methylpentane mixture over the NI-SFS-derived MFI membrane with 100 SCCM N₂ sweep gas.



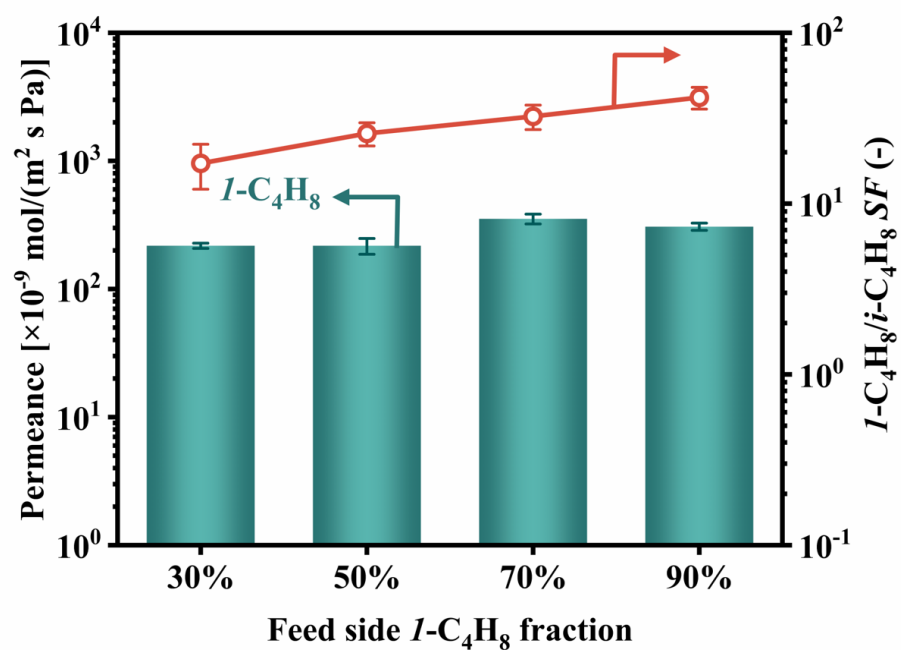
Supplementary Fig. 20. Effect of pressure drop across membrane on permeance and SF in a 50/50 n -butane/isobutane mixture at 303 K and feed flow rate of 400 SCCM without diluted feed gas and sweep gas.



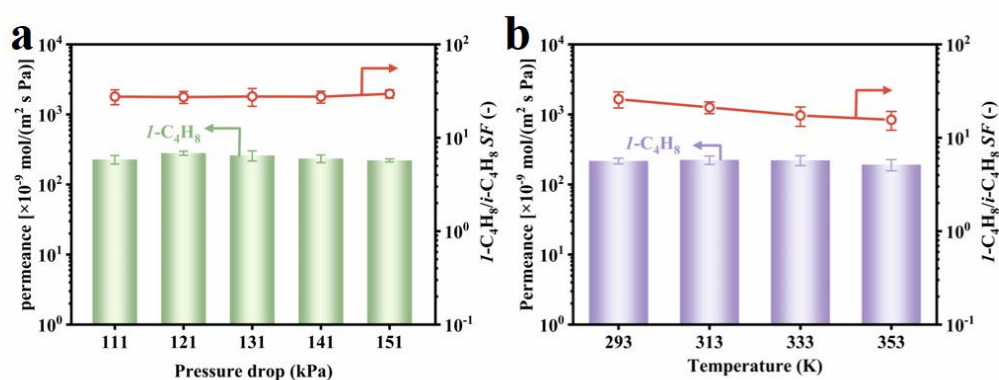
Supplementary Fig. 21. Effect of temperature on *n*-butane/isobutane separation performance of the NI-SFS-derived *b*-oriented MFI membrane in (a) 90/10 and (b) 50/50 *n*-butane/isobutane mixtures at 126 kPa and 400 SCCM without dilution or sweep gas.



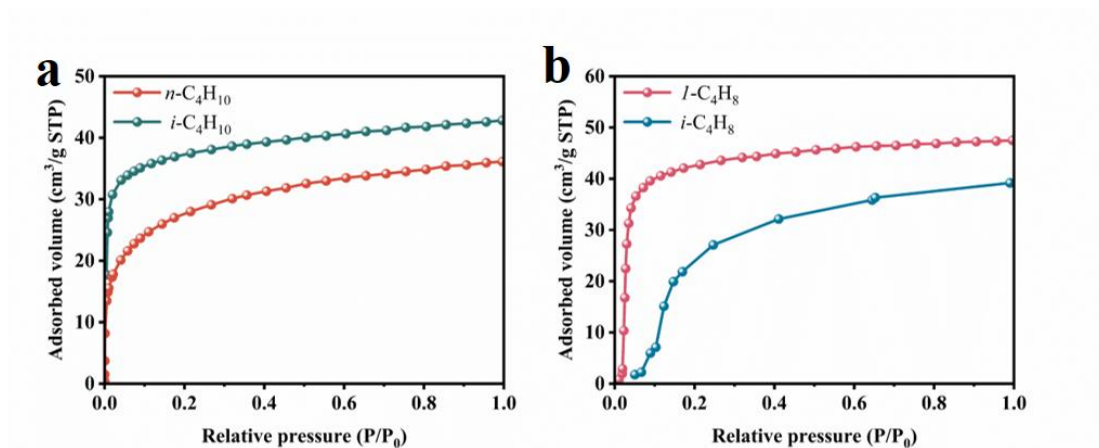
Supplementary Fig. 22. The *n*-butane/isobutane separation performance of MFI membrane prepared by NI-SFS: (a) long-term stability in a 50/50 *n*-butane/isobutane mixture, (b) effect of feed-side *n*-butane concentration on the separation performance of the NI-SFS membrane, at 303 K and 111 kPa feed pressure.



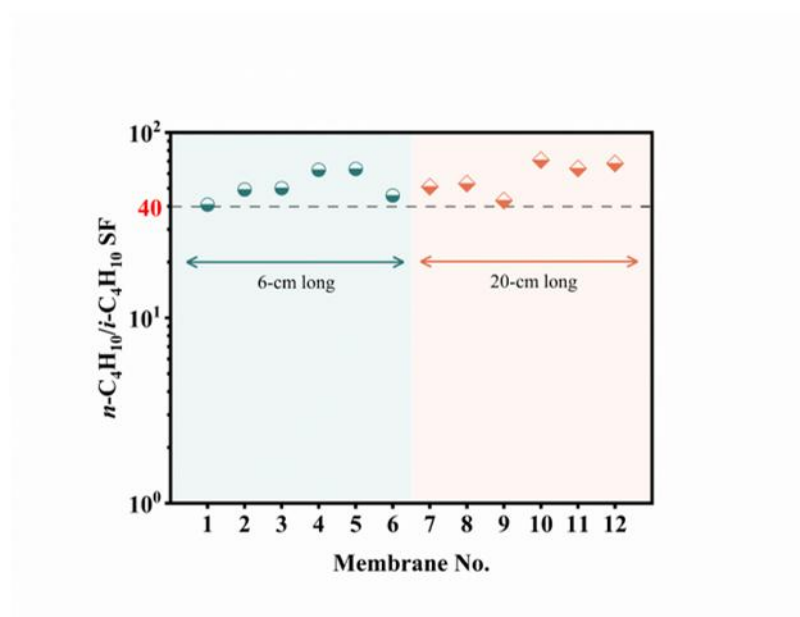
Supplementary Fig. 23. Effect of feed-side *l*-butene concentration on the separation performance of the NI-SFS membrane at 303 K and 111 kPa feed pressure.



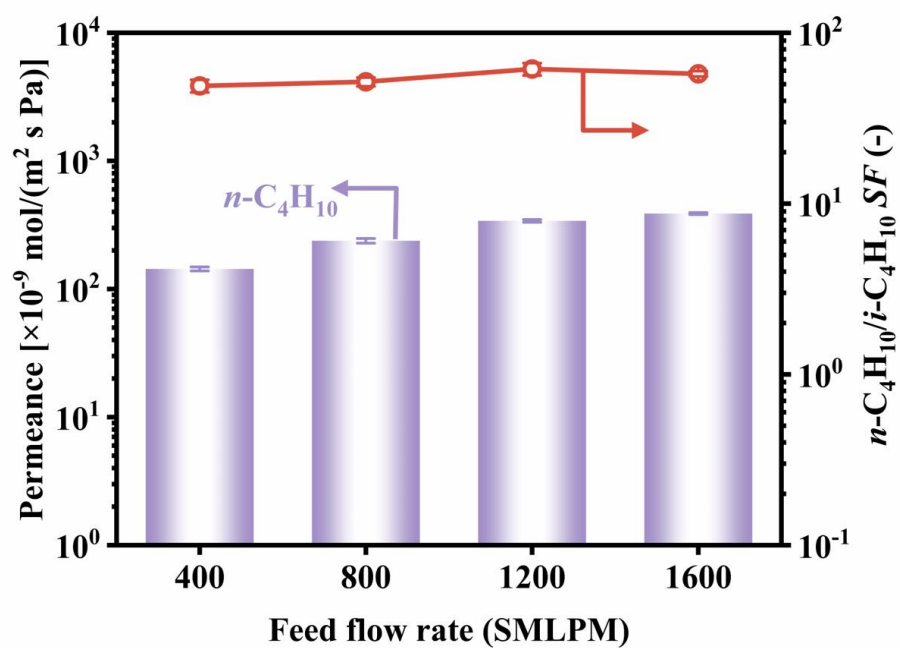
Supplementary Fig. 24. (a) Effect of pressure drop across membrane on permeance and SF in a 50/50 *I*-butene/isobutene mixture at 303 K, (b) effect of temperature on permeance and SF in a 50/50 *I*-butene/isobutene mixture at a feed pressure of 111 kPa, at a feed flow rate of 200 SCCM without diluted feed gas or sweep gas.



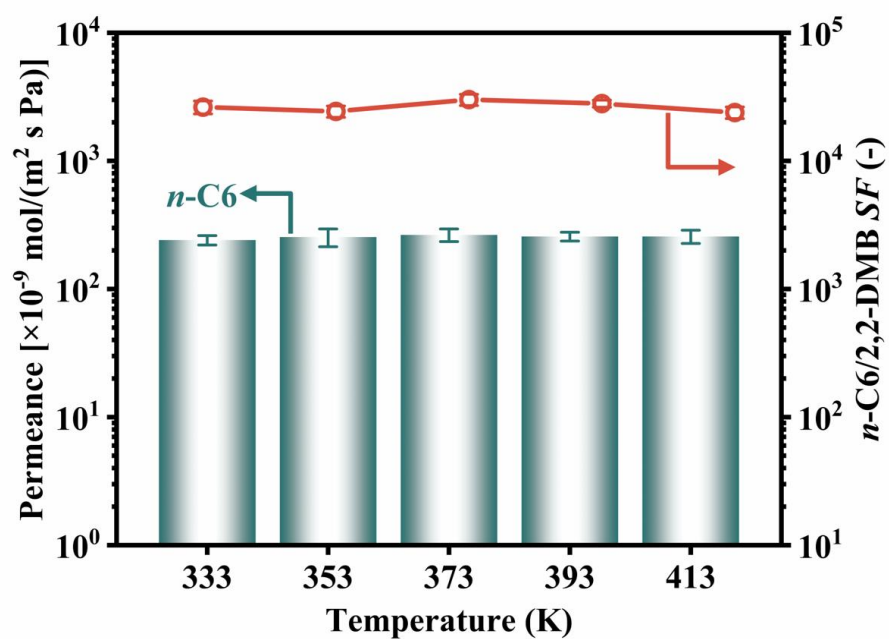
Supplementary Fig. 25. (a) *n*-Butane/isobutane and (b) *l*-butene/*i*-butene adsorption isotherms measured at 298 K acquired for zeolite MFI nanosheets after calcination.



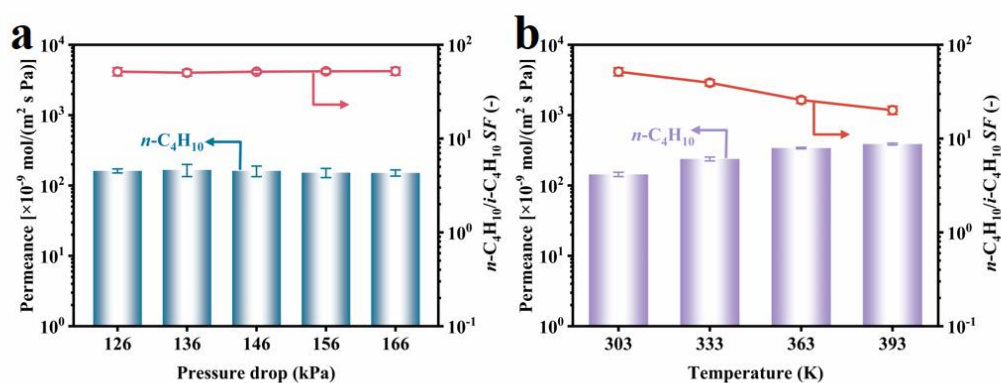
Supplementary Fig. 26. Comparison of *n*-butane/isobutane separation factors of 6-cm- and 20-cm-long NI-SFS-derived MFI membranes at 303 K and 126 kPa without diluted feed gas or sweep gas. The feed flow rates were 400 and 800 SCCM for the 6-cm- and 20-cm-long membranes, respectively. Detailed separation data are summarized in Supplementary Tables 1 and 3.



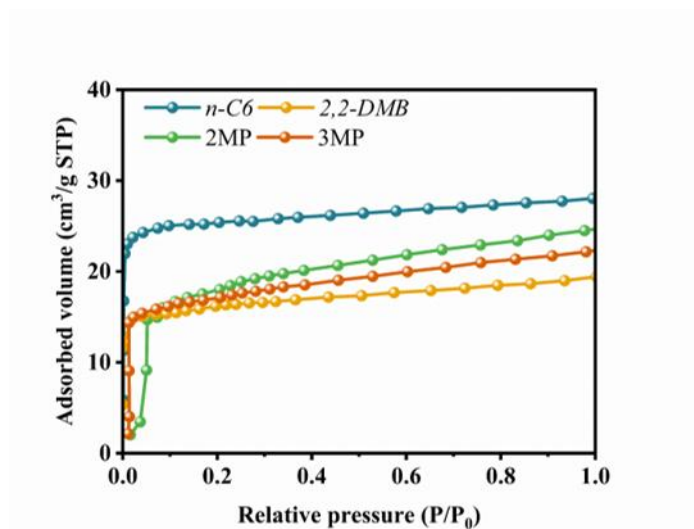
Supplementary Fig. 27. Effect of feed flow rate on *n*-butane/isobutane separation performance of a 20-cm-long MFI membrane prepared by NI-SFS at 303 K and a feed pressure of 126 kPa without diluted feed gas or sweep gas.



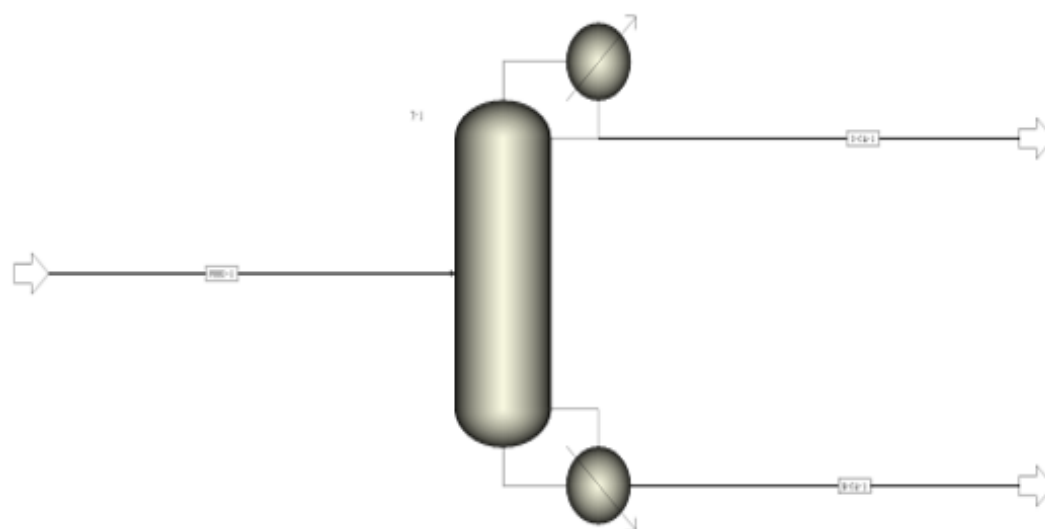
Supplementary Fig. 28. Effect of temperature on *n*-hexane permeance and *n*-hexane/2,2-dimethylbutane separation factor for a 50/50 *n*-hexane/2,2-dimethylbutane mixture over the 20-cm-long NI-SFS-derived MFI membrane with 200 SCCM N₂ sweep gas.



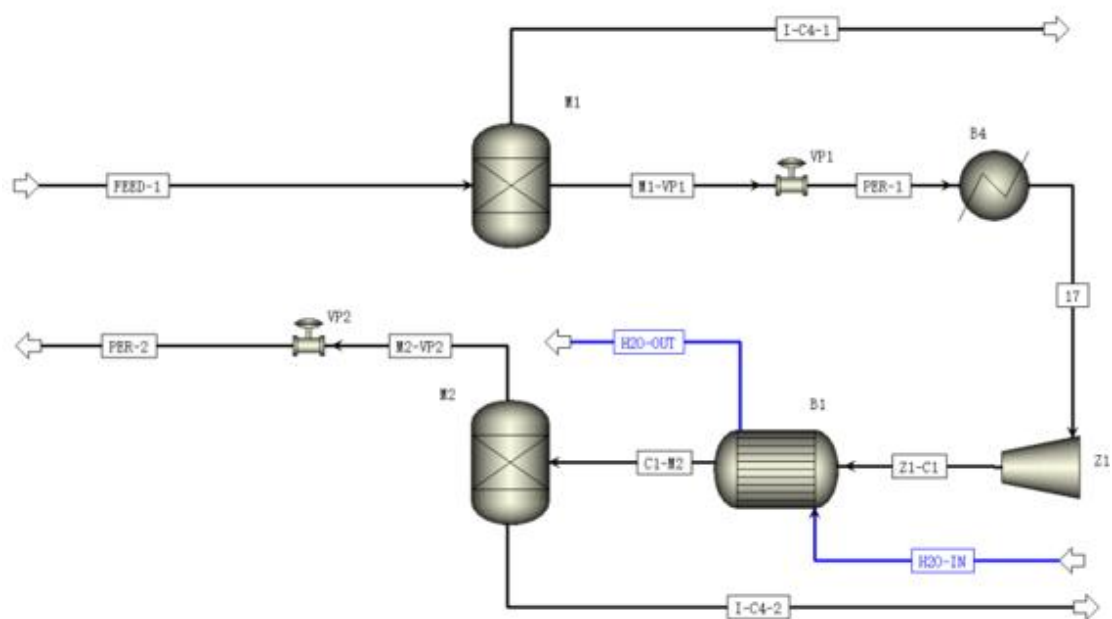
Supplementary Fig. 29. (a) Effect of pressure drop across membrane on permeance and SF of a 20-cm-long MFI membrane prepared by NI-SFS in a 50/50 *n*-butane/isobutane mixture at 303 K, (b) effect of temperature on permeance and SF of a 20-cm-long MFI membrane prepared by NI-SFS in a 50/50 *n*-butane/isobutane mixture at a pressure drop of 126 kPa; at a feed flow rate of 800 SCCM without diluted feed gas and sweep gas.



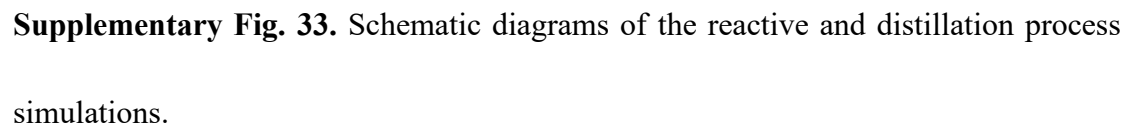
Supplementary Fig. 30. Adsorption isotherms of *n*-hexane, 2-methylpentane, 3-methylpentane and 2,2-dimethylbutane measured at 298 K on calcined MFI zeolite nanosheets. The adsorption uptake follows the order *n*-hexane > 2-methylpentane > 3-methylpentane > 2,2-dimethylbutane, confirming the preferential adsorption of less-branched C6 isomers in MFI nanosheets and supporting the molecular-sieving advantage of the oriented MFI nanochannels for C6 isomer separation.



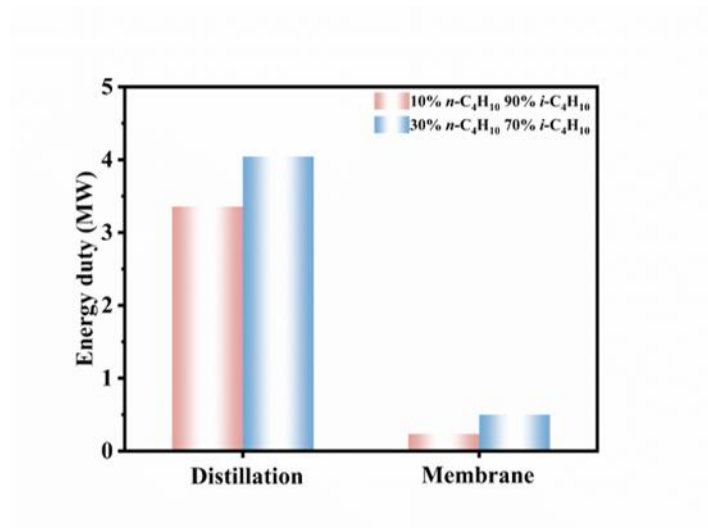
Supplementary Fig. 31. Schematic diagrams of distillation process simulations.



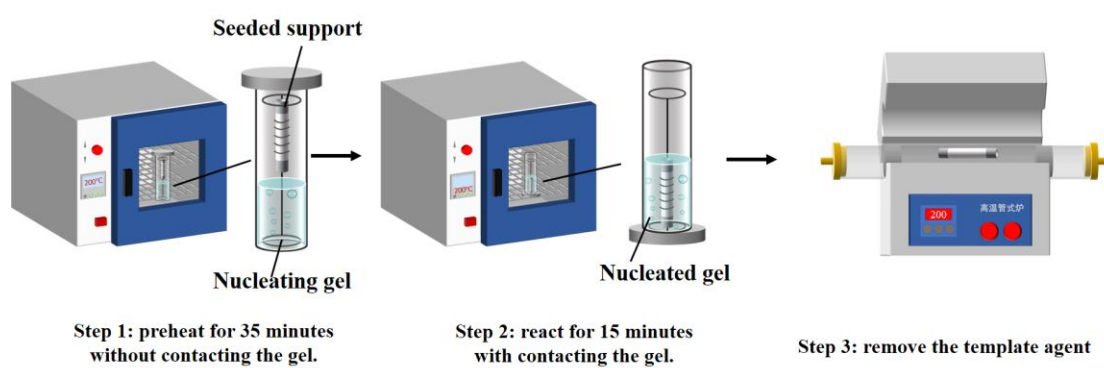
Supplementary Fig. 32. Schematic diagrams of the two-stage membrane separation process simulations.



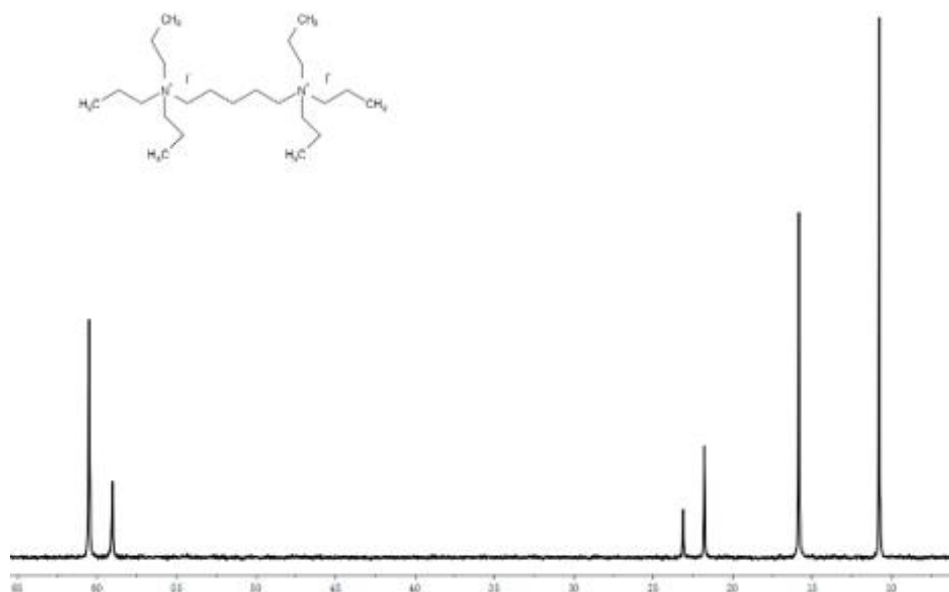
Supplementary Fig. 33. Schematic diagrams of the reactive and distillation process simulations.



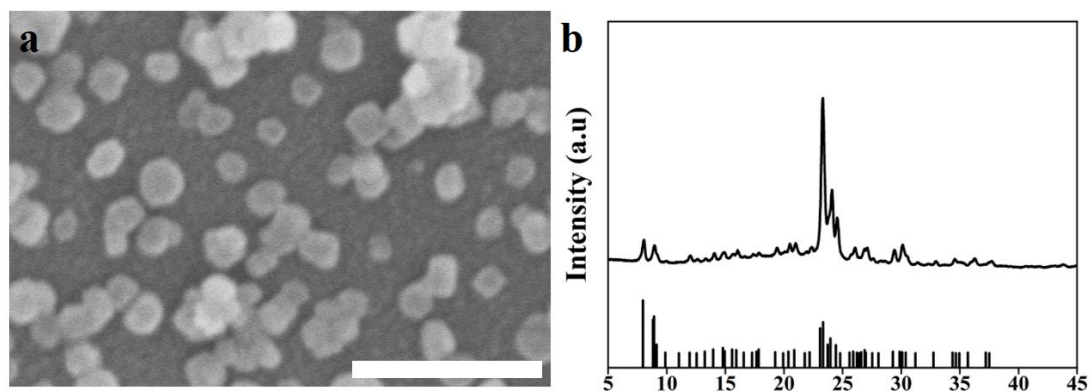
Supplementary Fig. 34. Comparison of specific energy consumption for distillation and membrane separation for *n*-butane/isobutane mixtures with different feed compositions (*n*-butane/isobutane: 10/90 and 30/70).



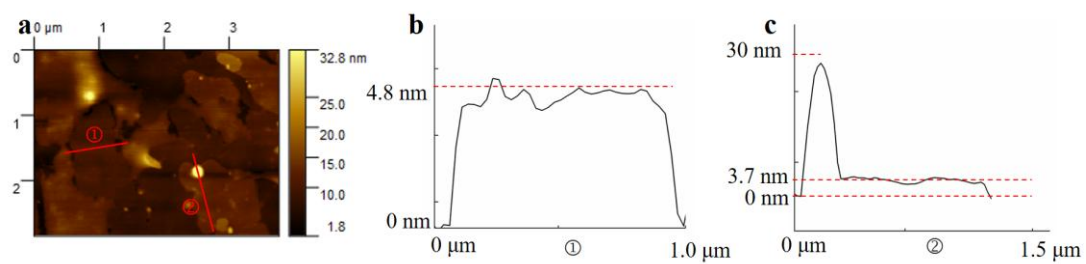
Supplementary Fig. 35. Schematic illustration of the nucleation-isolated superfast synthesis (NI-SFS) strategy in batch mode using air-oven heating, where the preheating and reaction steps are separated by a reactor flip-over process.



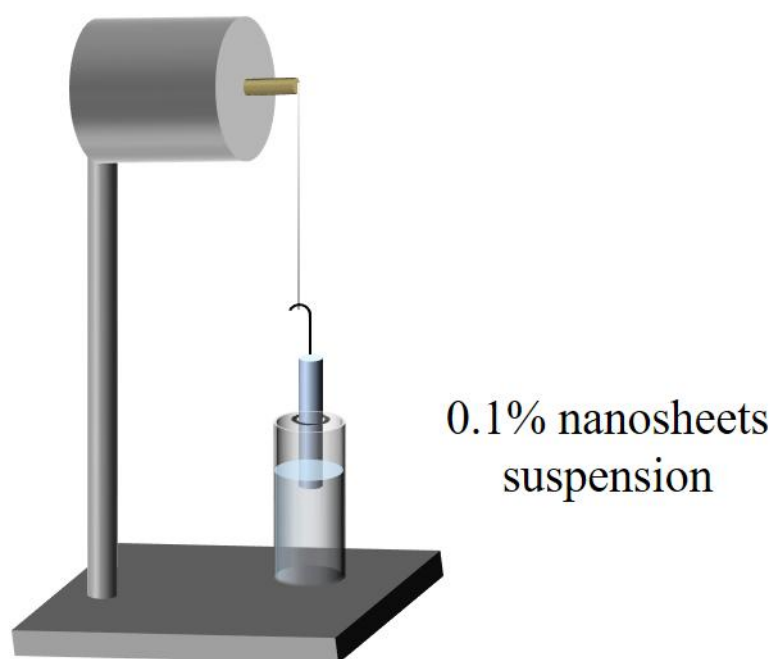
Supplementary Fig. 36. Molecular structure and the ¹³C nuclear magnetic resonance (NMR) liquid spectrum of dC5.



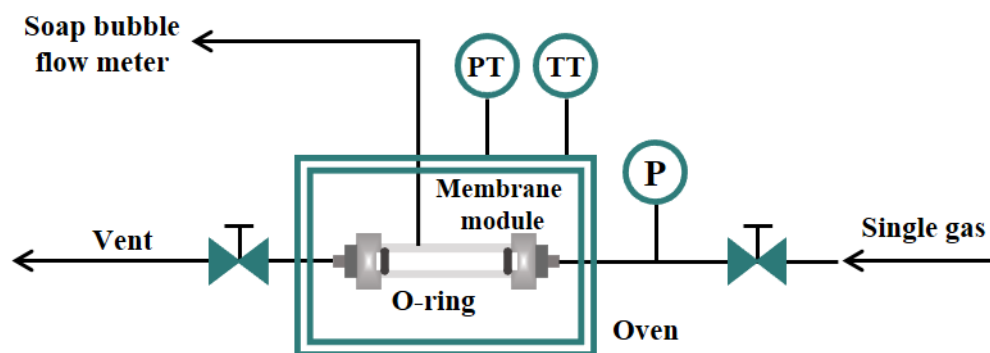
Supplementary Fig. 37. (a) Scanning electron micrograph (SEM) and (b) X-ray diffraction (XRD) profile of MFI nanoparticles employed as structural precursors in the MFI nanosheet synthesis.



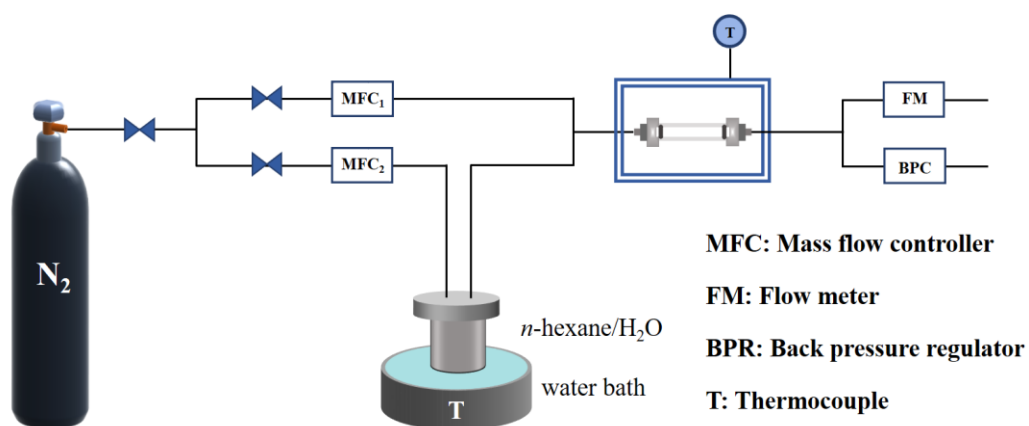
Supplementary Fig. 38. The atomic force microscope (AFM) image and AFM height profiles of MFI nanosheets.



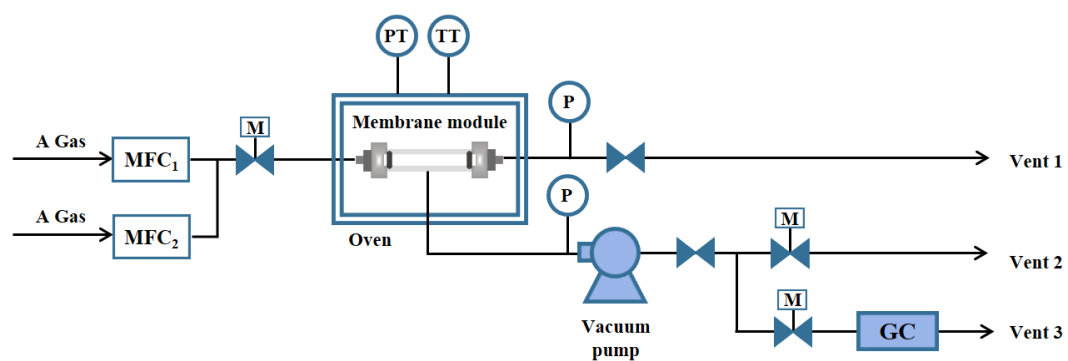
Supplementary Fig. 39. Schematic diagram of the dip-coating technique used for seeds coating on the support.



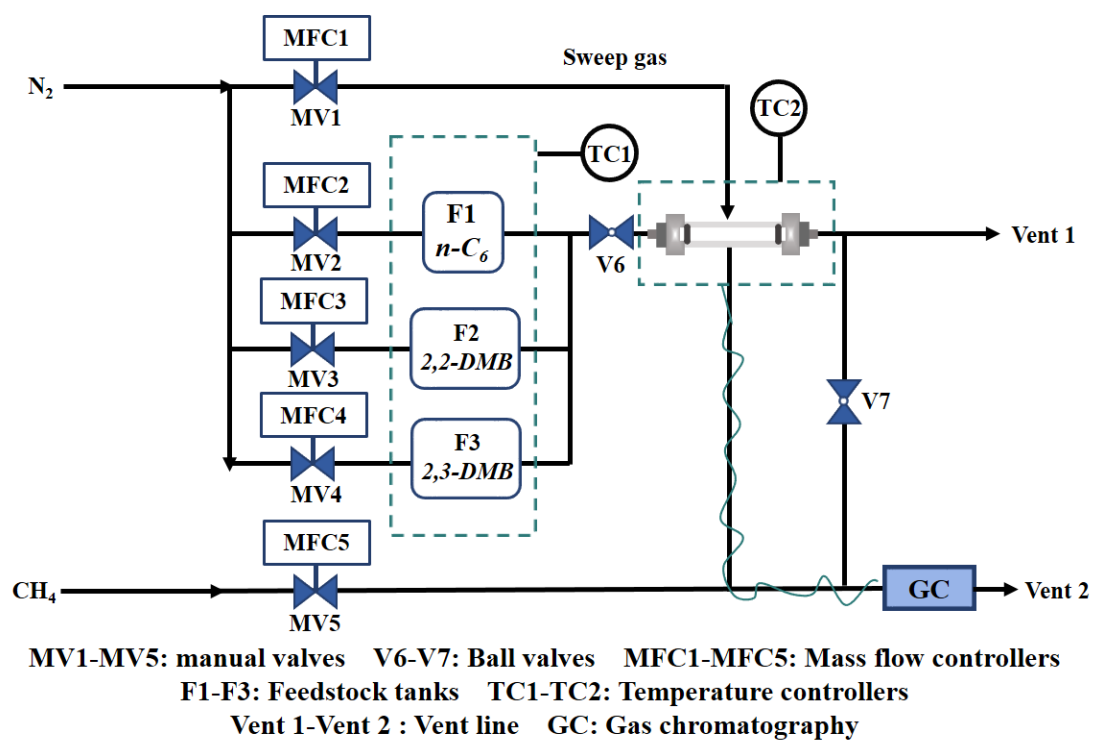
Supplementary Fig. 40. Schematic diagram of homemade single-gas permeation testing apparatus.



Supplementary Fig. 41. Schematic diagram of the homemade apparatus used for permporosimetry analysis.



Supplementary Fig. 42. Schematic of the homemade setup for testing the separation performance of MFI membranes with butane isomer mixtures, operated in permeate-vacuum mode.



Supplementary Fig. 43. Schematic diagram of the device for separating and testing hexane isomers in W-K mode.

Supplementary Table 1. *n*-Butane/isobutane separation performance of 6-cm-long MFI membranes prepared by NI-SFS under different synthesis temperatures and times.

Membrane No.	Heating time (min)	Synthesis time (min)	Synthesis temperature (K)	<i>n</i> -C ₄ H ₁₀ permeance ($\times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$)	<i>SF</i> (-)
M1	35	15	473	4.2	41
M2	35	15	473	3.2	49
M3	35	15	473	3.7	50
M4	35	15	473	2.7	63
M5	35	15	473	3.4	64
M6	35	15	473	3.2	46
M7	35	10	473	5.6	12
M8	35	20	473	1.8	33
M9	35	15	453	3.1	16
M10	35	15	493	1.6	28
M11	35	30	473	2.1	56
M12	90	30	473	-	-
M13	0	120	473	-	-

Notes: the separation tests were performed using a 50/50 *n*-butane/isobutane mixture at a feed pressure of 126 kPa and a feed flow rate of 400 SCCM.

Supplementary Table 2. *n*-Butane/isobutane separation performance of 6-cm-long MFI membranes prepared by CHS under different synthesis temperatures and times.

Membrane No.	Heating time (min)	Synthesis time (min)	Synthesis temperature (K)	<i>n</i> -C ₄ H ₁₀ permeance ($\times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$)	<i>SF</i> (-)
C1	35	360	473	2.1	33
C2	35	360	473	3.4	28
C3	35	720	413	1.7	42
C4	35	720	413	1.3	45

Notes: the separation tests were performed using a 50/50 *n*-butane/isobutane mixture at a feed pressure of 126 kPa and a feed flow rate of 400 SCCM.

Supplementary Table 3. *n*-Butane/isobutane separation performance of 20-cm-long MFI membranes prepared by NI-SFS under different synthesis temperatures and times.

Membrane No.	Heating time (min)	Synthesis time (min)	Synthesis temperature (K)	<i>n</i> -C ₄ H ₁₀ permeance ($\times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$)	<i>SF</i> (-)
N1	35	90	473	3	51
N2	35	90	473	2.5	72
N3	35	90	473	3	71
N4	35	90	473	2.4	64
N5	35	90	473	2.4	53
N6	35	90	473	2.8	44

Notes: the separation tests were performed using a 50/50 *n*-butane/isobutane mixture at a feed pressure of 126 kPa and a feed flow rate of 800 SCCM.

Supplementary Table 4. *n*-Hexane/2,2-dimethylbutane separation performance of 6-cm- and 20-cm-long MFI membranes prepared by NI-SFS.

Membrane No.	Membrane length (cm)	<i>n</i> -hexane permeance ($\times 10^{-7}$ mol m ⁻² s ⁻¹ Pa ⁻¹)	<i>SF</i> (-)
M1	6	2.4	25,000
M2	6	2.6	19,800
M3	6	2.4	23,700
M4	6	2.3	19,800
M5	6	2.5	21,600
N6	6	1.8	23,400
N1	20	1.8	20,900
N2	20	2	22,500
N3	20	1.7	21,300
N4	20	1.8	20,400
N5	20	1.9	19,400
N6	20	1.7	20,400

Notes: The separation tests were performed using a 50/50 *n*-hexane/2,2-dimethylbutane feed at 373 K with an *n*-hexane partial pressure of 4.6 kPa.

Supplementary Table 5. *I*-Butene/isobutene separation performance of 6-cm-long MFI membranes prepared by NI-SFS at 473 K.

Membrane No.	Heating time (min)	Synthesis time (min)	<i>I</i> -C ₄ H ₈ permeance ($\times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$)	<i>SF</i> (-)
M1	35	15	4.7	21
M2	35	15	2.7	27
M3	35	15	4.7	22

Notes: The membranes were tested with a 50/50 *I*-butene/isobutene mixture at a feed pressure of 111 kPa and a flow rate of 200 SCCM.

Supplementary Table 6. Summary of synthesis time, membrane thickness, orientation, and *n*-butane/isobutane separation performance of membranes.

Author	Synthetic time (min)	Orientation/type	Substrate	<i>n</i> -C ₄ H ₁₀ permeance (GPU)	<i>SF</i> (-)	<i>SPI</i>	Ref.
Vroon	4320	<i>random</i>	disc	90	52	4680	8
Verweij	4320	<i>random</i>	disc	90	52	4680	9
Tuan	4320	<i>random</i>	tube	150	25	3750	10
Tsapatsis	1440	<i>h0h</i>	disc	90	40	3600	11
Gump	900	<i>random</i>	tube	50	14	700	12
Li	720	<i>random</i>	tube	30	42	1260	13
Bernal	1440	<i>random</i>	tube	46	53*	2438	14
	1440	<i>random</i>	tube	209	28*	5852	
Jareman	1440	<i>random</i>	disc	2600	6	15600	15
	1380	<i>random</i>	tube	24	14*	336	
Coronas	2280	<i>random</i>	tube	21	11*	231	16
	1500	<i>random</i>	tube	54	11*	594	
Gora	1020	<i>random</i>	tube	418	45	18810	17
Chio	1200	<i>random</i>	disc	238	46	10948	18
Tsapatsis	1200	<i>c</i>	disc	299	35	10465	19

Kim	5760	<i>random</i>	disc	538	17	9146	20
Tsapatsis	2280	<i>c</i>	disc	329	30	9870	21
Zhou	1800	<i>h0h</i>	tube	597	27	16119	22
Nair	3600	<i>random</i>	tube	400	42	16800	23
Zhou	180	<i>h0h</i>	tube	299	45	13455	24
Liu	120	<i>b</i>	disc	597	33.2	19820.4	25
Qiu	180	<i>random</i>	tube	1284	17	21828	26
Min	1920	<i>random</i>	tube	433	60	25980	27
Saulat	1440	<i>b</i>	disc	328	41	13448	28
zhou	-	CMSM	-	2781	23	63963	29
Matsufuji	7200	composite	-	10	40	400	30
Liu	1440	MMM	-	10	21	210	31
	-	MMM	-	10	35	350	
Chernikova	-	MOF	-	46	55	2530	32
Eum	-	MOF	-	66	12	792	33
		<i>b</i>	tube	896	51	45,698	
This work ($S_m \geq 40 \text{ cm}^2$)	60	<i>b</i>	tube	746	72	43,010	(50/50 $n\text{-C}_4\text{H}_{10}/i\text{-C}_4\text{H}_{10}$)
		<i>b</i>	tube	896	71	53,016	
		<i>b</i>	tube	1045	86	92825	(90/10 $n\text{-C}_4\text{H}_{10}/i\text{-C}_4\text{H}_{10}$)
	60	<i>b</i>	tube	985	74	73966	

	<i>b</i>	tube	1075	78	85648	
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Supplementary Table 7. Summary of synthesis time, membrane thickness, orientation, and *I*-butene/isobutene separation performance of membranes.

Author	Synthetic time (min)	Membrane thickness (μm)	Substrate	<i>I</i> -C ₄ H ₈ permeance ($\times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$)	<i>SF</i> (-)	Ref.
Richter	2880	20	tube(TiO ₂)	1.9	5	³⁴
Voß	4320	20	tube(TiO ₂)	1.7	11	³⁵
50 mol% <i>I</i> -C ₄ H ₈	15	0.46	tube(α -Al ₂ O ₃)	2.7	28	This work
70 mol% <i>I</i> -C ₄ H ₈	15	0.46	tube(α -Al ₂ O ₃)	3	41	This work
90 mol% <i>I</i> -C ₄ H ₈	15	0.46	tube(α -Al ₂ O ₃)	2.4	62	This work

Supplementary Table 8. Summary of reported membrane performances for *n*-hexane/2,2-dimethylbutane separation compared with this work.

Membrane type	Test temperature (K)	<i>n</i> -C ₆ permeance (GPU)	<i>n</i> -C ₆ /2,2-DMB SF (-)	Ref.
MFI	373	302	30.5	36
	303	1,284	106	
Silicalite-1	373	568	10,000	19
B-ZSM-5	373	448	2,280	37
	373	448	1,950	
Silicalite-1	373	388	563	38
ZSM-5	374	747	500	39
	374	90	2,580	
Silicalite-1	373	60	47	15
	648	1,882	88	
ZSM-5	300	1,553	100	40
	375	60	1,260	
ZSM-5	358	597	680	41
	373	299	750	
B-ZSM-5	436	388	247	42
	497	102	171	
Silicalite-1	363	84	22.5	43
	370	538	21.1	
Silicalite-1	407	568	2.1	18
	373	627	2,490	
Silicalite-1	473	116	2,000	9

MOF	303	1,287	106	44
MOF	353	-	3.85	45
	373	538	20,900	
MFI	373	597	22,500	This work
	373	507	21,300	

Supplementary Table 9. Actual operating conditions and parameters for the 40,000-ton-per-year mixed butane separation unit (*n*-C₄H₁₀/*i*-C₄H₁₀).

Annual processing mass(t/y)	Mass flow rate (kg/h)	Temperature (K)	Pressure (kPa)	<i>n</i> -C ₄ H ₁₀ (mol%)	<i>i</i> -C ₄ H ₁₀ (mol%)
40,000	5000	318	600	10%	90%
40,000	5000	318	600	30%	70%

Supplementary Table 10. Simulation results for two-stage membrane process logistics calculations (*n*-C₄H₁₀/*i*-C₄H₁₀: 10%/90%).

Membrane process		Mass flow rate (kg/h)	<i>n</i> -C ₄ H ₁₀ (mol%)	<i>i</i> -C ₄ H ₁₀ (mol%)
First-stage	Permeate	997.43	46.12%	53.88%
	Retentate	4002.57	1.00%	99.00%
Secondary-stage	Permeate	543	83.88%	16.12%
	Retentate	454.44	1.00%	99.00%

Supplementary Table 11. Simulation results for two-stage membrane process logistics calculations (*n*-C₄H₁₀/*i*-C₄H₁₀: 30%/70%).

Membrane process		Mass flow rate (kg/h)	<i>n</i> -C ₄ H ₁₀ (mol%)	<i>i</i> -C ₄ H ₁₀ (mol%)
First-stage	Permeate	2006.92	73.26%	26.74%
	Retentate	2993.08	1.00%	99.00%
Secondary-stage	Permeate	1558.54	94.04%	5.96%
	Retentate	448.37	1.00%	99.00%

Supplementary Table 12. Actual operating conditions and parameters for the 40,000-ton-per-year mixed butene separation unit (*I*-C₄H₈/*i*-C₄H₈).

Annual processing mass (t/y)	Mass flow rate (kg/h)	Temperature (K)	Pressure (kPa)	<i>I</i> -C ₄ H ₈ (mol%)	<i>i</i> -C ₄ H ₈ (mol%)
40,000	5000	313	600	10%	90%
40,000	5000	313	600	30%	70%

Supplementary Table 13. Simulation results for two-stage membrane process logistics calculations(*l*-C₄H₈/*i*-C₄H₈:10%/90%).

Membrane process		Mass flow rate (kg/h)	<i>l</i> -C ₄ H ₈ (mol%)	<i>i</i> -C ₄ H ₈ (mol%)
First-stage	Permeate	1233.62	37.48%	62.52%
	Retentate	3766.38	1.00%	99.00%
Secondary-stage	Permeate	555.25	77.01%	22.99%
	Retentate	678.37	1.00%	99.00%

Supplementary Table 14. Simulation results for two-stage membrane process logistics calculations (*l*-C₄H₈/*i*-C₄H₈: 30%/70%).

Membrane process		Mass flow rate (kg/h)	<i>l</i> -C ₄ H ₈ (mol%)	<i>i</i> -C ₄ H ₈ (mol%)
First-stage	Permeate	2281.13	64.57%	35.43%
	Retentate	2718.87	1.00%	99.00%
Secondary-stage	Permeate	1676.55	87.49%	12.51%
	Retentate	604.57	1.00%	99.00%

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