Effective separation of hydrocarbon mixtures by zeolitic imidazolate frameworks-8 (ZIF-8) membranes

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The separation of hydrocarbon mixtures is an important but challenging process in the petrochemical industry. Thermally and hydrothermally stable microporous membranes with intrinsic high permeability and selectivity are highly demanded. ZIFs are microporous materials and belong to the new class of metal–organic frameworks (MOFs). ZIF-8 is formed by bridging 2-methylimidazolate anions and zinc cations resulting in a sodalite (SOD) topology with a pore size of about 0.34 nm. Herein, it was demonstrated that ZIF-8 membranes synthesized in aqueous solutions exhibited effective separation of ethane/propane and propylene/propane binary mixtures.

Dense ZIF-8 membranes supported on porous α-alumina discs (2 mm thickness and 22 mm diameter) were synthesized through a novel hydrothermal seeded growth method. The method mainly includes three steps: i) hydrothermal synthesis of ZIF-8 nanoparticles for seeding; ii) preparation of seed layers on porous support surface; and iii) secondary growth under hydrothermal synthesis conditions to convert the seed layer into a dense membrane. The detailed experiments are shown as follows. First, ZIF-8 seeds were prepared by stirring the synthesis solution \( \text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}: 2\text{-methylimidazole}: \text{H}_2\text{O} = 1: 70: 1200 \) at room temperature for 12 h. Then seeding process was conducted by the slip-coating technique. Finally, the seeded supports were immersed on the secondary solution \( \text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}: 2\text{-methylimidazole}: \text{H}_2\text{O} = 1: 70: 6000 \) for hydrothermal synthesis at 30 °C for 6 h.

Fig. 1. SEM pictures of (a) top-view and (b) cross-section view of the synthesized ZIF-8 membrane. (c) Single gas permeation measured on ZIF-8 membranes by Wicke-Kallenbach technique at room temperature (~23°C).\(^{11}\)

From the top-view of the ZIF-8 membrane, as shown in Fig. 1a, we can see that crystals are well inter-grown to form a continuous membrane. The thickness of the membrane is ca. 2.5 µm (Fig. 1b). The single-gas permeation results showed a clear cut-off between ethane and propane (Fig. 1c), further indicating that the membrane was compact. The permeances of ethane and propane are in the order of \( 10^{-8} \) and \( 10^{-10} \) mol/m² s Pa, respectively. The permeation experiments of \( \text{H}_2/\text{propane} \) and ethane/propane binary mixtures showed the separation factor were ca. 500 and 80, respectively. To the best of our knowledge, this is the first example for effective separation of ethane and propane by membrane technique. As for the separation of propylene/propane binary mixture, we also found that the performance of ZIF-8 membrane is
beyond the "upper-bound trade-off line" of both polymeric and carbon membranes (Fig. 2). This indicates that the overall performance of ZIF-8 membranes is superior and thus more commercially attractive.

In conclusion, thin and dense ZIF-8 membranes on porous α-alumina porous discs have been successfully prepared in aqueous solutions. The process is more economical and green compared to other synthesis procedures that are conducted in organic solvents. The membrane exhibited excellent separation performance for H₂/propane, ethane/propane and propylene/propane binary mixtures. The performance for separation of propylene/propane is beyond the "upper-bound trade-off line" of both polymeric and carbon membranes.

Reference


Keywords: Metal-organic framework, ZIF-8 membrane, propylene/propane separation, ethane/propane separation