Metal-Organic Frameworks (MOFs) based Mixed Matrix Membranes for aromatic and saturated hydrocarbons separation

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Abstract

Separation of aromatic and saturated hydrocarbons such as is one of the most challenging separations in chemical and petrochemical industries due to their tight boiling point and azeotrope formation. Separation of toluene from n-heptane mixture is useful to produce aromatic-lean motor fuels which are much recommended. The conventional process like extractive distillation, liquid-liquid extraction has been used. However, they require high energy input, multiple steps and need for specific reagents. Selective transport or affinity-based separation through membranes become alternative to the traditional energy-intensive process since the complete removal of toluene molecules is not necessary here [1-4].

In literature, pervaporation was the most common approach used for aromatic-aliphatic separation which exhibits lower flux. Here the specific affinity of toluene with membrane materials is exploited, and the membrane process is designed using transmembrane pressure as driving force. The solvent resistant polymer like polyimide and the filler made of metal-organic frameworks (MOFs) based on copper and silver showing specific interactions cation-π and π-π interactions between the aromatic functional groups have been selected. For this purpose, mixed matrix membrane (MMMs) incorporating MOFs involving Cu^{2+} and its reduced form Cu^{+} that exhibit an affinity for aromatic hydrocarbons have been selected. MOFs have been synthesized under solvothermal condition via conventional electrical heating. To control over crystal size as well as crystallization process, many alternative synthesis routes have been investigated including the use of modulator molecule [3-5].

The modulator assisted MOFs synthetic protocol illustrated the production of monodispersed MOFs whose size is entirely dependent on the concentration of lauric acid [6]. The addition of the modulator mainly suppresses the framework extension more efficiently by influencing the nucleation process due to the presence of the competitive interaction for the complexation of the Cu^{2+} cations thereby decreasing the oversaturation of the precursor materials. Figure 1 shows the scanning electron microscopic (SEM) image of MOFs (left) and the MMMs performance for separation of heptane and toluene (right). The non-doped PI membrane showed no affinity for heptane and toluene separation. The increase in toluene fractions in permeate is the clear indication of affinity of a benzene ring with Cu^{2+} or Cu^{+} moieties of MOFs.

A simple, straightforward method of modulator assisted MOF synthesis is cheaper and controlled process where uniform size and nanoscale is promised. The lower pressure based membrane separation process become alternative to expensive traditional process as well as pervaporation offering precise control over separation with ten-time higher membrane permeability compared to pervaporation mentioned previously in the literature [1,2].

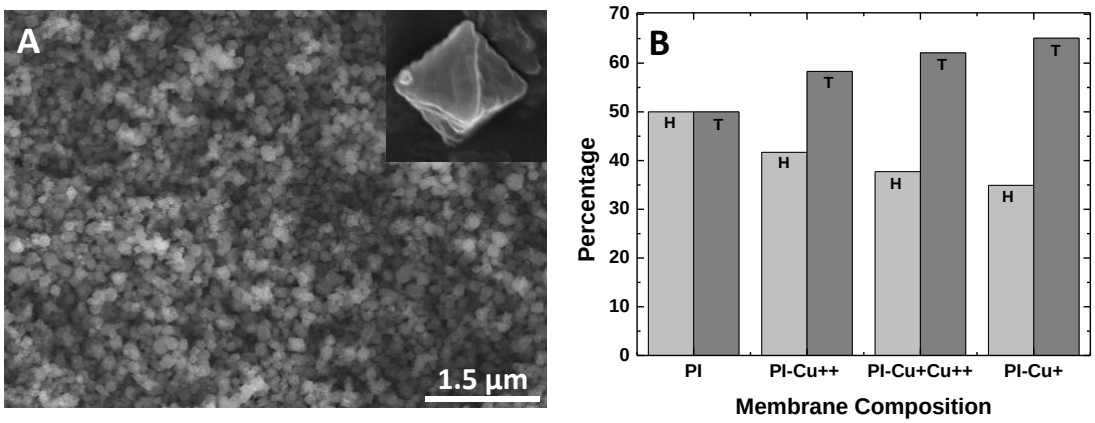


Figure 1. MOFs synthesis and membrane performance: (A) Cu^{2+} MOFs for [Lauric acid] = 0.01 M and (B) Membrane performance for polyimide (PI) with different proportions of Cu^{+} and Cu^{2+} fraction for n-heptane (H) and Toluene (T) separation

References

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