



Iron-containing carbon molecular sieve membranes for advanced olefin/paraffin separations



Yu-Han Chu^a, David Yancey^b, Liren Xu^c, Marcos Martinez^c, Mark Brayden^d, William Koros^{a,*}

^a School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

^b The Dow Chemical Company, Midland, MI 48667, USA

^c The Dow Chemical Company, Freeport, TX 77541, USA

^d The Dow Chemical Company, Plaquemine, LA 70765, USA

ARTICLE INFO

Keywords:

Carbon molecular sieve
Olefin/paraffin separation
Iron-containing membrane

ABSTRACT

In this work, carbon molecular sieve (CMS) dense film membranes derived from 6FDA-DAM:DABA (3:2) polyimide precursor were studied for separation of mixed olefins (C₂H₄ and C₃H₆) from paraffins (C₂H₆ and C₃H₈). Olefin-selective CMS membranes with high performance can be made by pyrolysis of metal-containing polymeric precursors. Pyrolyzed at 550 °C with a fast ramp rate, CMS membranes with integrated Fe²⁺ (2.2 wt% in the precursor) showed 19% higher C₂H₄/C₂H₆ and 11% higher C₃H₆/C₃H₈ sorption selectivity than that of the neat CMS membrane. Additional investigations with a quaternary mixture feed (C2 and C3 hydrocarbons) show that C₂H₄ permeability above 10 Barrers with C₂H₄/C₂H₆ permselectivity near 11 were achieved for the 3.2 wt% Fe loading case. Although Fe incorporation did not appear to promote C₃H₆/C₂H₆ permselectivity, Fe is useful to improve C2 pair olefin/paraffin separation. Deconvolution of the C₂H₄/C₂H₆ permselectivity for our more extensively studied 2.2 wt% loading case was also revealing. While both sorption and diffusion selectivity increased due to the Fe incorporation, a larger influence is seen on the diffusion selectivity versus the sorption selectivity. Hypotheses to explain this surprising outcome are offered to guide future work.

1. Introduction

Light olefins, such as ethylene (C₂H₄) and propylene (C₃H₆), are key building blocks for petrochemicals and polymers (e.g., polyethylene and polypropylene). For olefin production, separation of olefins from paraffins is required for subsequent use. The separation is typically carried out by distillation which is energy intensive due to the similar properties of the olefin and corresponding paraffin pairs. It is, therefore, appealing to develop alternative technology to replace or modify such conventional methods of olefin/paraffin separation.

Membrane separation is an attractive alternative to traditional thermally driven methods for gas separation because of potentially lower capital and operating costs [1]. Conventional polymeric membranes have been well studied and have shown good mechanical and chemical properties. Despite these advantages, solution-processable polymers have performance limited by a trade-off relationship (commonly referred to as the polymer upper bound) between productivity (permeability) and separation efficiency (selectivity) for common gas pairs, including C₂H₄/C₂H₆ and C₃H₆/C₃H₈ [2–4]. Hence, polymeric membranes are limited with respect to olefin/paraffin separation performance, and it is desirable to surpass these upper bounds.

Carbon molecular sieve (CMS) membranes, a new class of materials for gas separations, have been studied for binary olefin/paraffin separations (C₂H₄/C₂H₆ and C₃H₆/C₃H₈) [5–8], and it is found that CMS membranes with rigid size-selective ultramicropores are promising to surpass conventional polymer membranes. Xu et al. [9] have demonstrated that the ‘slit-like’ structures of CMS membranes enable separation of bulk olefins (C₂H₄ and C₃H₆) from paraffins (C₂H₆ and C₃H₈). A proof of concept study further demonstrated that a hybrid system with this olefin-selective membrane can not only debottleneck the current splitters but also potentially eliminate the need for them [9]. In this paper, we further pursue this approach and report novel CMS membranes containing metal ions for such separation of bulk olefins from paraffins.

As will be discussed, achieving this goal requires balancing more factors than is needed for a standard binary olefin/paraffin separation (C₂H₄/C₂H₆ or C₃H₆/C₃H₈) based solely on size. Specifically, the large olefin (C₃H₆) is only slightly more compact in molecular sieving size than the small paraffin (C₂H₆), which makes an olefin-selective membrane challenging. Previous studies showed that open metal sites in metal-organic framework (MOF) materials can selectively interact with olefins [10,11]. Therefore, it is envisioned that by including metal ions

* Corresponding author.

E-mail address: wjk@chbe.gatech.edu (W. Koros).

<https://doi.org/10.1016/j.memsci.2017.11.052>

Received 21 July 2017; Received in revised form 3 October 2017; Accepted 19 November 2017

Available online 22 November 2017

0376-7388/ © 2017 Elsevier B.V. All rights reserved.

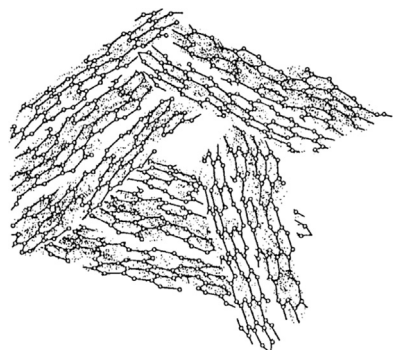


Fig. 1. Schematic of turbostratic structure of CMS membranes with disordered sp^2 hybridized carbon sheets [12,13].

into CMS membranes, the C_3H_6 has the potential for sorption selectivity enhancement to further promote its permselectivity relative to C_2H_6 . The advanced metal-containing CMS membranes made in this work have significantly improved bulk olefin/paraffin separation performance, which will be reported later.

2. Background and theory

2.1. Structure of CMS membranes

CMS membranes can be formed by thermal decomposition of polymer precursors through heating in an inert or vacuum environment. The residual material is primarily carbon after removal of volatile decomposition compounds during pyrolysis. Most CMS membranes used for gas separation have a disordered sp^2 hybridized carbon sheet morphology, which is amorphous and more or less isotropic; referred to as a so-called turbostratic structure as illustrated in Fig. 1 [12,13].

The resulting CMS membranes consist of ultramicropores ($< 7 \text{ \AA}$) within the carbon sheets while micropores (7–20 \AA) can be formed from packing imperfections between the carbon sheets. Unlike crystalline molecular sieve materials (e.g., zeolites), the pore structure of CMS materials is not sharply defined and can be idealized with a ‘slit-like’ structure, as shown in Fig. 2 (a). The micropores are connected by the ultramicropores, forming a selective passageway for gas to be transported. An idealized pore size distribution in a CMS membrane is envisioned as being bimodal, as illustrated in Fig. 2 (b) [14]. For gas separation applications, the ultramicropores offer selective molecular sieving, while micropores allow for sorption sites and high diffusion coefficients. The combination of ultramicropores and micropores make CMS membranes an attractive material for gas separations.

2.2. Transport in CMS membranes

Gas transport through either a non-porous polymer membrane or a

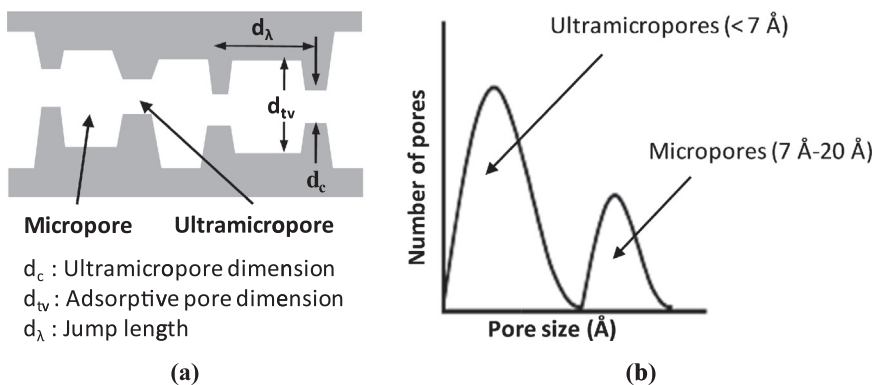


Fig. 2. (a) Idealized ‘slit-like’ pore structure of CMS membranes and (b) idealized bimodal pore size distribution in CMS membranes [14].

CMS membrane is described by the sorption-diffusion model [15,16]. Permeability (productivity) and selectivity (separation efficiency) are two intrinsic properties used to evaluate the membrane material performance. Permeability is defined as a partial pressure and thickness normalized flux, given in Eq. (1).

$$P_A = \frac{N_A \cdot \ell}{\Delta p_A} \quad (1)$$

where N_A is the flux of penetrant A through the membrane of thickness ℓ , and the partial pressure of A (Δp_A) is the driving force across the membrane. When significant non-ideality in the gas phase exists, the partial pressure is simply replaced by the component fugacity. Typically, Barrer is used as the unit of permeability, where

$$1 \text{ Barrer} = 10^{-10} \frac{\text{cm}^3(\text{STP}) \cdot \text{cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}} \quad (2)$$

Permeability can also be expressed as a product of an average kinetic diffusion coefficient (\bar{D}_A), and a thermodynamic sorption coefficient (\bar{S}_A), as shown below.

$$P_A = \bar{D}_A \cdot \bar{S}_A \quad (3)$$

The ideal permselectivity of a membrane with negligible downstream pressure is equal to the ratio of single-component gas permeabilities, which is also the product of diffusion selectivity ($\frac{\bar{D}_A}{\bar{D}_B}$) and sorption selectivity ($\frac{\bar{S}_A}{\bar{S}_B}$). Separation factors or selectivity (when stage cut is low and the downstream pressure is negligible compared to the upstream pressure) for multi-component gas mixture are defined as a ratio of permeate-side (y) and feed-side (x) mole fractions of components A and B . Hence,

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{\bar{D}_A}{\bar{D}_B} \right) \cdot \left(\frac{\bar{S}_A}{\bar{S}_B} \right) = \alpha_D \cdot \alpha_S \quad (4)$$

$$\alpha_{A/B} = \frac{(y_A/y_B)_{\text{permeate}}}{(x_A/x_B)_{\text{feed}}} \quad (5)$$

The average sorption coefficient (\bar{S}_A) in Eq. (6) is defined as pressure normalized equilibrium concentration of gas penetrant (C_A) sorbed by a material at a given partial pressure (p_A), and depends on the condensability of the gas penetrant as well as the interaction with the sorbent material.

$$\bar{S}_A = \frac{C_A}{p_A} \quad (6)$$

For CMS membranes, Langmuir void filling sorption is considered to be the mechanism in which gas penetrants sorb into micropores in the CMS membranes. The sorption coefficient is, therefore, given by:

$$\bar{S}_A = \frac{C_A}{p_A} = \frac{C'_{HA} \cdot b_A}{1 + b_A \cdot p_A} \quad (7)$$

where C'_{HA} is the Langmuir saturation constant and b_A is the Langmuir

Download English Version:

<https://daneshyari.com/en/article/7020326>

Download Persian Version:

<https://daneshyari.com/article/7020326>

[Daneshyari.com](https://daneshyari.com)