



Matrimid[®] derived carbon molecular sieve hollow fiber membranes for ethylene/ethane separation

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ARTICLE INFO

Article history:

Received 29 May 2011

Received in revised form 22 June 2011

Accepted 26 June 2011

Available online 1 July 2011

Keywords:

Carbon molecular sieve
Hollow fiber membrane
Olefin-paraffin separations
Glass transition
Defect-free

ABSTRACT

Carbon molecular sieve (CMS) membranes have shown promising separation performance compared to conventional polymeric membranes. Translating the very attractive separation properties from dense films to hollow fibers is important for applying CMS materials in realistic gas separations. The very challenging ethylene/ethane separation is the primary target of this work. Matrimid[®] derived CMS hollow fiber membranes have been investigated in this work. Resultant CMS fiber showed interesting separation performance for several gas pairs, especially high selectivity for C₂H₄/C₂H₆. Our comparative study between dense film and hollow fiber revealed very similar selectivity for both configurations; however, a significant difference exists in the effective separation layer thickness between precursor fibers and their resultant CMS fibers. SEM results showed that the deviation was essentially due to the collapse of the porous substructure of the precursor fiber. Polymer chain flexibility (relatively low glass transition temperature (T_g) for Matrimid[®] relative to actual CMS formation) appears to be the fundamental cause of substructure collapse. This collapse phenomenon must be addressed in all cases involving intense heat-treatment near or above T_g . We also found that the defect-free property of the precursor fiber was not a simple predictor of CMS fiber performance. Even some precursor fibers with Knudsen diffusion selectivity could be transformed into highly selective CMS fibers for the Matrimid[®] precursor. To overcome the permeance loss problem caused by substructure collapse, several engineering approaches were considered. Mixed gas permeation results under realistic conditions demonstrate the excellent performance of CMS hollow fiber membrane for the challenging ethylene/ethane separation.

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1. Introduction

Olefin/paraffin separation is a large potential market for gas separation membranes. In 2008, the global ethylene production capacity was 126.7 million tons, which represents an increase of nearly 6% from the 2007 capacity [1]. The currently dominant olefin/paraffin separation technology, cryogenic distillation, is highly energy intensive due to the very low and close boiling points of ethylene (169.4 K) and ethane (184.5 K) [2,3]. For example, a typical ethylene/ethane separation is performed at around $-25\text{ }^\circ\text{C}$ and 320 psig in a column containing over 100 trays [4].

Extensive research has been devoted to identifying alternative separation technologies for the C₂H₄/C₂H₆ pair, and membranes have emerged as a promising choice due to low capital, operating and maintenance costs [5]. Currently, replacing distillation columns with membrane modules is still not feasible due to the relatively low selectivity and stability of current membranes for

ethylene and ethane separation. Nevertheless, a hybrid distillation-membrane system has been proposed by several researchers [2,6]. The hybrid system, which consists of a distillation column and a parallel membrane unit, provides a practical way for retrofitting current distillation units. Substantial savings in total costs and energy can be obtained based on simulation results [2].

Current processible polymeric membrane materials appear to have reached an upper limit in the productivity–selectivity trade-off [7,8]. Especially, due to the very similar physical properties of ethylene and ethane, the current best performing polymers can only deliver relatively low C₂H₄/C₂H₆ separation selectivity. Seeking novel membranes that can overcome the trade-off limits is of great interest. Recently, carbon molecular sieve (CMS) membranes have shown permeation and separation properties exceeding those of their polymeric precursor membranes. Such high performance has been observed in O₂/N₂, CO₂/CH₄, C₃H₆/C₃H₈, etc. [9–14]. The C₂H₄/C₂H₆ separation by CMS membranes has also been investigated by some researchers [15,16]; however, the inherent difficulty in separating this gas pair has retarded the progress for this challenging separation case. In addition, CMS membranes exhibit excellent thermal and chemical stability as well as stability under high pressure gas exposure, while for the polymer membrane case,

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plasticization caused by CO₂ or other hydrocarbons is detrimental to the membrane performance. Although CMS membrane is more brittle, previous work by Vu and Koros showed CMS hollow fiber module could be used for natural gas separation very stably under high feed pressure up to 1000 psi [17]. Thus, the CMS membrane for aggressive C₂H₄/C₂H₆ separations is also expected to be practical.

Highly permeable micropores, coupled with molecular sieving ultramicropores, enable the intrinsically high performing CMS versus polymeric membranes [12,13]; however, CMS materials are not yet viable for high performance asymmetric hollow fibers, which provide high surface area/volume ratio. Such fibers show improved stability over dense films, and are expected to be less expensive and easier to produce than supported zeolite membranes [18], however, most CMS research still focuses on dense films or supported membranes on prefabricated porous support [19,20]. Only a few literature reports consider the pyrolysis of dense flat films for comparison to actual asymmetric hollow fibers of the same precursor material. This important comparative topic is considered in the current paper.

As noted above, this work focuses on application of CMS membrane for the relatively little studied gas pair (C₂H₄/C₂H₆). The fundamental relationship between dense films and hollow fibers is also considered in this work. As a commercially available high-performing polyimide, Matrimid® was used in this study as the precursor material for CMS membranes. The Matrimid® derived CMS dense films were formed under a wide range of pyrolysis temperatures, and the permeation properties were compared with currently available polymer material performance. Further comparison between dense film and hollow fibers clarifies the relationship between the two membrane configurations. The impact of Matrimid® precursor fiber properties on CMS hollow fiber performance is discussed in detail.

2. Experimental

2.1. Materials

The polymer used in this work, Matrimid® 5218 (BTDA-DAPI), was purchased from Huntsman International LLC. The polymer was dried before use.

2.2. Pyrolysis setup

The pyrolysis setup was similar to previously reported systems [9,17]; however, some modifications were made to achieve a better control of the pyrolysis parameters. A 3-zone furnace (Thermcraft, Inc., model XST-3-0-24-3C, Winston-Salem, NC) was well controlled by a multi-channel temperature control (Omega Engineering, Inc., model CN1504TC, Stamford, CT). With 3 thermocouples independently connected to 3 channels of the controller, the temperature profile inside the quartz tube (National Scientific Company, GE Type 214 quartz tubing, Quakertown, PA) is quite uniform. Sealing of the quartz tube was insured by an assembly of a metal flange with silicon O-rings (MTI Corporation, Richmond, CA), which was applied to both ends of the quartz tube. The furnace can be operated under vacuum or inert gas purge mode. Under vacuum operations, the vacuum level was insured to be ≤15 mtorr, and was monitored by a 0–1000 mtorr range pressure transducer (MKS, model 628 Absolute Capacitance Manometer, Andover, MA).

2.3. Preparation of dense flat CMS membranes

Precursor dense flat films were fabricated by a solution casting method. The preparation procedure of film casting and pyrolysis is similar to that in previous work [9,12,13].

Table 1

Pyrolysis temperature protocol A1: for comparative study of dense films and hollow fibers (final temperature up to 550 °C).

	Start temperature (°C)	End temperature (°C)	Ramp rate (°C/min)
Step 1	50	250	13.3
Step 2	250	$T_{\max}-15$	3.85
Step 3	$T_{\max}-15$	T_{\max}	0.25
Step 4	T_{\max}	T_{\max}	Soak for 2 h

Table 2

Pyrolysis temperature protocol A2: for comparative study of dense films and hollow fibers (final temperature above 550 °C up to 800 °C).

	Start temperature (°C)	End temperature (°C)	Ramp rate (°C/min)
Step 1	50	250	13.3
Step 2	250	535	3.85
Step 3	535	550	0.25
Step 4	550	$T_{\max}-15$	3.85
Step 5	$T_{\max}-15$	T_{\max}	0.25
Step 6	T_{\max}	T_{\max}	Soak for 2 h

A quartz plate with 2 mm deep and 2 mm wide ribs (United Silica Products, Franklin, NJ) was used as the support for films in the tube furnace. Pyrolysis was performed under vacuum for a range of temperatures between 500 °C and 800 °C, specifically at 500 °C, 525 °C, 550 °C, 650 °C, 675 °C and 800 °C. For final temperatures up to 550 °C, the temperature protocol A1 listed in Table 1 was used; for final temperatures above 550 °C up to 800 °C, the temperature protocol A2 listed in Table 2 was used. The temperature protocols above were selected based on a typical 550 °C protocol used in previous studies of our group [9,17,21,22].

After the heating cycle was complete, the furnace was allowed to cool down naturally to below 50 °C before venting and unloading samples. After each pyrolysis, the quartz tube and plate were rinsed with acetone (VWR International LLC., ACS grade) and then baked in air at 800 °C for 2 h in order to remove deposited materials.

2.4. Preparation of CMS hollow fiber membranes

Asymmetric precursor hollow fiber membranes were fabricated by a dry-jet/wet-quench spinning process. Matrimid® precursor hollow fiber spinning was mostly performed as described in detail by Clausi and Koros [23] with some minor changes for the specific polymer batch used to study permeance and selectivity of the precursor. Matrimid® polymer power was first dried in a vacuum oven at 110 °C overnight to remove moisture and residual organics. A spinning dope was then made in a Qorpak® glass bottle sealed with a Teflon® cap and dissolved by placing on a roller at room temperature. A typical dope consists of 26.2 wt% Matrimid®, 53 wt% 1-Methyl-2-pyrrolidinone (NMP, Sigma-Aldrich Inc., 99.5%), 14.9 wt% Ethanol (Sigma-Aldrich Inc., ≥99.5%), 5.9 wt% Tetrahydrofuran (THF, Sigma-Aldrich Inc., 99.5%). Once the dope was homogeneous based on visual inspection (usually several days), it was loaded into a 500-mL syringe pump (ISCO Inc., Lincoln, NE) and allowed to degas overnight. Bore fluid was loaded into a separate 100-mL syringe pump. The dope and bore fluid were then co-extruded through a spinneret. Both the dope and the bore fluid were filtered in-line between the delivery pumps and the spinneret with 60 μm and 2 μm metal filters, respectively. Temperature control was applied for the spinning process. Thermocouples were placed on the spinneret, the dope filter and the dope pump. After passing through an air gap, the nascent membrane was immersed into a water quench bath. The phase-separated fiber spin line was collected by on a 0.32 m diameter rotating polyethylene cylinder after passing over Teflon® guides. Once cut from

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