Fluorine-containing polyimide/polysilsesquioxane carbon molecular sieve membranes for C_3H_6/C_3H_8 separation

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Herein, we investigated the effect of thermo-oxidative crosslinking of siloxanes on the C_3H_6/C_3H_8 separation performance of carbon molecular sieve (CMS) membranes derived from polymer blends containing a fluorine-containing polyimide and a ladder-structured polysilsesquioxane (P/LPSQ). The P/LPSQ precursors self-generated fluorinated gases, which possibly lead to cleavage of the double-stranded siloxanes during pyrolysis. At the same time, residual siloxanes underwent thermo-oxidative crosslinking, which resulted in the densification into nonporous inorganic SiO_2 phases. Such impermeable SiO_2 phases adversely affected the gas diffusion, decreasing C_3H_6 permeability, but contributed to the significant enhancement in the C_3H_6/C_3H_8 selectivity up to as much as 67 because of the substantially enhanced diffusivity selectivity. Density functional theory-based pore size distribution analysis exhibited that the modality of the pore distributions sharpened in the ultramicropore regime with increase in LPSQ content, supporting the enhancement in selectivity.