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Plasticization-resistant Ni₂(dobdc)/polyimide composite membranes for the removal of CO₂ from natural gas⁺

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We demonstrate that the incorporation of Ni₂(dobdc) metalorganic framework nanocrystals into various polyimides can improve the performance of membranes for separating CO₂ from CH₄ under mixed-gas conditions. Four upper-bound 6FDA-based polyimides, as well as the commercial polymer Matrimid[®], show improved selectivity under mixed-gas feeds when loaded with 15–25 wt% Ni₂(dobdc), while the neat polyimides show diminishing selectivity upon increasing feed pressure. This approach presents an alternative to chemical crosslinking for achieving plasticization resistance, with the added benefit of retaining or increasing permeability while simultaneously reducing chain mobility.

The substitution of high carbon fuels with natural gas, along with the increased use of renewables, is an integral part of reducing CO_2 emissions in the electric power sector. Due to its domestic abundance, the consumption of natural gas is expected to grow considerably through 2040.¹ In response to these environmental and economic drivers, innovations in natural gas purification technology are needed to increase availability. Indeed, many natural gas reservoirs are contaminated with CO_2 that must be removed before delivery to the pipeline, and at least 10% of U.S. natural gas reserves exceed the maximum 2% CO_2 pipeline specification.² While the removal of CO_2 from natural gas has traditionally been accomplished by amine-based absorber-stripper units, advances in membrane design highlight the potential of this technology for carrying out more cost-effective separations.³

Various membrane technologies have been developed for natural gas purification, although the only commercial membrane materials are derived from organic polymers. Inorganic membranes⁴

Broader context

The efficient separation of CO_2 from various gas streams, in processes such as natural-gas purification and post-combustion carbon capture, presents major opportunities for advancing clean energy technologies. Membrane-based gas separations are less energy intense compared to conventional CO_2 separation methodologies, but new membrane materials with improved separation performance under realistic process conditions are needed. Here, we utilize strong metal-organic framework nanoparticle/polymer interactions to improve membrane performance under realistic feed environments, which tend to diminish the separation properties of neat polymer membranes.

and metal-organic framework membranes⁵ have been studied extensively for CO₂/CH₄ separations; however, challenges associated with membrane formation have prohibited their realworld application. Similarly, carbon molecular sieving (CMS) membranes⁶ and thermally rearranged (TR) polymer membranes⁷ display excellent separation properties, but are brittle and susceptible to defects. Unlike these inorganic and metal-organic framework-based crystalline membranes, polymer materials are solution-processable, and thus the membrane formation process is highly scalable. Additionally, the mechanical behavior of polymeric materials is superior to that of alternative membrane materials, which allows them to be formed into hollow fiber or spiral-wound modules. Due to these desirable characteristics, hundreds of polymer structures have been developed for CO2/CH4 separations, with all materials bounded by an upper-bound tradeoff between CO2 permeability and CO2/CH4 selectivity.8

A major pitfall of polymer membranes for natural gas purification, however, is their susceptibility to plasticization, which leads to an undesirable and often unpredictable loss in selectivity under the high pressures of a mixed-gas feed environment. This loss in selectivity is especially problematic for natural gas purification, where the high pressure of CO_2 in the feed gas will swell the polymer and accelerate the permeation of CH_4 .⁹ This process effectively shifts the transport properties of the polymer away from the upper bound and decreases its glass

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transition temperature, and polymers that exhibit a high CO₂ uptake are more susceptible to plasticization.¹⁰ In practice, then, commercialized and high performance polymers have lower mixed-gas selectivities relative to the values estimated from pure-gas measurements. A number of the upper-bound polymers for CO₂/CH₄ separations are glassy polyimides composed of a 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) monomer polymerized with a diamine.¹¹⁻¹³ These 6FDA-based polyimides show both diffusivity- and solubilitybased selectivities for CO₂ over CH₄, bestowing them with excellent separation factors and CO₂ permeabilities. Due to their high CO₂ uptake, however, they are susceptible to plasticization and their excellent pure-gas properties are diminished under mixed-gas conditions. Similarly, the polymers already commercialized for this application, cellulose acetate and Matrimid[®], exhibit reduced performance due to plasticization.^{3,14}

One reliable way to impart plasticization resistance is to crosslink polymer chains, which can decrease their mobility and prohibit them from swelling upon adsorption of CO₂.¹⁵⁻¹⁸ Although effective at mitigating plasticization, crosslinking has the undesired effect of reducing CO_2 permeability. An alternative route to plasticization resistance, which retains membrane permeability, is to incorporate porous, CO₂ selective metal-organic framework nanocrystals, which have exposed Ni²⁺ cations on the particle's surface that can interact strongly with the polymer chains. This strategy has recently been shown to improve mixedgas separation properties for C2H4/C2H6 as well as CO2/CH4 separations.¹⁹ Metal-organic frameworks have also been shown to be effective materials for adsorptive-based gas separations, including specifically CO2-based gas separations.²⁰⁻²³ Indeed M_2 (dobdc) has a higher isosteric heat of adsorption compared to other metal-organic frameworks with open metal sites.²² More recently, metal-organic frameworks have been used as fillers to form composite membranes targeting various gas separations, including many materials for CO₂-based separations.²⁴⁻²⁹ While most of the studies on metal-organic framework/polymer composite membranes have focused only on selective transport through the framework phase, the interactions between the framework and polymer can also be leveraged to improve transport properties.19

Here, we study the plasticization response of Matrimid[®], cellulose acetate, and four upper bound 6FDA-based polyimides (Fig. 1), both as neat polymers and as composites with Ni_2 (dobdc) (dobdc^{4–} = dioxidobenzenedicarboxylate) nanocrystals. In the case of the polyimides, the introduction of strong metalorganic framework/polyimide interactions substantially reduces plasticization, while, additionally, CO₂ selectivity improves for both the polyimide and Matrimid[®] composites over the neat polymers.

Nanocrystals of Ni₂(dobdc), neat polymer films, and Ni₂(dobdc)/ polymer composite membranes were synthesized using a method described previously.¹⁹ The purity of the Ni₂(dobdc) nanocrystals (15–20 nm particles from this method) was confirmed by powder X-ray diffraction (ESI,† Fig. S1), and porosity was confirmed using N₂ and CO₂ adsorption. The capacity of the nanocrystals for CO₂ at 1 bar was determined to be 4.94 mmol g⁻¹, comparable to previously reported values (ESI,† Fig. S2).²¹



Fig. 1 Representative structures of polymers employed for membrane preparation in this study.

Adsorption of CO_2 and CH_4 further revealed that the Ni₂(dobdc) nanocrystals have a strong adsorption selectivity for CO_2 over CH_4 , with an IAST selectivity of 38 under an equimolar mixture and 1 bar total pressure (ESI,† Fig. 3).

The loading of Ni₂(dobdc) nanocrystals in the polymer films was determined by thermogravimetric analysis in a method developed previously (ESI,† Fig. S4 and S5).³⁰ The loading was found to range from 15–23 wt% (Table 1), thus deviating only slightly from the target amount of 20 wt%. Carbon dioxide and CH₄ equilibrium adsorption isotherms were also measured on the neat polymer and Ni₂(dobdc)/polymer composites (ESI,† Fig. S6). The observed adsorption of CO₂ and CH₄ in the composites matched closely with the weighted average of the neat polymer and Ni₂(dobdc) nanocrystals, indicating that the pores of the nanocrystals are still fully accessible to gas molecules.

One pronounced effect of polymer rigidification is an increase in the glass transition temperature, T_{g} , which was measured for all neat and composite films using differential scanning calorimetry. For all polyimides there was a 6–10 $^\circ\mathrm{C}$ increase in T_g upon Ni₂(dobdc) incorporation (Table 1), although no increase in T_g was observed for cellulose acetate. Variation in molecular weight cannot explain this exception, as the cellulose acetate sample has a similar molecular weight to other polymers tested (ESI,† Table S1). This result suggests that there is an interaction between the polymer and nanocrystal that is specific to the imide functionality. Further, an increase in $T_{\rm g}$ of this magnitude is similar to what is observed upon crosslinking of polymer films and indicative of a reduction in polymer chain mobility.^{17,18} Unfortunately, the composite infrared spectra exhibited no changes from that of the pure Ni₂(dobdc) or polymer that might elucidate the specific interactions at play. This result is perhaps not surprising though, in view of the limited number of specific nanocrystal surface contacts compared to the bulk polymer phase.

Single-component gas permeation experiments were conducted with a CO_2 or CH_4 feed pressure of 1 bar. These pure

Table 1 Membrane sample characterization and pure gas transport parameters showing comparison of neat polymers with Ni₂(dobdc) loaded membranes. Ni₂(dobdc) loading was measured by thermogravimetric analysis and the glass transition temperature by differential scanning calorimetry. CO_2 permeabilities and CO_2/CH_4 selectivities were measured by single component permeation tests at a feed pressure of 1 bar. Errors on CO_2 permeability are propagated from errors in film thickness, area, and upstream pressure. Solubility was determined from the equilibrium adsorption isotherm and diffusivity by the solution diffusion model

Polymer	Ni ₂ (dobdc) (wt%)	$T_{\rm g}$ (°C)	$P_{\rm CO_2}$ (barrer)	$S_{\rm CO_2}$ (cm ³ (STP) cm ⁻³ bar ⁻¹)	$D_{\rm CO_2} \ (10^{-8} \ {\rm cm}^2 \ {\rm s}^{-1})$	$P_{\rm CO_2}/P_{\rm CH_4}$	$S_{{ m CO}_2}/S_{{ m CH}_4}$	$D_{\rm CO_2}/D_{\rm CH_4}$
Cellulose acetate	_	193	3.50 ± 0.30	4.0	0.67 ± 0.06	30.6	6.4	4.7
	23	193	3.78 ± 0.17	22.9	0.13 ± 0.01	30.3	12.7	2.4
Matrimid [®]		320	9.55 ± 0.51	8.5	0.86 ± 0.05	34.5	9.8	3.5
	23	330	9.31 ± 0.56	25.5	0.28 ± 0.02	29.5	13.0	2.3
6FDA-DAT	_	319	55.8 ± 3.1	9.0	4.70 ± 0.26	50.1	7.9	6.3
	15	326	63.9 ± 3.6	20.9	2.32 ± 0.13	51.9	14.9	3.5
6FDA-DAM:DAT	_	372	191 ± 9	12.1	11.9 ± 0.6	31.3	6.1	5.1
	18	377	220 ± 10	25.0	6.71 ± 0.31	30.5	6.7	4.5
6FDA-DAM	_	393	518 ± 21	13.2	30.0 ± 1.2	18.7	6.7	2.8
	23	402	715 ± 51	29.8	18.2 ± 1.3	14.5	12.1	1.2
6FDA-durene	_	422	626 ± 35	15.5	30.7 ± 1.7	18.0	7.0	2.6
	21	428	1035 ± 56	30.1	26.1 ± 1.4	12.3	12.1	1.0
Single component,	35 °C, 1 bar fe	eed pressui	e.					

component permeation tests revealed that CO₂ permeability is similar between the composite and the neat low-permeability commercial polymers. However, for the more permeable 6FDA-based polyimides, the CO₂ permeability increased upon Ni₂(dobdc) incorporation. Additionally, a modest decrease in the permselectivity for CO2 over CH4 was observed for these composites. In order to determine the origins of the transport behavior in these systems, the solution-diffusion model was used to deconvolute the solubility and diffusivity components of the permeability.³¹ Here, the solubility component of the diffusivity (S) was determined from the quantity adsorbed in the gas adsorption isotherm at 1 bar, and the diffusivity (D) was determined from the equation, D = P/S, where P is permeability. Based on this analysis, it can be readily seen that the increase in the solubility selectivity (S_{CO}/S_{CH}) mostly offsets the decrease in the diffusivity-based selectivity (D_{CO_2}/D_{CH_4}) to yield a similar or slightly lower permselectivity. It is important to note here that this analysis does not take into account competitive adsorption. The solubility-selectivity observed in a single-component gas adsorption measurement is lower than the actual composition of the adsorbed phase in a binary mixture, in much the same way as Ideal Adsorbed Solution Theory (IAST) predicts a higher selectivity for Langmuir-shaped isotherms than does a simple ratio of the amounts adsorbed.32 Because of this, we would expect that an even larger boost in the solubility-selectivity would be observed in a mixed-gas permeation experiment.

Variable-pressure, mixed-gas permeation tests were carried out in order to resolve the effects of competitive adsorption, as well as nanoparticle-induced polymer rigidification. These experiments were performed on all five polyimides and cellulose acetate. Fig. 2 shows the mixed-gas permselectivity as a function of the feed pressure of an equimolar mixture for composite and neat polymer membranes. Indeed, all polymers that exhibited an increase in T_g also showed resistance to plasticization upon exposure to high pressures of CO₂, as seen by the retention of CO₂/CH₄ selectivity at high feed pressures. Additionally, the mixed-gas permselectivity was greater than the pure-component permselectivity, indicating that competitive adsorption effects are substantial. For example, CO₂/CH₄ selectivity for the Ni₂(dobdc)/6FDA-DAT composite increased from an ideal selectivity of 51.9 to a mixed-gas selectivity of 55.5 \pm 3.2, whereas the neat 6FDA-DAT decreased in selectivity from an ideal selectivity of 50.1 to a mixed-gas selectivity of 40.3 ± 1.7 . The drop in selectivity under mixed-gas conditions for the neat polymer is typical for CO₂-induced plasticization, and a similar effect was observed for all polymers tested. The increase in CO₂/CH₄ selectivity in the composite material from pure to mixed-gas tests is a rare and very beneficial attribute in polymer-based membrane materials,³³ and is enabled primarily by the reduction in plasticization with competitive adsorption contributing slightly to the overall improvement. The only polymer that did not show this advantageous effect was cellulose acetate, consistent with the observation that the $T_{\rm g}$ values for this composite and the neat polymer membrane are similar.

By comparing permeabilities of CO2 and CH4 under a mixed-gas feed at low pressure (1 bar) and high pressure (55 bar), the origin of the plasticization resistance can be readily understood (Fig. 3). In the neat polyimide, the CO_2 permeability decreases or remains constant, while the CH₄ permeability greatly increases between 1 and 55 bar of feed pressure. The change in CO₂ permeability with increasing feed pressure is influenced by two main factors: dual-mode transport and polymer plasticization. Dual-mode adsorption of CO2 causes the permeability to decrease with increasing feed pressure,³⁴ while plasticization causes permeability to increase. The net effect is a slightly lower or similar CO2 permeability at 55 bar compared to 1 bar. In the case of CH₄, however, the Langmuir component of solubility is minor relative to the Henry's Law component, so plasticization effects are dominant. Thus, an overall increase in CH₄ permeability occurs with increasing feed pressure. On the other hand, Ni₂(dobdc)/polyimide composites are plasticizationresistant, and so changes in permeability with pressure are



Fig. 2 Variation of CO_2/CH_4 permselectivity as a function of the total feed pressure of a binary gas mixture measured at 35 °C for each membrane material studied. Open circles represent the neat polymer film and closed circles represent the Ni₂(dobdc)-loaded film with a weight fraction corresponding to the value in Table 1.



Fig. 3 Permeability of CO₂ (top) and CH₄ (bottom) in neat polyimides (a) and Ni₂(dobdc)/polyimide composites (b) at a low (grey) and high (blue) feed pressure of an equimolar mixture of CO₂ and CH₄.

dominated by dual-mode transport over the entire pressure range. In this case, CH_4 adsorption in the composites is more Langmuirian than in the neat polyimide, which explains the decrease in CH_4 permeability with increasing feed pressure.

Finally, the polyimide polymers and their $Ni_2(dobdc)$ containing composites were compared on the CO_2/CH_4 upper bound plot. Fig. 4 shows the CO_2/CH_4 selectivities and CO_2 permeabilities for membranes composed of the neat polyimides (open colored circles) and their composites (filled colored circles) over the range of pressures tested, and also includes various upper-bound polymers from the literature (grey circles). The neat polymers consistently move away from the upper bound with increasing feed pressure, whereas the Ni₂(dobdc) composites retain high selectivities. These high mixed-gas selectivities, along with the solution processability of the mixed-matrix format, make Ni₂(dobdc)/ polyimides intriguing materials for commercial membrane applications.



Fig. 4 Mixed-gas CO_2/CH_4 separation properties on the Robeson upper bound. Grey crosses represent literature data measured under pure gas conditions. Open colored circles represent mixed-gas permeation properties of the neat polyimides studied here, and closed colored circles represent the Ni₂(dobdc) loaded polyimides. Selectivity decreases with increasing pressure, with highest selectivity corresponding to 1–2 bar upstream pressure and lowest selectivity corresponding to 55–60 bar upstream pressure.

Conclusions

We have shown that the incorporation of relatively small amounts (~20 wt%) of Ni₂(dobdc) nanocrystals into a range of polyimides can improve the membrane performance under realistic process conditions. Improved CO_2/CH_4 selectivities were observed for these composites at high pressures (up to 55 bar) of a binary feed mixture, along with increases in the T_g that are consistent with a crosslinking effect. Importantly, the improvement in CO_2/CH_4 selectivity is not accompanied by a decrease in permeability, setting this approach apart from conventional crosslinking strategies. Indeed, the incorporation of strongly adsorbing nanocrystals appears generally to improve the properties of imide-based polymers, helping to overcome one of the most substantial barriers to the application of this important class of materials.

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