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# Pure- and mixed-gas $CO_2/CH_4$ separation properties of PIM-1 and an amidoxime-functionalized PIM-1

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## ABSTRACT

The prototypical solution-processable polymer of intrinsic microporosity, PIM-1, and derivatives thereof offer combinations of permeability and selectivity that make them potential candidate materials for membrane-based gas separations. Paramount to the design and evaluation of PIMs for economical natural gas sweetening is a high and stable $CO_2/CH_4$ selectivity under realistic, mixed-gas conditions. Here, amidoxime-functionalized PIM-1 (AO-PIM-1) was prepared and examined for fundamental structure/property relationships. Qualitative NLDFT pore-size distribution analyses of physisorption isotherms ($N_2$ at -196 °C; $CO_2$ at 0 °C) reveal a tightened microstructure indicating size-sieving ultra-microporosity ($<7$ Å). AO-PIM-1 demonstrated a three-fold increase in $\alpha_D(CO_2/CH_4)$ over PIM-1, surpassing the 2008 upper bound with $P(CO_2)=1153$ Barrer and ideal $\alpha(CO_2/CH_4)=34$. Under a 50:50 $CO_2$:$CH_4$ mixed-gas feed, AO-PIM-1 showed less selectivity loss than PIM-1, maintaining a mixed-gas $\alpha(CO_2/CH_4)$ $\sim 21$ across a 20 bar pressure range. Conversely, PIM-1 endured up to 60% increases in mixed-gas $CH_4$ permeability over pure-gas values concurrent with a selectivity of only $\sim 8$ at 20 bar. A pervasive intermolecular hydrogen bonding network in AO-PIM-1 predominantly yields a rigidified microstructure that mitigates $CO_2$-induced matrix dilations, reducing detrimental mixed-gas $CH_4$ copermeation.

## 1. Introduction

Natural gas is the world's fastest growing primary energy source [1]. For corrosion-free pipeline delivery to residential and industrial end-users, crude gas is dehumidified and sweetened to remove entrained acid gases like $CO_2$. Hence, among the most rapidly emerging applications of polymeric membrane gas separation technology today is natural gas sweetening [2–4]. Because natural gas is often extracted from offshore and other remote locations, significant advantages of membrane technology include simple and continuous operation, small footprint, low weight and minimal operator attention [5]. Ideal, cost-effective polymer candidates are solution-processable into defect-free asymmetrical or thin-film composite membranes that are highly permeable and, more importantly, highly selective. That is, high selectivity, defined as the ratio of the permeability of the fast gas ($P_A$) to that of the slow gas ($P_B$) such that $\alpha_{A/B}=P_A/P_B$, ensures fulfillment of product-purity criteria while minimizing operational costs associated with co-permeation of $CH_4$ (the product) from the crude gas. In natural gas upgrading, highly selective materials reduce the cost associated with co-permeating $CH_4$ in two ways [6]: (i) less re-compression of the $CH_4$ recoverable by a second membrane stage and (ii) less $CH_4$ loss. However, an inherent trade-off exists between permeability and selectivity embodied by Robeson upper-bound relationships [7] representing limits to the separation performance achievable by state-of-the-art polymer membranes.

Solution-processable polymers of intrinsic microporosity (PIMs) [8–21] are a rapidly emerging class of materials which possess microporosity (IUPAC: pore diameter $<20$ Å) by virtue of rigid fused-ring backbones that are kinked to promote inefficient packing in the solid state. They are interesting candidates for membrane-based gas separation because of their unique ability to combine the microporosity characteristics of inorganic materials with both the functional tunability offered by organic chemistry and solution-processability of polymers. The prototypical PIM-1 offered combinations of permeability and selectivity that surpassed Robeson's upper bounds from 1991 and redefined those in 2008 for important gas pairs, including $O_2/N_2$ and $CO_2/CH_4$. Strong research efforts have subsequently produced PIMs that continue to challenge the state-of-the-art with more developed microporosity, surface areas exceeding 1000 $m^2/g$ and commendable gas separation performance [22,23].

In particular, researchers have taken three core directions to manipulate the structural platform, and thus gas transport properties, of ladder-type PIM-1: (i) varying the spiro-carbon contortion

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site via novel monomers [16,22,24–27], (ii) varying the benzodioxane arms between contortion sites via novel monomers [18,19,21,27], and (iii) post-polymerization modification at the nitrile groups [13,20,28,29]. Post-polymerization modification is a convenient means of introducing $CO_2$-philic functionalities – i.e., nitrogen containing heterocycles or hydroxyl moieties – onto the main chain that can improve Lewis acid–Lewis base interactions with $CO_2$ [30]. Only a few reports provide successful post-polymerization reactions using hydrophilic functionalities at the nitriles of PIM-1 because it often yields intractable products [13,20,28,31]. Du et al. [28] prepared a carboxylated PIM-1 (COOH-PIM-1) via base hydrolysis of the nitriles to carboxylic acids. The gas transport properties were tunable depending on the degree of hydrolysis, obeying a tradeoff relationship where ideal $\alpha$ $(CO_2/N_2)=26$ increased up to 136% relative to PIM-1 but $P(CO_2)=$ 620 Barrer decreased by 92%. Du et al. [20] also reported a tetrazole-functionalized PIM-1 (TZ-PIM-1), prepared by azide-based ‘click-chemistry’, which demonstrated significant improvement in $\alpha$ $(CO_2/N_2)=41$ over PIM-1 in mixed-gas experiments and a modest increase in $\alpha(CO_2/CH_4)$ $\sim 22$ concurrent with a loss in $P(CO_2)$ $\sim 3000$ Barrer. Mason et al. [13] prepared a thionated PIM-1 (Thio-PIM-1) using phosphorous pentasulfide in the presence of sodium sulfite to yield an ideal $\alpha(CO_2/CH_4)=20$ with $P(CO_2)=1120$ Barrer – again, improved selectivity over PIM-1 for $CO_2$ at the acceptable expense of permeability [13]. Recently, Patel and Yavuz reported [31] an amidoxime-functionalized PIM-1 (AO-PIM-1) prepared by rapid reaction of the nitriles with hydroxyl amine under reflux conditions, introducing ample basic nitrogen and hydroxyl groups while maintaining high surface area ( $>500$ $m^2/g$). Structurally similar to the monoethanolamine (MEA) used in power plant $CO_2$ scrubbing processes, the amidoxime functionality has been integrated into sorbents, including solution-processable porous polymers, with $CO_2$ capture properties surpassing those of activated charcoal [32,33]. To date, however, the gas transport properties of membranes derived from such promising amidoxime-containing polymers have not been reported.

Based on the pure-gas testing summarized above, a major effect of the addition of pendant polar functionalities onto the backbone of PIM-1 is apparently a tightening of the microstructure, due to enhanced intermolecular interactions, by which favorable increases in selectivity for $CO_2$ are accompanied by acceptable reductions in permeability. However, except for the TZ-PIM-1, no studies regarding the stability of separation performance for these functionalized PIMs under more realistic, mixed-gas feeds have been carried out. Pure-gas testing cannot reveal the potentially detrimental effects of non-ideal phenomena such as competitive sorption and plasticization, which can elicit significant reductions in $CO_2/CH_4$ selectivity [34–42]. That is, the pure-gas permeability/selectivity trade-off performance assessments typically used for novel membrane materials can be misleading when gas mixtures containing highly sorbing feed components like $CO_2$ are involved. This may be particularly prominent when the $CO_2$ sorption capacity of the matrix is enhanced by interactions with the basic and polar functionalities, as conventionally postulated for the functionalized PIMs noted above. Few reports exist on the organic vapor/gas mixture transport properties of various PIMs [36,37,39,42] and their mixed-gas $CO_2/CH_4$ performance [17,20,23,43,44]. Only one of these reports addresses the stability of $CO_2/CH_4$ mixed-gas selectivity for the prototypical PIM-1, but without mention of mixed-gas permeabilities [43]. Knowledge of these mixed-gas permeabilities is required for fundamental insights into the reasons for the selectivity behavior as well as how well the polymer copes with plasticization or competitive sorption phenomena.

Here, we report the structure/property relationships of PIM-1 and its microporous amidoxime-functionalized counterpart AO-PIM-1. A qualitative assessment of the microstructural changes was obtained via NLDFT-based analysis of physisorption isotherms ($N_2$ at -196 °C; $CO_2$ at 0 °C) as well as pure-gas transport properties for He, $H_2$, $N_2$, $O_2$, $CH_4$ and $CO_2$ at 2 bar and 35 °C for both PIM-1 and AO-PIM-1. Pure- and mixed-gas permeability and selectivity isotherms for $CO_2$ and $CH_4$ are presented for both polymers at 35 °C under aggressive conditions involving 50:50 $CO_2/CH_4$ mixtures up to high pressures (20 bar), spanning the range of typical wellhead $CO_2$ partial pressures (5–10 bar). The effect of the basic and polar amidoxime functionality on performance improvements and stability is evaluated in direct comparison to the parent ladder-type PIM-1 polymer, with special attention to mitigation of plasticization.

## 2. Experimental

### 2.1. Polymer synthesis

The parent PIM-1 polymer (Fig. 1) was synthesized according to a high-temperature, high-concentration method [45] reported by Du

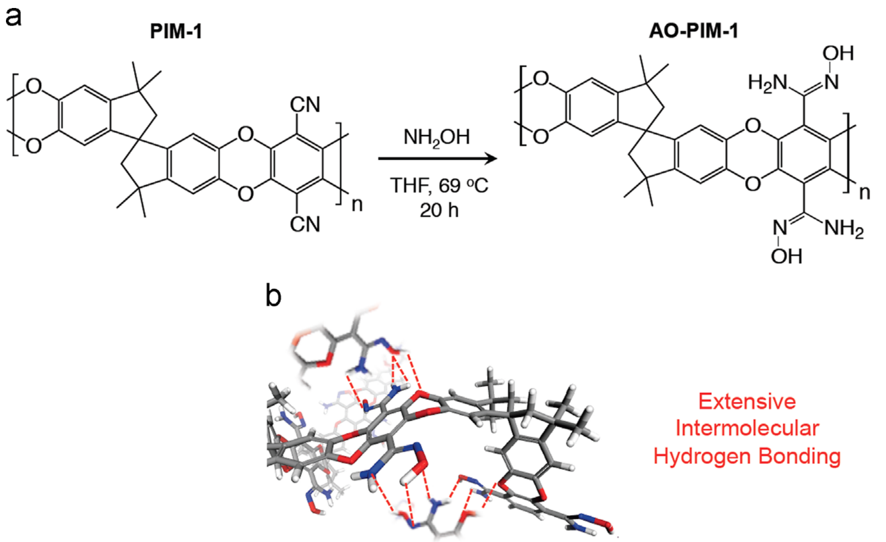

**Fig. 1.** (a) Synthetic scheme for amidoxime-functionalized PIM-1 (AO-PIM-1); (b) potential intermolecular hydrogen-bonding in the contorted energy-minimized structure of AO-PIM-1 (Forcite module, Materials Studio 6.0, Accelrys).