Enhanced CO₂/CH₄ Separation Performance of a Mixed Matrix Membrane Based on Tailored MOF-Polymer Formulations

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Membrane-based separations offer great potential for more sustainable and economical natural gas upgrading. Systematic studies of CO₂/CH₄ separation over a wide range of temperatures from 65 °C (338 K) to as low as −40 °C (233 K) reveals a favorable separation mechanism toward CO₂ by incorporating Y-fum-fcu-MOF as a filler in a 6FDA-DAM polyimide membrane. Notably, the decrease of the temperature from 308 K down to 233 K affords an extremely high CO₂/CH₄ selectivity (≈130) for the hybrid Y-fum-fcu-MOF/6FDA-DAM membrane, about four-fold enhancement, with an associated CO₂ permeability above 1000 barrers. At subambient temperatures, the pronounced CO₂/CH₄ diffusion selectivity dominates the high permeation selectivity, and the enhanced CO₂ solubility promotes high CO₂ permeability. The differences in adsorption enthalpy and activation enthalpy for diffusion between CO₂ and CH₄ produce the observed favorable CO₂ permeation versus CH₄. Insights into opportunities for using mixed-matrix membrane-based natural gas separations at extreme conditions are provided.

Natural gas consisting primarily of methane (CH₄) is an important commodity and chemical feedstock with a relatively low CO₂ footprint.[1] Nevertheless, raw natural gas contains various impurities, and a key step in natural gas treatment is the removal of acid gases, e.g., CO₂, to prevent corrosion of the pipelines.[2] Conventional amine absorption, a mature technology for CO₂ removal with high selectivity, suffers from a number of well-documented drawbacks.[3] Nowadays, membrane-based technology is recognized as a highly promising and energy-efficient alternative to amine-based technology, as it offers flexible design, smaller footprint, and is relatively eco-friendly.[2b,3] However, present organic polymer membranes face a limit of trade-off between permeability and selectivity,[4] while inorganic membranes face scalability and cost limitations.[5] Hybrid membranes, also called mixed matrix membranes (MMMs), combining a dispersed molecular sieving phase (filler particles) and a continuous polymer (matrix), offer opportunities to overcome the drawbacks associated with pure polymer- or inorganic-based membranes. Various dispersed fillers, such as zeolites,[6] mesoporous silicas,[7] activated carbons,[8] carbon nanotubes,[9] and metal organic frameworks (MOFs),[10] have been incorporated into polymers to produce MMMs. Such MMMs must display compatibility between the dispersed and continuous constituents.[11] In this regard, MOFs are especially attractive in terms of compatibility with polymers due to their integrated organic moieties in organic linkers.[11,12] Nevertheless, relatively few reported MOF-based MMMs (MOF-based MMMs) exhibit enhanced CO₂ permeability and CO₂/CH₄ selectivity as compared to the associated parent pure polymer membrane.[13]

The ability to increase the loading ratio of MOFs to polymers offers the opportunities to improve the separation performance of MOF MMMs if aggregation of MOF particles at high loadings in the polymers matrix can be controlled and avoided.[1b] The choice of the matrix polymer with the appropriate and intrinsic permeability are vital for the successful integration of the filler properties in the MMM. Kulkarni and co-workers developed a novel hollow fiber membrane process at subambient temperatures offering an enhancement in the CO₂/N₂ selectivity for custom-synthesized pure polyimide membranes by twofold to fourfold at temperatures below −20 °C with negligible CO₂ permeance loss as compared to ambient temperature values.[14] It is important to note that feed streams in natural gas separation processes can be heated to 65 °C or higher (to prevent condensation in membrane modules) and cooling pretreatment can be used to capture and remove valuable ethane and higher hydrocarbon components. On this basis, evaluating...
the natural gas separation at extreme temperatures, beyond typical temperatures (25–35 °C) is of practical importance.

This communication reports a novel approach to achieve exceptionally high CO₂/CH₄ separation performance for pre-selected MOF-based MMMs without altering the composition of the integrated MOF or polymer. Principally, we report the high performance of the MOF-based MMM derived from Y-fum-fcu-MOF with interconnected tetrahedral (5.2 Å) and octahedral (7.6 Å) cages (Figure 1a). The engineered fcu-MOFs have triangular windows as the sole entrance for guest molecules to the MOF pore system.[15] Our previous work had demonstrated the good CO₂/CH₄ separation performance of Y-fum-fcu-MOF incorporated 6FDA-DAM polyimide membrane at 35 °C (308 K).[16] In this work, we extend our investigation to show that controlling the temperature is a promising way to further fine-tune the performance attributes of hybrid membranes.

Single gas permeation tests for pure CO₂ (at 1.38 bar) and CH₄ (at 4.14 bar) were performed on the Y-fum-fcu-MOF/6FDA-DAM membrane with 20 wt% MOF loading (Figure 1b) and pure 6FDA-DAM membrane at various temperatures ranging from 233 to 338 K, as shown in Figure 1c. As expected, decreasing the temperature significantly affects the CO₂/CH₄ separation performance, especially selectivity, for both pure 6FDA-DAM membrane and hybrid Y-fum-fcu-MOF/6FDA-DAM membranes. The CO₂/CH₄ permselectivity dramatically increases with decreasing temperature, and interestingly, the CO₂ permeability does not change much, resulting in a notable enhancement of the membrane performance exceeding the upper-bounds reported by Robeson.[17] Comparing with the parent 6FDA-DAM membrane, the hybrid Y-fum-fcu-MOF/6FDA-DAM membrane exhibits a higher CO₂/CH₄ separation performance especially at subambient temperatures, such as 253 and 233 K, surpassing the pure polymer upper bounds pertaining to temperature effects.[18]

At 233 K, the hybrid Y-fum-fcu-MOF/6FDA-DAM membrane exhibits an exceptionally high CO₂/CH₄ selectivity (=126) associated with a high CO₂ permeability (=855 barrers), reflecting approximately a fourfold enhancement in CO₂/CH₄ selectivity with only 10% reduction in the CO₂ permeability as compared to corresponding values at 308 K (Figure 1d).

Furthermore, mixed gas permeation tests corroborated the good performance of the hybrid Y-fum-fcu-MOF/6FDA-DAM membrane at subambient temperatures, as shown in Figure 1e. The hybrid membrane has a CO₂/CH₄ selectivity as high as =130 with CO₂ permeability of =1050 barrers at 233 K and 3.5 bar. Additionally, the membrane performs well under high pressures, even up to 55 bar, at 308 K (Figure 1f). As the pressure increases, CO₂ permeability and CO₂/CH₄ selectivity decreases only gradually indicating minimal plasticization effects. The evaluated membranes sustained their associated performances, thereby affirming that: i) the membrane is mechanically strong and ii) the interface compatibility/interactions between
the constituents of the films are sufficient to be maintained and remain operational under wide-range temperatures. The observed enhancement in the CO\textsubscript{2}/CH\textsubscript{4} separation performance for the evaluated membranes by fourfold at low temperatures, below ambient temperature, offers great opportunities to combine a membrane system with an appropriate pretreatment to capture condensable components\cite{12a,b,19}.

To gain a better understanding on the fundamentals governing the excellent CO\textsubscript{2}/CH\textsubscript{4} separation performance at subambient temperature, permeability of CO\textsubscript{2} and CH\textsubscript{4} were deconvoluted into diffusivities and sorption coefficients based on sorption–diffusion theory, as shown in Figure 2a,b. As expected, the change in temperature exhibits opposite influences on the gases (CO\textsubscript{2} and CH\textsubscript{4}) sorption and diffusivity in the membranes. Specifically, gas sorption increases with the decrease of temperature, while gas diffusivity decreases, resulting in minor changes in CO\textsubscript{2} permeability with temperature variation (Figure 1d) since gas permeability is the product of solubility and diffusivity. Lowering the temperature dramatically increases the CO\textsubscript{2} sorption in the glassy polymer 6FDA-DAM, which has excess free-volume providing abundant sorption sites for CO\textsubscript{2} at extreme conditions. Interestingly, addition of Y-fum-fcu-MOF into 6FDA-DAM promoted this effect on CO\textsubscript{2} and CH\textsubscript{4} solubility when the temperature is lowered. In contrast, lowering the temperature resulted in reduction of CO\textsubscript{2} and CH\textsubscript{4} diffusivities due to decreased motions of flexible polymer segments at subambient temperature. The enhanced CO\textsubscript{2} sorption contributes to the high CO\textsubscript{2} permeability at subambient temperatures for 6FDA-DAM and Y-fum-fcu-MOF/6FDA-DAM membranes.

Nevertheless, the sorption factor contributes only in a minor way to the CO\textsubscript{2}/CH\textsubscript{4} selectivity of the membranes at subambient conditions. Since CH\textsubscript{4} sorption also increases with decreasing temperature, only small enhancement in CO\textsubscript{2}/CH\textsubscript{4} sorption selectivity is seen, as shown in Figure 2c. Notably, as the temperature decreases, CO\textsubscript{2}/CH\textsubscript{4} diffusion selectivity increases rapidly, despite reductions in both CO\textsubscript{2} and CH\textsubscript{4} diffusivity (Figure 2a,b). The trend is further strengthened by the addition of Y-fum-fcu-MOF, so diffusivity dominates the high CO\textsubscript{2}/CH\textsubscript{4} selectivity of the membranes at subambient conditions.

Considering diffusion activation enthalpies of CO\textsubscript{2} and CH\textsubscript{4} in the membranes provides fundamental understandings on the transport processes. Typically, the activation enthalpy for diffusion is larger in absolute magnitude than the sorption enthalpy, so permeability decreases, and selectivity usually increases with

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Figure 2. Transport mechanisms of pure 6FDA-DAM and hybrid 20% Y-fum-fcu-MOF/6FDA-DAM membranes: solubility and diffusivity of a) CO\textsubscript{2} and b) CH\textsubscript{4} at 233–338 K. c) Sorption and diffusion based CO\textsubscript{2}/CH\textsubscript{4} selectivity. Sorption enthalpy, activation enthalpy for diffusion and for permeation of d) CO\textsubscript{2} and e) CH\textsubscript{4}.  

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decreasing temperature.\[^{20}\] Nonetheless, in this case interaction between the membrane and penetrant promotes high sorption enthalpy, making the sorption enthalpy similar in magnitude or even higher than the activation enthalpy for diffusion. Figure 2d,e shows that the comparable sorption enthalpy and activation enthalpy for diffusion makes CO\(_2\) permeation high. On the other hand, the much higher activation enthalpy for diffusion than sorption enthalpy induces a high energy barrier for CH\(_4\) permeation through the membranes. Apparently, the differences between CO\(_2\) and CH\(_4\) transport behavior in 6FDA-DAM membrane can be attributed to: 1) favorable interactions between CO\(_2\) molecule and the polyimide chains; and 2) lower energy barrier of CO\(_2\) molecule than that of CH\(_4\) molecule to execute an effective jump. Furthermore, the addition of Y-fum-fcu-MOF increases the diffusive discrimination between these two gas molecules, thereby making the hybrid membrane exhibit a remarkable CO\(_2\)/CH\(_4\) separation performance at subambient temperatures.

In order to better understand the diffusion process, the CO\(_2\)/CH\(_4\) diffusion selectivity of the membranes were deconvoluted into energetic selectivity and entropic selectivity, as shown in Figure 3a. The values for pure MOF membrane were also evaluated by back-calculation using the Maxwell equation.\[^{5a}\] Detailed descriptions of the deconvolution method can be found in the Supporting Information. Interestingly, unlike carbon molecular sieving (CMS) membranes with slit-shaped pores showing significant entropic selectivity for CO\(_2\)/CH\(_4\) separation,\[^{21}\] the polymer and hybrid membranes evaluated in this study showed a noteworthy energetic selectivity. This trend is clear from the large differences in diffusion activation enthalpy between CO\(_2\) and CH\(_4\) (Figure 2d,e) and low intercepts in Figure 3a. The CO\(_2\)/CH\(_4\) energetic selectivity of the polymer and hybrid membranes are less than unity, indicating less shape discrimination, versus overall size discrimination as the dominant factor in diffusion selectivity. In fact, the Y-fum-fcu-MOF with rigid triangle aperture (4.7 Å) has a reverse geometrical sieving effect on CO\(_2\) over CH\(_4\), e.g., condensability and kinetic diameter, as well as the intrinsic properties of the glassy polymer and the MOF structure, resulting in different levels of activation energies. Moreover, the CO\(_2\)/CH\(_4\) diffusion selectivity of the membranes is dominated by energetic selectivity. Due to the ultrahigh CO\(_2\)/CH\(_4\) selectivity and high CO\(_2\) permeability of the membranes, hybrid natural gas shapes. Specifically, CH\(_4\) molecule is tetrahedral in shape with little difference on three dimensions: \(a = 3.829\ \text{Å}, b = 4.101\ \text{Å}, c = 3.942\ \text{Å}\), while CO\(_2\) molecule is linear in shape with large difference on its dimensions: \(a = 3.339\ \text{Å}, b = 3.189\ \text{Å}, c = 5.361\ \text{Å}\). Thus the tetrahedral CH\(_4\) molecule can pass through the aperture without losing any rotational freedom in three axis; however, the long linear CO\(_2\) molecule has to give up two of its rotational degrees of freedom and some vibrational degrees of freedom to pass through the aperture since its c-dimensional size (5.361 Å) is larger than the aperture size (4.7 Å), as shown in Figure 3b. In this case, traditional kinetic size measured by experiments loses its standard meaning to evaluate the molecular sieving effects. Detailed atomistic understanding of these exceedingly complicated phenomena must await further developments in simulation capabilities.

With decreasing temperature, CO\(_2\)/CH\(_4\) energetic selectivity increases, while CO\(_2\)/CH\(_4\) entropic selectivity remains almost constant, as shown in Figure 3a. This behavior agrees well with fundamental analysis of transition state theory (Supplementary Information). Compared to molecules with higher diffusion activation enthalpy, molecules with lower diffusion activation enthalpy can more easily execute effective jumps. Obviously, by decreasing temperature, this effect due to the diffusion activation enthalpy difference between CO\(_2\) and CH\(_4\) is magnified, thereby significantly increasing CO\(_2\)/CH\(_4\) separation performance of the membranes.

In summary, Y-fum-fcu-MOF incorporated 6FDA-DAM polyimide membrane offers a high CO\(_2\)/CH\(_4\) separation performance at subambient conditions, overcoming the 2008 Robeson upper bound and the theoretical pure polymer upper bound, even when accounting for the temperature effect. Solution and diffusion play different roles in such a process, dominating the high CO\(_2\) permeability and high CO\(_2\)/CH\(_4\) selectivity, respectively. This is attributed to the different physical properties between CO\(_2\) and CH\(_4\), e.g., condensability and kinetic diameter, as well as the intrinsic properties of the glassy polymer and the MOF structure, resulting in different levels of activation energies. Moreover, the CO\(_2\)/CH\(_4\) diffusion selectivity of the membranes is dominated by energetic selectivity. Due to the ultrahigh CO\(_2\)/CH\(_4\) selectivity and high CO\(_2\) permeability of the membranes, hybrid natural gas

![Figure 3](https://www.advancedsciencenews.com/)

**Figure 3.** a) CO\(_2\)/CH\(_4\) diffusion selectivity, energetic selectivity, and entropic selectivity of 6FDA-DAM, Y-fum-fcu-MOF/6FDA-DAM, and predicted Y-fum-fcu-MOF membranes. b) Illustration of Y-fum-fcu-MOF aperture as well as CO\(_2\) and CH\(_4\) molecules.
separation process combining membrane with low temperature capture of valuable condensable hydrocarbons may be practical to lower processing cost in comparison with a pure ambient temperature membrane system. Detailed studies involving capital investments evaluation, operation temperature optimization, and robust condition tests are needed in future.

Experimental Section

Preparation of Membranes: The Y-fum-fcu-MOF crystals were synthesized as reported in the literature.[13] The as-synthesized micron-sized Y-fum-fcu-MOF crystals were nonideal to form MMMs directly, and thus a mild manual grinding method carrying out at ultralow temperature (e.g., −196 °C using liquid nitrogen) was applied to reduce the crystal sizes as described elsewhere.[16] The submicron-sized Y-fum-fcu-MOF/THF suspension was added to the 6FDA-DAM/THF solution to form a mixed-matrix dope, which was then mixed thoroughly on a rolling mixer overnight. Excess solvent (~60 vol%) in the mixed-matrix dope was removed by slowly purging dry nitrogen to achieve a higher concentration. Y-fum-fcu-MOF/6FDA-DAM mixed matrix dense films with 20 wt% MOF loading were then formed by casting the mixed-matrix solution. More details can be found in Supplementary Information.

Gas Sorption and Permeation Tests: Gas sorption isotherms at pressure up to 1 bar and temperatures ranging from 233 to 338 K were measured using a pressure decay method. The method and apparatus has been described in detail elsewhere.[22] The gas permeation was conducted in a variable pressure, constant-volume apparatus. The membrane was housed between an upstream, capable of high-pressure gas introduction, and a downstream, which was kept under vacuum until experiments were initiated. The permeation temperature for CO₂ and CH₄ ranged from 233 to 338 K as described earlier.[14c] A 50/50 (molar) CO₂/CH₄ mixture was used for mixed-gas permeation of Y-fcu-MOF/6FDA-DAM membrane. The downstream composition was determined using a gas chromatograph (Varian 450-GC). The stage cut (the flow rate ratio of permeate to feed) was maintained below 1% to avoid concentration polarization on the upstream side of the permeation cell, keeping the driving force across the membrane constant throughout the course of the experiment.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

mixed-matrix membranes, metal organic frameworks, natural gas separation, subambient conditions

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