**Title:** Sorption and permeation of H2S, CO2, CH4, and N2 in amine-functionalized microporous polymers.

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**Abstract:**

Current industrial gas separations, such as CO2 removal from natural gas, rely primarily on energy-intensive and environmentally unfriendly processes. Polymer membranes offer a more sustainable alternative due to their energy-efficiency and ease of operation. However, membranes are infrequently deployed because of separation performance and lifetime limitations of industrial polymers. In this work, the effect of backbone functionalization and polymer packing structure on transport performance was investigated for a high-performance polymer of intrinsic microporosity, PIM-1, and a new microporous polymer based on a poly(aryl ether) (PAE) backbone. Generally, PIMs have shown excellent pure-gas separation performance due to their rigid backbones, inefficient packing, and high free volume. However, their out-of-equilibrium structures make PIMs susceptible to physical aging (i.e., densification of structure overtime) and plasticization (i.e., swelling when in contact with CO2 or H2S), and the pure-gas transport performance for PIMs rarely matches mixed-gas performance for industrially relevant conditions.

 Recently, we reported on the mixed-gas and high-pressure gas transport properties of six functionalized PIMs for CO2 capture and purification. Low-pressure mixed-gas tests indicated a relationship between CO2 sorption affinity and increased CO2/CH4 mixed-gas selectivity compared to pure-gas calculations for PIMs considered. The best results were found for amine-functionalized PIM-1 (PIM-NH2), which shows a 2.4- and 3.5-fold increase in mixed-gas CO2/CH4 and CO2/N2 selectivity, respectively. PIM-NH2 also retained high mixed-gas selectivity up to a total mixed-gas pressure of 26 bar. Our results demonstrated the promise of amine functionalization for developing sorption-selective and plasticization-resistant membranes for natural gas separations as well as CO2 capture. Here, we extend this work as we probe the generalizability of our findings with an amine-functionalized PAE. PAE-NH2 shows exceptional increases in CO2/CH4 and CO2/N2 mixed-gas selectivities (compared to pure-gas) similar to those observed for PIM-NH2. Moreover, pure-gas CO2 sorption for PAE-NH2 was significantly higher than that of PAE-CN, which suggests that increases in mixed-gas performance were driven by sorption. The strength of the CO2-polymer interactions were quantified through calculation of isosteric heats of sorption for CO2 in PIM-1, PIM-NH2, PAE-CN, and PAE-NH2. Amine-functionalized samples showed significantly more exothermic interactions compared to those of nitrile-functionalized analogues, indicating stronger interactions for the amine with CO2. Notably, PAE-NH2 also showed exceptional plasticization resistance up to a total mixed-gas pressure of 26 bar.

 Finally, to evaluate the performance of the polymers in aggressive, toxic gas conditions, the H2S sorption capacity as well as pure- and mixed-gas transport of all four sampleswas tested. Compared to nitrile-functionalized analogues, amine-functionalized samples did not show as strong of an affinity increase with H2S as was observed with CO2 up to 10 bar. Taken together, our results indicate the development of H2S resistant and highly CO2-selective polymers for CO2 capture and natural gas purification.