Research on Common Technical Methods Based on Metal-organic Framework Membranes

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Abstract

Against the backdrop of the greenhouse effect exacerbated by the escalating global concentration of greenhouse gases, coupled with the urgent demand for carbon capture technologies driven by China's "carbon neutrality" strategy, this paper centers on the application of metal-organic framework (MOF)-based mixed matrix membranes (MMMs) in CO_2 capture. It systematically reviews the prevalent bottlenecks constraining membrane technology, including inadequate stability, interfacial defects, challenges in large-scale fabrication, and agglomeration issues under high-loading conditions. This paper takes the CH_4/N_2 separation system as a technical prototype to extract common technical methods that can be borrowed, which specifically include four aspects: First, MOF is modified by high vacuum resistance calcination to build a carbon layer on the surface of zeolitic imidazolate framework-8 (ZIF-8) to enhance its acid stability, and at the same time, to amorphize university of oslo framework-66 (UiO-66) to expose its unsaturated metal sites and enhance the affinity for the target gas. Second, the "dual-site synergy" interface design is achieved by matching the surface functionalization of MOF with the functional groups of the polymer to eliminate interface gaps and improve selectivity. Third, the hydrophilic modification of the support and the coating process are optimized, and mesoporous structures are introduced to achieve a MOF loading of over 95.000 wt%, effectively suppressing the agglomeration phenomenon. Fourth, based on large-area membranes, a roll-type membrane module is successfully developed to achieve a controllable performance transformation from membrane sheets to modules. This research provides a practical technical path for MOF-based mixed matrix membranes from material design to component integration, and has significant reference value for promoting the research on membrane-based CO_2 capture.

Keywords

Metal-organic framework, Mixed matrix membrane, Membrane amplification, Interface engineering

Introduction

Membrane-based gas separation has emerged as a promising alternative to conventional absorption processes owing to its low energy consumption, small footprint, and operational simplicity. However, the deployment of high-performance membranes for CO_2 capture remains hindered by material limitations, particularly the trade-off between permeability and selectivity. In this context, MOF-based MMMs offer a viable pathway to overcome these limitations by combining the processability of polymers with the superior sieving properties of MOFs. This paper focuses on extracting generic technical solutions from CH_4/N_2 separation studies and transferring them to CO_2 capture systems.

Carbon capture demand and challenges

The average concentration of CO_2 in the global atmosphere has risen from 280 one part per million (ppm) before the Industrial Revolution to over 420 ppm in 2024. The resulting greenhouse effect has become the most pressing environmental issue of this century. To address this challenge, China proposed the "carbon peak, carbon neutrality" strategic goal in 2020, indicating a deep low-

carbon transformation of the energy structure and industrial processes. In this context, the CO_2 capture, utilization, and storage (CCUS) technology has been given a core mission. Among them, the capture process is considered the core part of the CCUS technology, accounting for 70.00%-80.00% of the energy consumption in the entire CCUS chain, and is the key to technological breakthroughs [1,2].

The flue gas from coal-fired power plants is the main source of CO_2 emissions, accounting for 30.00% to 40.00 % of the global CO_2 emissions. This type of gas source has three inherent characteristics: The partial pressure of CO_2 is low (10.00%-15.00%), it is under normal pressure, and it contains acidic impurities such as SO_x and NO_x. These characteristics lead to high energy consumption becoming the primary obstacle for the industrialization of carbon capture technology. Taking the mature amine method as an example, its regeneration energy consumption can reach 3-5 GJ/t CO_2, accounting for approximately 20.00%-30.00% of the power plant's electricity generation.

Positioning and bottlenecks of membrane separation technology

Compared with absorption methods, membrane separation technology is based on the physical permeation principle and does not require a phase change process. Theoretically, it can reduce the capture energy consumption to below 1 GJ/t CO_2. Moreover, the modular nature of the membrane device enables it to be flexible in terms of processing scale and can adapt to the needs of different capacity power plants. These advantages have made membrane-based carbon capture continuously receive attention over the past two decades. However, as the core of membrane technology, membrane materials have long been constrained by the trade-off relationship between permeability and selectivity. This phenomenon was systematically summarized as an upper limit curve for polymer membrane separation performance, which has been subsequently updated. Although CO_2-affinity polymers represented by polyethylene oxide (PEO) have enhanced CO_2 solubility by introducing polar ether oxygen bonds, their permeability coefficients are mostly distributed in the range of 100-500 Barrer. These still fall short of the economic threshold for industrial applications [3].

Proposal of MOF-based hybrid matrix membranes

The concept of mixed matrix membranes (MMMs) aims to reconcile these contradictions. By dispersing highly selective porous fillers into an easily processable polymer matrix, it is expected to achieve a synergistic effect beyond that of a single component. Metal-organic frameworks (MOF) materials, due to their highly ordered pore structures, tunable chemical structures, and large specific surface areas. Due to these properties, they can simultaneously achieve high permeability and high selectivity, and are regarded as one of the most promising candidate fillers. Although MOF-based MMMs at the laboratory scale have repeatedly demonstrated remarkable performance improvements, when it comes to practical applications for CO_2 capture, four common challenges gradually emerge.

Challenge 1: The chemical stability of MOF does not match the environment of the flue gas. The flue gas contains SO_2, NO_x and water vapor, which cause the coordination bonds of MOF to hydrolyze or the ligands to be replaced [4]. ZIF-8 has stable performance in a pure CO_2/N_2 system, but its specific surface area decreases by more than 30.00% when exposed to an atmosphere containing SO_2. If the MOF structure partially collapses during membrane preparation or operation, the gas transmission path will undergo uncontrollable changes.

Challenge 2: Interface defects of MOF-polymer result in loss of selectivity. In an ideal MMMs, gases should flow through both the polymer matrix and the MOF pores simultaneously. However, when nanoscale voids form at the interface between MOF and polymer, gases preferentially penetrate through the voids, bypassing the selective sieving function of MOF. This phenomenon is particularly prominent in glassy polymers, such as polysulfone and polyimide, where the rigid chain segments are difficult to closely adhere to the surface of MOF.

Challenge 3: Loss of structural uniformity during membrane amplification. In the laboratory, membranes of the cm^2 size are typically prepared using the spin coating method, with thickness deviation controlled within 5.00%. When transitioning to the scraping and coating method for preparing membranes larger than 1000 cm^2, the spatial differences in solvent evaporation rate lead to uneven membrane thickness. The

sedimentation of MOF particles causes a longitudinal distribution gradient. This ultimately resulting in local defects in the effective separation layer [5].

Challenge 4: Agglomeration effect under high filler loading. Theoretically, increasing the MOF loading can enhance the gas permeation flux. However, experiments often show the opposite trend. When the loading exceeds a certain threshold (typically 30.000-40.000 wt%), the fillers begin to form agglomerates. The MOF pores within the agglomerates are blocked, and larger non-selective voids are generated at the interface between the agglomerates and the polymer, resulting in a sharp decline in selectivity.

Problem transfer and technological borrowing

The above four challenges are not unique to the CO_2 capture system. In the CH_4/N_2 separation process, the acidic components in natural gas require metal-organic frameworks (MOFs) to have acid resistance.

The similarity in molecular size between CH_4 and N_2 makes the interface defects more sensitive, and membrane area expansion also encounters the problem of uniformity. Aggregation phenomena also exist at high loading levels.

This paper conducts a comprehensive and systematic study on these key common issues in the field of CH_4/N_2 separation, and has successfully developed a set of effective technical solutions covering MOF modification, interface regulation, process scaling, and component integration. These four distinct levels of technology together constitute a complete chain from materials to components, and the detailed logical framework is also clearly shown in Figure 1.

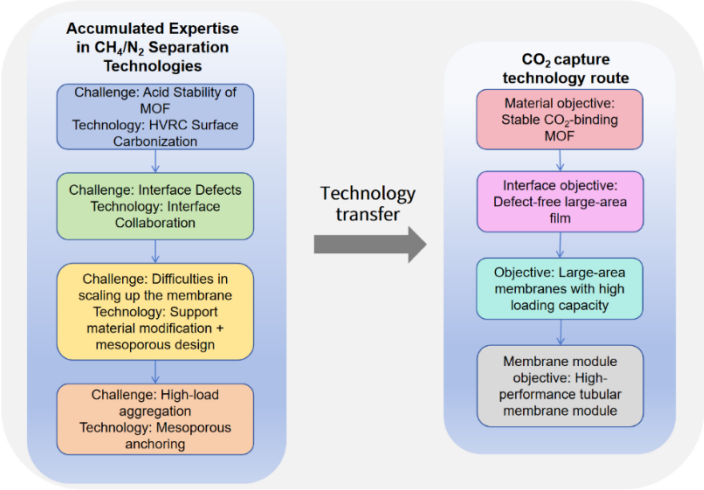

Figure 1. Technical route framework diagram of this paper.

MOF modification and CO_2-adhesive materials

Challenges and approaches

In the flue gas environment targeted by CO_2 capture, there are two factors that pose challenges to the MOF materials. The first is chemical corrosiveness. When SO_2 and NO_x dissolve in water vapor, they form sulfurous acid and nitric acid, which can cause the coordination bonds between the MOF metal nodes and ligands to break [6]. The second is competitive adsorption. The concentration of N_2 in the flue gas is approximately 4.0-6.0 times that of CO_2. If the MOF also has a considerable affinity for N_2, the separation selectivity will be difficult to meet the standards.

The high vacuum resistance calcination (HVRC) method provides a technical framework for addressing these issues. This method is based on two fundamental principles. First, the vacuum environment can significantly reduce the oxygen partial pressure, thereby inhibiting the oxidation and decomposition of the MOF framework at high temperatures. Second, under vacuum conditions, the solvent molecules adsorbed in the MOF pores, the unreacted ligands, and some less coordinated organic components can be selectively removed.

During the treatment, the MOF powder is placed in a tungsten boat, and the vacuum is reduced to the set pressure before applying an electric current. The current intensity is linearly related to the temperature.

Cases of surface carbonization and amorphization

ZIF-8 is formed by the coordination of Zn^{2+} with 2-methylimidazole.

When HVRC treatment is carried out at 88 A current for 3 hours, two observable changes occur in the ZIF-8 particles. The first change is a transformation in the surface morphology and structure. The Raman spectrum shows the characteristic peaks of carbon materials, D band and G band. The X-ray diffraction (XRD) spectrum indicates that the diffraction peaks of the ZIF-8 core still exist, indicating that a carbon thin layer was formed on the surface but the main skeleton structure was retained. The second change is the reconstruction of the surface chemical composition. Elemental analysis shows that the carbon content decreased from 42.26% to 38.16%, while the Zn content increased from 26.14% to 28.54%, indicating that the Zn sites were relatively enriched on the surface. The presence of the carbon layer significantly enhanced the acid stability of ZIF-8@VR. The enrichment of Zn sites enhanced the adsorption capacity for CH_4, and at 298 K and 1 bar conditions, the CH_4 adsorption capacity of ZIF-8@VR was 63.00% higher than that of ZIF-8, and the adsorption selectivity was increased by 1.4 times [7].

UiO-66 is composed of $Zr_6O_4(OH)_4$ clusters as nodes and is coordinated with phthalic acid ligands. When HVRC treatment is carried out at a current of 120 A for 30 minutes, the XRD pattern of UiO-66 undergoes a fundamental change. The original two strong diffraction peaks completely disappear and are replaced by broad "breadfruit-like peaks". This characteristic indicates that the long-range ordered crystal structure no longer exists and the material transforms into an amorphous state. Gas adsorption tests reveal a seemingly contradictory phenomenon.

However, at 298 K and 1 bar conditions, the adsorption capacity of CH_4 for non-crystalline UiO-66 is 2.400 cm^3/g, while the adsorption capacity of N_2 is only 0.400 cm^3/g. The difference in the magnitude of the decrease leads to an increase in the CH_4/N_2 selectivity. The surface carbonization of ZIF-8 by HVRC treatment forms a carbon layer, and the non-crystallization transformation of UiO-66 by HVRC treatment occurs.

Interface engineering and compatibility regulation mechanism

Formation and impact of interface defects

The interface compatibility issue between MOF and polymers is a common problem in the field of mixed matrix membranes. From a thermodynamic perspective, the surface of MOF usually has a relatively high surface energy, while the polymer chain segments tend to reduce the free energy of the system. When they come into contact, it is difficult for them to form a stable interface bond. From a kinetic perspective, during the solvent evaporation process, the difference in shrinkage rates between MOF particles and polymers will generate stress at the interface. This stress will subsequently lead to the formation of micrometer or nanometer-sized voids.

The influence of these interface gaps on membrane separation performance can be explained by the change in the gas transmission path. In an ideal situation, gas molecules should flow through both the polymer matrix and the MOF pores simultaneously, allowing the MOF's selectivity to be exerted. However, when interface gaps exist, gas preferentially permeates through the narrower gaps with lower resistance, bypassing the MOF. More seriously, once the gaps are formed, they may expand due to pressure fluctuations during the membrane operation, resulting in continuous performance degradation.

Surface functionalization strategy of MOF

One fundamental approach to solving the interface compatibility problem is to perform functionalization on the surface of MOF, so that its surface chemical properties match those of the polymer. The core of surface functionalization lies in introducing functional groups on the surface of MOF that can form interactions with the polymer chain segments. These interactions can be hydrogen bonds, coordination bonds, or van der Waals forces.

The case of the composite of amorphous UiO-66 and polyvinyl alcohol (PVA) demonstrates the effectiveness of this strategy. The surface of the original UiO-66 is mainly composed of the benzene rings and carboxylate oxygen atoms of the phthalic acid ligand, and has limited interaction with PVA. After HVRC non-crystallization treatment, the surface of UiO-66 exposes a large number of coordinatively unsaturated Zr^{4+} sites. The Zr sites on the non-crystalline UiO-66 surface form hydrogen bond interactions with the hydroxyl groups of PVA. Gas separation tests further confirm this difference. Under the same test conditions, the CH_4/N_2 selectivity of PVA/non-crystalline UiO-66 mixed matrix membrane (MMM) is approximately 40.00% higher than that of PVA/original

UiO-66 MMM [8].

Polymer selection and synergistic effects

The surface functionalization of MOFs has addressed the issue of "whether MOFs can interact with polymers", and the choice of the polymer determines "the strength and mode of the interaction". An ideal polymer should possess two characteristics. First, it should contain functional groups that can form interactions with the surface sites of MOFs. Second, it should have a certain affinity for the target gas and can form a "relay transmission" effect with MOFs.

The case of the calcia-stabilized zirconia (CSZ) and polyvinylamine (PVAm) composite demonstrates the importance of polymer selection. CSZ is ZIF-8 that has been carbonized by HVRC treatment and has a surface rich in Zn sites. PVAm is a polymer containing a large number of -NH_2 functional groups, with a polyethylene backbone as the main chain and a primary amine hanging on the side chain. This calculation result indicates that CH_4 can be spontaneously adsorbed by the Zn sites and -NH_2, while N_2 is not easily adsorbed. In other words, CSZ and PVAm have a common preference for CH_4 and a common repulsion for N_2.

The synergy resulting from this common preference is manifested in the gas separation performance. The difference between the two sets of data can be attributed to the HVRC treatment, which exposes more Zn sites on the CSZ surface. These sites interact with the -NH_2 of PVAm, strengthening the adsorption and transport of CH_4. DFT calculations confirm that the binding energies of CH_4 to the Zn sites and -NH_2 are all negative, while that of N_2 is positive. This dual-site cooperative adsorption mechanism is shown in Figure 2.

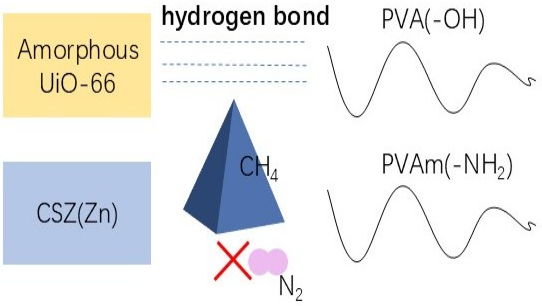

Figure 2. Schematic diagram of the interface engineering strategy for MOF-polymer.

Principle of dual-point synergistic design

The success of the CSZ-PVAm system has revealed a more universal design principle: dual-site synergy. This principle has three levels of meaning. First, site matching. The active sites on the surface of the MOF should have chemical complementarity with the functional groups of the polymer. For the CO_2 capture system, CO_2 acts as a Lewis acid. The ideal match is that the MOF provides Lewis acid sites and the polymer provides Lewis base sites. The interaction between acid and base can not only strengthen the interface bonding but also enhance the adsorption of CO_2. Second, transmission relay. The transmission path of gas molecules within the membrane can be described as follows: They enter the polymer surface from the gas phase, diffuse within the polymer matrix, then enter the MOF pores, exit the MOF pores and enter the polymer matrix again, and finally reach the permeation side. If both the MOF and the polymer have affinity for the target gas, then gas molecules do not need to overcome the energy barrier when entering the MOF from the polymer, and vice versa. This "relay transmission" can effectively reduce the diffusion resistance.

Applying these principles to the CO_2 capture system can lead to the following design concept: Selecting MOFs with unsaturated metal sites and combine them with polymers containing -NH_2 or -OH functional groups. If the inherent stability of the MOF is insufficient, carbon layers can be introduced on its surface through HVRC treatment to protect the metal sites while exposing them. The constructed MMMs are expected to benefit simultaneously in terms of interfacial compatibility and CO_2 selectivity [9].

Membrane amplification and component integration

The core issue of membrane scaling

The transition from laboratory-scale to industrial application often involves an increase in membrane area from the centimeter-square level to the square-meter level. During this process, three issues frequently arise.

The first issue is the agglomeration of the fillers. In the preparation of small-area membranes in the laboratory, the spin-coating method can enable MOF particles to be uniformly dispersed under the action of centrifugal force. When the slurry-coating method is used to prepare large-area membranes, the residence time of the slurry on the substrate is prolonged, and the MOF particles may settle under the influence of gravity.

This results in a longitudinal gradient in the distribution

of fillers within the membrane. More seriously, during the solvent evaporation process, particle migration forms local enriched areas, where MOF particles come into contact with each other and form aggregates. The pores within the aggregates are blocked, and larger-sized voids will be generated at the interface between the aggregates and the polymer [10].

The second issue is the loss of uniformity in thickness. During large-area coating, the solvent evaporates from the surface of the film and also from the edges towards the center. The spatial differences in evaporation rates cause the viscosity of the slurry to change asynchronously. In regions with higher viscosity, the film layer is thicker, while in regions with lower viscosity, the film layer is thinner. When the thickness deviation exceeds 20.00%, there will be significant differences in the spatial distribution of gas flux. The overall performance of the film will be determined by the thinnest or thickest region, failing to reflect the intrinsic properties of the material.

The third issue is the increase in defect density. Small-area membranes can be screened under a microscope to identify defect-free areas for testing. However, large-area membranes cannot be screened as a whole. Any local defect will become a short-circuit channel for gas preferential penetration. Taking CO_2/N_2 separation as an example, if there is a pinhole defect with an area of 0.1 mm^2 in a membrane with a total area of 2,400 cm^2, the non-selective flux contributed by this defect may reach more than 30.00% of the total membrane flux [11].

Modification and coating process of the supporting body

The support is the physical carrier of the membrane, and its surface properties directly affect the film-forming quality of the membrane. The surface of the unmodified polysulfone (PSf) ultrafiltration membrane contains micropores with diameters of 50.0-200.0 nm. If the MOF/polymer slurry is directly coated, some of the slurry will penetrate the micropores, resulting in an uncontrollable thickness of the effective separation layer. Moreover, the PSf surface is hydrophobic, and its spreadability with water-based slurry is poor, making it prone to form coatings with uneven thickness.

To address these issues, a preparation method for the modified polysulfone (MPSf) support was established. The first step was to coat 0.400 wt% of the polydimethylsiloxane (PDMS) solution on the surface of the PSf. The role of PDMS is twofold. Firstly, it seals the large pores on the PSf surface to prevent the leakage of the subsequent casting solution. Secondly, after PDMS solidifies, it forms a smooth surface, providing a uniform base for the subsequent coating. The second step was to immerse the PDMS/PSf membrane in a 0.025 wt% PVA solution for 6 hours. PVA is rich in -OH groups and can form a hydrophilic layer on the PDMS surface. The presence of this hydrophilic layer enables the subsequent water-based MOF/polymer slurry to spread uniformly. Additionally, the -OH groups of PVA can act as anchor points, forming hydrogen bonds with the subsequent MOF or polymer.

The parameter control of the coating process is also crucial. The distance between the scraper and the substrate directly determines the thickness of the wet film, which in turn affects the thickness of the dry film and the defect density. Taking CSZ-based MMMs as an example, when the scraper spacing increased from 100 μm to 300 μm, the CH_4 permeability decreased from 2,233 gas permeation unit (GPU) to 510 GPU, a reduction of 77.00%. The CH_4/N_2 selectivity decreased from 3.19 to 2.53, a decrease of 21.00%. The decrease in permeability can be attributed to the increase in membrane thickness, which leads to an extension of the mass transfer path. The decrease in selectivity is related to the increase in the probability of defect formation during the increase in membrane thickness.

Design of mesoporous structure and achievement of high loading capacity

Increasing the loading capacity of MOFs is an intuitive approach to enhancing the performance of MMMs. However, traditional MOFs often experience agglomeration when the loading capacity exceeds 40.000 wt%. It has been discovered that introducing mesoporous structures into MOFs can overcome this limitation.

The preparation process of CSZ-H_3 embodies this design concept. ZIF-8 was treated with HVRC at 95 A current for 3 hours. Thermal evaporation of some 2-methylimidazole ligands occurred. Consequently, while the original microporous structure of ZIF-8 was retained, mesopores of about 3.9 nm in diameter formed inside and on the particle surfaces. The Brunauer-Emmett-Teller

(BET) analysis indicated that the specific surface area of CSZ-H_3 was 922 m^2/g, and the total pore volume was 1.477 cm^3/g.

The presence of these mesopores has changed the interface bonding mode between MOF and polymers. Traditionally, the interaction between MOF and polymers mainly relied on the chemical interaction of surface functional groups, with limited strength. The existence of mesopores enables the polymer chain segments to "embed" inside the MOF particles, forming physical interlocking structure. During membrane drying process, when the polymer chains contract, they are "hooked" by the mesopores and are less likely to detach from the surface of the MOF. This combination of physical interlocking and chemical interaction significantly enhances interface bonding strength [12].

The experimental results show that the PVA/CSZ-H_3 MMMs remain uniformly dispersed even when the CSZ-H_3 loading reaches as high as 95.000 wt%. The cross-sectional SEM images reveal that the MOF particles are tightly encapsulated by PVA, and there are no visible voids at the interface. The gas separation test indicates that the CH_4 permeability of this MMM reaches 7,283 GPU, and the CH_4/N_2 selectivity reaches 4.44. In contrast, the PVA/ZIF-8 MMM shows significant agglomeration when the ZIF-8 loading is only 75.000 wt%, with the CH_4 permeability dropping to 5584 GPU and the selectivity reducing to 2.59.

Achieving high loading capacity requires both chemical compatibility between MOF and polymers and physical anchoring via mesopores to maintain interface stability.

Development of roll-type membrane modules and optimization of flow field

Based on the large-area membrane fabrication technology, the literature reported the development of roll-type membrane modules. A roll-type membrane module with an effective area of 2,000 cm^2 was successfully fabricated using 1,120 cm^2 CSZ-based MMMs. The preparation process consists of three key steps: membrane bag fabrication, winding, and encapsulation. Gas separation tests showed that the CH_4 permeability of this roll-type membrane module was approximately 5,500 GPU, and the CH_4/N_2 selectivity was approximately 3.8, which was basically comparable to that of the flat membrane. This result verified the reliability of the component fabrication process and also indicated that the performance degradation from the membrane sheet to the module can be controlled within an acceptable range through process optimization [13].

To transfer the above component technologies to the CO_2 capture system, parameter adjustments need to be made based on the physical properties of the CO_2/N_2 mixture. The molecular weight of CO_2 is greater than that of N_2, and the concentration polarization phenomenon near the membrane surface is more significant. Turbulence needs to be enhanced through the design of the flow channels to thin the boundary layer. Additionally, the flue gas contains water vapor, which may affect the long-term stability of the sealant, so a water-resistant adhesive system needs to be selected. The complete process flow from the modification of the support material to the roll-type membrane module is shown in Figure 3.

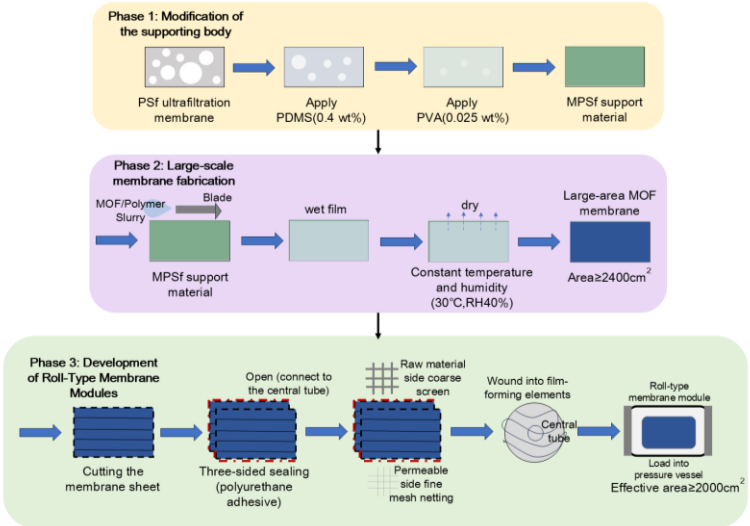

Figure 3. Flowchart for large area membrane preparation and roll-type membrane assembly.

Conclusion

In summary, this paper systematically reviews the common technical methods in the research of CH_4/N_2 separation from three aspects: MOF modification, interface engineering, and membrane amplification.

For MOF modification, approaches such as surface carbonization and amorphization are employed to enhance chemical stability and gas affinity. For interface engineering, a dual-site synergy strategy is developed by matching functionalized MOF surfaces with polymer groups to eliminate interfacial defects and improve selectivity. For membrane amplification, techniques including support modification, mesoporous structure design, and roll-type module fabrication are demonstrated to enable high-loading, defect-controlled large-area membranes.

The applicability of these methods to the CO_2 capture system is discussed, with necessary adjustments for flue gas conditions. Collectively, this work provides practical technical references for MOF-based mixed matrix membranes from material design to component integration.

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Conflict of Interest

The authors declare no conflict of interest.

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