Chemical Engineering Doctoral Defense

Stability, Transport and Modification of Zeolitic Imidazolate Framework-8 Membranes for Light Hydrocarbon Separations

School for Engineering of Matter, Transport and Energy

Joshua B. James
Advisor: Dr. Jerry Lin

abstract

The separation of light hydrocarbon mixtures produced after hydrocarbon cracking is of significant economic importance. Membrane technology is a viable option to debottleneck light hydrocarbon distillation technology and greatly reduce the energy burden associated with such separations. Zeolitic imidazolate frameworks (ZIFs) are a new subclass of microporous metal-organic frameworks (MOFs) containing zeolitic topologies that enable precise control of the framework's steric and electronic properties. ZIF-8 has already proven to be superior to most membrane materials in terms of separation performance and room temperature stability at the lab scale for propylene/propane (C3) mixtures. However, to date, little is known about the static thermal stability ZIF-8 for high temperature separation applications. Additionally, ZIF-8 is an attractive material and template framework for surface modification to separate other light hydrocarbon mixtures such as ethylene/ethane (C2) and hydrogen/hydrocarbon gasses. In this work, the thermal stability and C2 transport properties of ZIF-8 membranes were analyzed and elucidated. ZIF-8 crystals maintain their crystallinity up to 200○C while alumina supported ZIF-8 membrane thin films are thermally stable below 150○C under static conditions. At temperatures above 250○C, this work enables postulation that the ZIF-8 framework partially carbonizes into an imidazole-Zn-azirine structure. Ethylene/ethane separation studies show that the transport mechanism is controlled by adsorption rather than diffusion. Low activation energy of diffusion values for both C2 molecules and limited energetic/entropic diffusive selectivity are observed for both molecules despite being larger than the nominal ZIF-8 pore aperture and is due to pore flexibility. Finally, post-synthetic membrane surface ligand exchange was performed using 5,6 dimethylbenzimidazole (5,6 DMBIm) to modify the ZIF-8 membrane surface for light hydrocarbon separation enhancement. A ligand exchange mechanism was proposed for the incorporation of 5,6 DMBIm into the ZIF-8 structure. C3 olefin/paraffin and H2/C2 separation performances were improved after modification.

October 10, 2017; 9:30 AM; ECG 215