Coordination-driven structure reconstruction in polymer of intrinsic microporosity membranes for efficient propylene/propane separation

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GRAPHICAL ABSTRACT

PUBLIC SUMMARY
- Coordination-driven reconstruction (CDR) strategy in polymer of intrinsic microporosity (PIM) membranes was proposed
- Reduced micropore sizes and narrowed pore size distribution were obtained
- CDR strategy enhanced molecular sieving ability and membrane stability remarkably
- K⁺ incorporated amidoxime-functionalized PIM membrane exhibited high ideal C₃H₆/C₃H₈ selectivity up to 50
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Polymers of intrinsic microporosity (PIMs), integrating unique microporous structure and solution-processability, are one class of the most promising membrane materials for energy-efficient gas separations. However, the micropores generated from inefficient chain packing often exhibit wide pore size distribution, making it very challenging to achieve efficient olefin/paraffin separations. Here, we propose a coordination-driven reconstruction (CDR) strategy, where metal ions are incorporated into amidoxime-functionalized PIM-1 (AO-PIM) to in situ generate coordination crosslinking networks. By varying the type and content of metal ions, the resulting crosslinking structures can be optimized, and the molecular sieving capability of PIM membranes can be dramatically enhanced. Particularly, the introduction of alkali or alkaline earth metals renders more precise micropores contributing to superior C3H6/C3H8 separation performance. K⁺ incorporated AO-PIM membranes exhibit a high ideal C3H6/C3H8 selectivity of 50, surpassing almost all the reported polymer membranes. Moreover, the coordination crosslinking structure significantly improves the membrane stability under higher pressure as well as the plasticization resistant performance. We envision that this straightforward and generic CDR strategy could potentially unlock the potentials of PIMs for olefin/paraffin separations and many other challenging gas separations.

INTRODUCTION

Light olefins, such as ethylene and propylene, are the most produced organic chemicals with output capacities exceeding 200 million tons/ year.1 Meanwhile, the downstream polyolefin industries require high-purity olefins, so highly efficient olefin/paraffin separations are in great demand.2–5 The dominant thermal-based cryogenic distillation of olefin/paraffin mixture is one of the most energy-intensive processes because of the phase changes and close volatility. By comparison, membrane technology is highly energy efficient for olefin/paraffin separations owing to the non-thermal process without phase changes, which potentially can greatly contribute to carbon neutrality in chemical industries.5–12

Membrane materials lie in the core of membrane technology. Conventional polymers and metal-organic frameworks (MOFs) have been widely explored toward olefin/paraffin separations.13–22 Especially, MOF membranes, represented by ZIF-8 membranes, exhibit outstanding propylene/propane separation performance owing to their ordered micropore structures and appropriate molecular-sieving apertures.16,20,23 However, MOF membranes often have poor processability, and their scalable fabrication remains elusive. By comparison, polymer membranes possess excellent solution processability and thus have high scale-up potential. Nevertheless, conventional polymer membranes often yield low olefin/paraffin selectivity and low permeability due to their dense, disordered polymer chain packing.

The emergence of polymers of intrinsic microporosity (PIMs) brings about new opportunities to prepare advanced membranes by integrating both excellent processability of conventional polymers and well-developed microporosity of MOFs.24–26 PIMs, composed of rigid fused-ring backbones, possess large surface areas and abundant micropore structures.27–31 As such, PIM membranes exhibit extraordinary gas separation performance, which, for example, show CO2 permeability nearly two orders of magnitude higher than conventional polymer membranes.32–34 However, until now, few studies have explored PIM membranes for olefin/paraffin separation, and particularly, the gas selectivity is often far away from the practical application requirement.34,35–37 The low selectivity is mainly due to the fact that the micropores, originating from inefficient chain packing, are usually irregular with large sizes (~6 Å) and widely distributed. To address this issue, it is crucial to reduce the micropore sizes and narrow the pore size distribution (PSD) of PIMs. One common solution is designing novel monomers.35,39–44 However, so far, attractive olefin/paraffin selectivity has not been reached.

Herein, we envisage the structure reconstruction as an alternative strategy for PIM membranes to optimize micropore structures. To efficiently reconstruct a polymer membrane toward olefin/paraffin separations, the following criteria should be satisfied: (1) precise and controllable manipulation of micropore sizes can be achieved, allowing significantly enhanced molecular sieving selectivity; (2) the interchain interactions should be enhanced to inhibit the unfavorable plasticization and physical aging effect; and (3) the methods should be simple and generic without sacrificing the excellent processability and scaling-up potential of polymers. Based on the criteria, we design a coordination-driven reconstruction (CDR) strategy by utilizing metal ions in the membrane fabrication formula to induce coordination crosslinking structures in situ in PIM membranes, leading to optimized micropore structures and ultrahigh C3H6/C3H8 separation performance. Although structure reconstruction strategy has recently been applied in various fields with remarkable performance enhancement, including materials science and biology, our study for the first time proposes this strategy for membrane separation.45–47 Several studies about metal ion-induced membrane structure modification have been reported, including metal ion-modified carboxylated PIM-1 membranes and metal-induced ordered microporous polymers.25,48,49 However, based on the mentioned three criteria, there are significant differences between these studies and our CDR strategy. More specific discussion about the difference is presented in the Note S1.

In detail, amidoxime-functionalized PIM-1 (AO-PIM) was first synthesized and then loaded with metal ions to prepare AO-PIM-M membranes. AO-PIM was utilized owing to the well-developed microporosity and abundant functional groups.34,50,51 Strikingly, the fine-tuning of micropore structures can be realized by altering the type and loadings of metal ions, including alkali metal ions (Na⁺ and K⁺), alkaline earth metal ion (Ca²⁺), and transition metal ions (Zn²⁺, Ag⁺, Cu²⁺, and Fe³⁺). Meanwhile, various structure characterizations, including X-ray diffraction (XRD), gas molecule adsorption, and positron annihilation lifetime spectroscopy (PALS), binding energy calculation, and systematic evaluation of gas separation performances were conducted to verify the fabrication of PIM membrane structures. The resulting more ordered micropore structures with appropriate sizes afford the higher selectivity in separating C3H6 from C3H8 (Figure 1A). The AO-PIM-K membranes exhibited superior separation performance with C3H6 permeability of 147 Barrer and ideal C3H6/C3H8 selectivity of 50, which is nearly eight times as high as that of PIM-1 membranes and surpasses the performance of almost all polymer membranes.
RESULTS AND DISCUSSION

Fabrication and characterization of AO-PIM-M membranes

PIM-1 polymers with a $M_n$ of 87,000 and a polydispersity index of 1.6 were synthesized through a high-temperature method. AO-PIM polymers were synthesized by the reaction of PIM-1 with hydroxylamine for 20 h, which converted the cyano groups (-CN) to amidoxime groups (Figure 1B). In this study, we dissolved AO-PIM polymers in dimethylacetamide, and then a certain amount of metal ions were introduced into the AO-PIM solution, where the molar ratio between the repeated unit of AO-PIM and the metal ions was fixed at 16:1. After the evaporation of the solvent, AO-PIM-M membranes were obtained with uniform metal ion distributions and similar cross-sectional morphology (Figures 1Da and 1S1–S3), where the M represents the type of metal ions, including Na+, K+, Ca²⁺, Zn²⁺, Ag⁺, Cu²⁺, and Fe³⁺.

The successful synthesis of PIM-1 and the complete conversion of cyano groups using a reaction time of 20 h were verified by the liquid state $^1$H nuclear magnetic resonance spectra of PIM-1 and AO-PIM polymers (Figure 1C). The disappearance of characteristic -CN peak in the Fourier transform infrared (FT-IR) spectra of the AO-PIM membrane further verified the complete modification of PIM-1 polymers (Figure 1S4). Thus, the reaction time of 20 h was chosen to synthesize AO-PIM polymers. Meanwhile, the amidoxime groups were confirmed by the emerging bands at 3,487 and 3,380 cm⁻¹ (the asymmetric and symmetric stretching vibration of -NH₂ groups) and 1,650 and 914 cm⁻¹ (the stretching vibration of C=N and N-O groups). Moreover, amidoxime groups endow the AO-PIM polymers with the capability of post-modification. As is known, amidoxime groups exhibit strong coordination capacity and are broadly utilized to adsorb metal ions, conduct ions, extract uranium from seawater, and remove heavy metal ions from aquatic environments. In this study, metal ions were employed to crosslink polymer chains of AO-PIM by the coordination with amidoxime groups, which subsequently can lead to the in situ generation of coordination crosslinking networks and micropore structure reconstruction of AO-PIM membranes.

Further, we calculated the binding energy between polymer chains and the metal ion to quantify the influence of metal ions on polymer chain packing based on density functional theory (DFT). As shown in Figures 2B, 1S5, and 1S6, transition...
Metal ions possess much higher binding energy than alkali and alkaline earth metal ions, suggesting that strong coordination bonds would be formed between transition metal ions (e.g., Cu$^{2+}$ and Fe$^{3+}$) and amidoxime groups, while only weak coordination bonds would be generated for the cases of using Na$^+$, K$^+$, and Ca$^{2+}$. Meanwhile, the closer distance between transition metal ions and amidoxime groups also indicates stronger coordination bonds. The trend of binding energy versus metal ion type is identical with the ionic potential, suggesting the validity of the DFT calculations.

The coordination capacity of different metal ions is also reflected by the mechanical properties of corresponding membranes (Figure S7 and Table S2). As the coordination capacity of metal ions increased, the Young's modulus of AO-PIM-M membranes increased slightly. These results also indicate that the metal ions with different coordination capacity would exert different influences on the AO-PIM polymer chain packing and the micropore sizes. The trend of binding energy versus metal ion type is identical with the ionic potential, suggesting the validity of the DFT calculations.

The coordination capacity of different metal ions is also reflected by the mechanical properties of corresponding membranes. As shown in Figures S7 and S2, as the coordination capacity of metal ions increased, the Young's modulus of AO-PIM-M membranes increased slightly. These results also indicate that the metal ions with different coordination capacity would exert different influences on the AO-PIM polymer chain packing and the micropore sizes. The weak or moderate coordination bonds would endow AO-PIM-M membranes with relatively large micropores, while the strong coordination bonds would bind adjacent polymer chains tightly and form small micropores. Such deduction is further evidenced by the following micropore structure characterizations.

The reconstruction of pore structures in PIM membranes is verified by the characterizations of XRD, gas adsorption tests, and PALS. As shown in Figures 2C and S8, amidoxime functionalization considerably reduces the interchain spacing, while the subsequent introduction of metal ions increases the interchain spacing slightly. Gas adsorption tests using CO$_2$ as a probe molecule were conducted to further characterize the micropore sizes of the as-prepared membranes. As shown in Figures 2D and S9, the ultramicropore sizes in PIM-1 membranes are mainly located at 5.0 Å, accompanied by a small proportion of micropores with a size of 10.2 Å. In contrast, the AO-PIM-M membranes show smaller pore sizes at around 4.4 and 6.7 Å, respectively. Strikingly, the micropore sizes of the AO-PIM-M membranes exhibit unimodal distribution, mainly concentrated on 5.0–5.2 Å, which is larger than the ultramicropore size of AO-PIM membranes. Meanwhile, the elimination of micropores with larger sizes, such as those of 6.7 Å in AO-PIM membranes and those of 10.2 Å in PIM-1 membranes, narrows the PSD of AO-PIM-M membranes.

PALS is an effective technology to characterize the pore (or free volume) sizes and PSD of a solid material. As shown in Figures 2E and S10, AO-PIM-K membranes exhibit the highest intensity for the peak at around 4 ns and the narrowest PSD compared with other membranes. This might be attributed to the moderate coordination capacity between amidoxime groups and K$^+$, which is favorable for polymer chains to repack and for optimization of micropore structures. In addition, the peak locations in these spectra decrease in the following order: AO-PIM-Cu < AO-PIM-K ≈ AO-PIM < PIM-1, indicating that the metal ions with stronger coordination capacity lead to smaller micropore sizes. Thus, the PALS results prove that the stronger interchain interactions generally contribute to narrower PSD, while too strong interchain interactions is unfavorable to the PSD, as well as the microporosity. These results are also consistent with those obtained from CO$_2$ isothermal adsorption tests. Overall, the above

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**Figure 2.** The structure characterizations of AO-PIM-M membranes. (A) The FT-IR spectra of PIM-1, AO-PIM, and AO-PIM-M membranes. (B) The optimized structure of AO-PIM-K membranes through DFT calculations. The polymer chains of AO-PIM and K$^+$ are shown in ball-and-stick model, where carbon, oxygen, nitrogen, and hydrogen atoms are presented in gray, red, blue, and white, respectively; K$^+$ is presented in purple. The distances between adjacent atoms are presented in angstroms. (C) The XRD spectra of PIM-1, AO-PIM, and AO-PIM-M membranes. (D) The pore size distributions of PIM-1, AO-PIM, and AO-PIM-M membranes calculated through grand canonical Monte Carlo (GCMC) model based on the CO$_2$ sorption isotherms at 298 K. (E) The positron annihilation lifetime distributions of PIM-1, AO-PIM, AO-PIM-K, and AO-PIM-Cu membranes. Error bars represent the ($\sigma_x$)$^{1/2}$, where $\sigma_x$ is the covariance matrix of the solution for the probability distribution function in the CONTIN analysis of each PALS spectrum.
results confirm that the CDR strategy is effective in tailoring the pore size of PIM membranes and achieving much narrower PSD, which can contribute to the enhancement of diffusion selectivity for C3H6/C3H8 separation, as revealed in the following section.

C3H6/C3H8 separation performances of AO-PIM-M membranes

The gas permeation properties of PIM-1, AO-PIM, and AO-PIM-M membranes were evaluated by single-gas permeation tests toward C3H6/C3H8 gas pair. The PIM-1 membranes exhibited a high C3H6 permeability of about 1,300 Barrer owing to the well-developed microporosity, while their ideal C3H6/C3H8 selectivity of PIM-1 membrane was only about 6, consistent with the literature (Figure 3A and Table S3). The amidoxime functionalization of PIM-1 remarkably increased the ideal selectivity by about three times to 23. Meanwhile, the C3H6 permeability of AO-PIM membranes dramatically decreased to about 50 Barrer. The separation performances of AO-PIM membranes suggested a significant decrease in micropore sizes with improved size-sieving effect, in agreement with the gas adsorption and PALS results (Figures 2D and 2E). The CDR of micropore structures in PIM-1 membranes endowed AO-PIM-M membranes with improved separation performances. In detail, the introduction of alkali and alkaline earth metals significantly enhanced both the C3H6 permeability and the C3H6/C3H8 selectivity. The C3H6 permeabilities of AO-PIM-Na, AO-PIM-K, and AO-PIM-Ca membranes were 92, 147, and 171 Barrer, respectively, while corresponding ideal C3H6/C3H8 selectivities were 60, 50, and 24, respectively. Such a remarkably improved separation performance is attributed to the following reasons: (1) The metal ions exhibit weak coordination capacity toward amidoxime groups (Figure 2B and Figure S5), and they could effectively expand the interchain spacing and thus enhance the C3H6 permeability, as evidenced by the results of XRD, isothermal adsorption, and PALS. (2) The moderate coordination crosslinking could optimize the polymer chain packing, contributing to a narrower PSD and thus increased molecular sieving effect. (3) The C3H8 permeability of AO-PIM-Na and AO-PIM-K membranes was close to that of AO-PIM membranes, indicating that the micropore sizes were still sufficiently smaller than the size of C3H8 molecules. Thus, the AO-PIM-Na and AO-PIM-K membranes exhibited high ideal selectivity, while the AO-PIM-Ca membranes exhibited relatively low ideal selectivity because of the larger interchain spacing.

The introduction of transition metal ions generally led to lower C3H6 permeability and ideal C3H6/C3H8 selectivity because of stronger coordination bonding, in comparison with the AO-PIM-M with alkali metal ions. As a result, the C3H6 permeability of the AO-PIM-Zn membranes was 92 Barrer. With regard to the AO-PIM-Ag, AO-PIM-Cu, and AO-PIM-Fe membranes, the stronger coordination bonds with amidoxime groups could significantly reduce the interchain spacing, as indicated by the PALS and gas adsorption results. Consequently, these three
membranes exhibited very low C3H6 permeability. For example, AO-PIM-Fe membranes only showed a C3H6 permeability of 15 Barrer. The ideal C3H6/C3H8 selectivity of AO-PIM-Cu and AO-PIM-Fe membranes was also very low, only about 5, attributing to the smaller micropore sizes also efficiently blocking the diffusion of C3H6 molecules. It should be noted that the AO-PIM-Ag membranes showed a high ideal selectivity of 31, most likely owing to the fact that the Ag+ can promote the C3H6 transport through facilitated transport mechanism and the AO-PIM-Ag membranes with smaller pore size inhibited the transport of C3H8 molecules.65,66

Furthermore, the mixed-gas permeation tests were performed to evaluate the membrane separation performances toward practical applications. As shown in Figure S11 and Table S4, the C3H6 permeability of the as-prepared membranes in mixed-gas tests was lower than that in single-gas tests because of the competing adsorption effect. Notably, the membranes exhibited much lower C3H6/C3H8 selectivities in mixed-gas tests (molar ratio of 1/1). We further measured the C3H6/C3H8 mixture separation performance with different compositions in the feed gas wherein molar ratios of 1/9 and 3/7 for C3H6/C3H8 gas pair were utilized. It could be observed that the less the content of propylene in the feed gas, the higher the C3H6/C3H8 mixed-gas selectivity of the AO-PIM-K membranes was close to that in the single-gas tests. These results indicate that propylene molecules can induce significant plasticization effect and thus reduce the mixed-gas selectivity.

Gas adsorption is weakened at higher temperatures, so the propylene-induced plasticization could be alleviated with increasing the temperatures. As shown in Figure 3B and Table S5, when the temperature was increased to 50°C, the resulting membranes exhibited higher mixed-gas selectivity than that at 25°C. For example, the mixed-gas selectivity of AO-PIM-K membranes was improved from 6.7 to 14. Especially, AO-PIM-Ag membranes possessed the highest mixed-gas selectivity of 21, which could be attributed to the facilitated transport effect of Ag+. This indicates that integration of solution-diffusion and facilitated transport mechanisms may be a feasible strategy to overcome the plasticization effect and improve the mixed-gas selectivity.

Besides, PIM-1 membranes exhibit a serious pressure-induced plasticization effect, which is indicated by the increase in permeability and loss at selectivity. This is because the interchain interaction among PIM-1 polymers is weak and the micropore structures could not be preserved at high pressure. The metal ion-induced structure reconstruction converts the weak interaction to stronger coordination bonding in AO-PIM-M membranes, which is promising to improve the plasticization-resistance performance. Herein, we evaluated the membrane separation performances up to an absolute pressure of 6 bar (Figures 3C and S13). As shown in Figure 3C, we chose the C3H6 permeability at 1.5 bar as the benchmark and normalized the C3H6 permeability at higher pressure. AO-PIM-M membranes exhibited a smaller increase in C3H6 permeability and a prominent plasticization resistance effect at a higher pressure. For example,
the C$_3$H$_6$ permeability of the AO-PIM-K membrane at 6 bar was only about two times of that at 1.5 bar. Moreover, AO-PIM-K membranes exhibited a stable separation performance over 30 days with a permeability loss of 11% (Figure S14). The significantly enhanced structure stability at high feed pressure makes AO-PIM-M membranes a promising alternative membrane material for practical applications.

In Figure 3D, we compare the C$_3$H$_6$/C$_3$H$_8$ separation performance of AO-PIM-M, AO-PIM, and PIM-1 membranes with other polymer-based membranes. It is observed that the AO-PIM-K membrane exhibited an optimized comprehensive separation performance, with a C$_3$H$_6$ permeability higher than 100 Barrer and an ideal C$_3$H$_6$/C$_3$H$_8$ selectivity higher than 35. Moreover, the separation performance of AO-PIM-Na and AO-PIM-K membranes could surpass almost all the reported polymer-based membranes, indicating the high efficiency of structure reconstruction strategy. Overall, the AO-PIM-M membranes show great potential of practical application owing to the high separation performance and excellent processability. To realize the scale-up of AO-PIM-M membranes in the future, we envision that studies could focus on two aspects: (1) fabricating composite membranes with AO-PIM-M as the thin selective separation layer to achieve high C$_3$H$_6$ permeance by spin-coating, dip-coating, or blade-casting and (2) enhancing the mixed-gas C$_3$H$_6$/C$_3$H$_8$ selectivity. It would be feasible to incorporate MOF materials into AO-PIM-M matrix to significantly improve the molecular sieving effect or further optimize the content of silver ions to facilitate the transport effect.

Mechanisms of C$_3$H$_6$/C$_3$H$_8$ selective separation in AO-PIM-M membranes

The solution-diffusion model is widely used to elucidate the transport mechanism for gas separations in polymeric dense membranes. In order to decouple the solubility and diffusivity, isothermal adsorption tests of C$_3$H$_6$ and C$_3$H$_8$ were conducted. As shown in Figures 4A and S15, the PIM-1 membrane exhibited almost the identical adsorption quantity of C$_3$H$_6$ and C$_3$H$_8$ at 25°C and 1 bar, and thereby the solubility selectivity was close to 1. This means that the ideal C$_3$H$_6$/C$_3$H$_8$ selectivity of the PIM-1 membrane mainly depended on diffusivity selectivity. However, the amidoxime functionalization led to a significant difference in the adsorption behavior between C$_3$H$_6$ and C$_3$H$_8$. It could be found that for AO-PIM and all the AO-PIM-M membranes, the C$_3$H$_6$ adsorption quantity was almost 1.38 times higher than C$_3$H$_8$ at 25°C and 1 bar. As shown in Table S6, the dual-mode adsorption model, especially the b values, indicates that the lower adsorption quantity of C$_3$H$_8$ in AO-PIM and AO-PIM-M membranes is mainly resulted from the inhibition adsorption of C$_3$H$_8$ molecules in the micropores because of the smaller micropore sizes and enhanced size sieving effect. Thus, the high ideal selectivity of AO-PIM and some of the AO-PIM-M membranes could be ascribed to the reconstructed micropore structures.

We further calculated the diffusivity and solubility coefficients of C$_3$H$_6$/C$_3$H$_8$ gas pair based on the corresponding adsorption isotherms and membrane density (Table S7) for PIM-1, AO-PIM, and AO-PIM-M membranes. As shown in Figure 4C and Table S8, compared with PIM-1 membranes, AO-PIM and AO-PIM-M membranes possessed lower solubility for both C$_3$H$_6$ and C$_3$H$_8$ molecules because of smaller specific surface areas and fewer adsorption sites. Whereas, the C$_3$H$_6$/C$_3$H$_8$ solubility selectivity of AO-PIM and AO-PIM-M membranes was improved from 1.06 for PIM-1 to about 1.3. As explained for the adsorption difference, the enhanced solubility selectivity may be attributed to the reduced micropore sizes and narrow PSD. However, we should note that the solubility selectivity was still close to 1. Therefore, the high ideal selectivity of AO-PIM-M membranes could be owing to the diffusivity selectivity. As shown in Figure 4B and Table S8, the diffusivity selectivity of AO-PIM and AO-PIM-M membranes was significantly enhanced compared with that of PIM-1 membranes. Particularly, AO-PIM-Na membranes exhibited the highest diffusivity selectivity of 47.4, almost 8 times and 2.6 times as high as that of PIM-1 membranes and AO-PIM membranes, respectively. When Zn$^{2+}$ and Ag$^+$ were introduced, moderate diffusivity selectivity could be obtained. With respect to the metal ions with strong coordination capacity, the corresponding membranes exhibited low diffusivity selectivity because of the undersized micropores and low microporosity (Figure 2D). Thus, we could conclude that diffusion process dominates the highly efficient C$_3$H$_6$/C$_3$H$_8$ separation in AO-PIM and AO-PIM-M membranes, and it is possible to manipulate the diffusion process by altering metal ions.

Then, the role of metal ions in AO-PIM-M membranes was further evaluated by changing the amount of incorporated metal ions. Herein, we chose the AO-PIM-K membrane as a model because of its higher separation performance. The molar ratio between the repeated unit of AO-PIM and K$^+$ was fixed at 32:1, 16:1, and 8:1, and these membranes were labeled as AO-PIM-K(X), where X was 32, 16, and 8. As shown in Figure 4D, with the increasing of the content of K$, the C$_3$H$_6$ permeability increased initially and then decreased, and the AO-PIM-K(16) membrane exhibited the optimum separation performance. The ideal C$_3$H$_6$/C$_3$H$_8$ selectivity showed a similar trend. Such a trend suggests that metal ions play two roles in AO-PIM-M membranes, coordination crosslinking and blocking the micropores. The former dominates the separation performance at a low metal ion content, and the latter is the dominant role at a high metal ion content. These two roles compete and coordinate to determine the final separation performances of AO-PIM-M membranes.

CONCLUSION

In summary, we explored a CDR strategy to in situ generate coordination crosslinking networks in PIM membranes toward highly efficient C$_3$H$_6$/C$_3$H$_8$ separation. Seven kinds of metal ions were utilized to construct crosslinking networks in amidoxime-functionalized PIM-1 membranes. The incorporation of alkali or alkaline earth metals rendered moderate micropore sizes and narrow size distribution in the membranes, resulting in outstanding ideal C$_3$H$_6$/C$_3$H$_8$ selectivity with relatively high C$_3$H$_6$ permeability. Especially, AO-PIM-K membranes exhibited superior separation performance with a C$_3$H$_6$ permeability of 147 Barrer and an ideal C$_3$H$_6$/C$_3$H$_8$ selectivity of 50, surpassing almost all the polymer-based membranes. Strikingly, the fortified interchain interaction greatly contributed to the superior structure stability and plasticization-resistant performance even at 6 bar. Our strategy may stimulate the thinking about the fabrication of polymer membranes through structure reconstruction for highly efficient molecular separations.

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