Multidimensional MOFs Mixed Matrix Membranes for Efficient Gas Separation

by

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Abstract

Membrane separations are crucial in the chemical industry, with polymeric materials traditionally used due to their cost and mechanical benefits. However, they face challenges in permeability–selectivity trade-off, and in stability. Metal–organic frameworks (MOFs) offer potential solutions with their customizable properties but are difficult to manufacture. Mixed-matrix membranes (MMMs), which incorporate MOFs into polymers, mitigate some issues, yet high MOF loading can lead to aggregation and voids. This thesis investigates the promising potential of MMMs for efficient and improved gas separation, leveraging unique morphologies and understanding the dynamics of MOF–polymer interactions. First, the novel branch-shaped ZIF-8 (BZ) was developed and incorporated into polymer matrix, which successfully established a percolated network at loadings as low as 20 wt%, showing permeability boost. Also, it showed suppressed polymer chain dynamics and a smaller diffusion cut-off than traditional ZIF-8, which resulted in an enhanced membrane stability and superior performance in H_2-based separations. BZ was studied further by investigating temperature-dependent properties of MMMs. BZ and control ZIF-8 (CZ) MMMs exhibited unique gas transport behaviour in relation to temperature shifts, with BZ MMM demonstrating more significant temperature dependence for H_2-based separations. As temperature decreases, the H_2/CH_4 permselectivity of BZ MMMs drastically increases, with minor changes in H_2 permeability. Conversely, at higher temperatures, separation performance aligns with that of CZ MMM, showing continuous yet broad control over the gas performance. To understand the origin of this selectivity difference, facet-specific gas transport in polymer nanocomposites was studied with the hypothesis of BZ consist of facet 100, which characterize less thermally stable polymorph, cubes. A key finding is the interaction between 100 facet and polyimides, which enhances hydrogen-based and ethylene/ethane separation, particularly at subambient temperatures, which is consistent with the trend observed for BZ MMMs. In conclusion, this thesis addresses the enhancement of MMMs through innovative morphological approaches, where percolated network enhances permeability and 100 facet termination may restrict the MOF–polymer interphase confinement, leading to high selectivity for small gas pairs, which is very difficult to achieve at the same time. The temperature effects and facet-termination effects on gas transport in MMMs can also offer substantial contributions to the development and optimization of mixed matrix membranes for efficient gas separations.

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