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Preparation of carbon molecular sieve membranes on low-cost alumina hollow fibers for use in C_3H_6/C_3H_8 separation

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ABSTRACT

We herein report the preparation of thin carbon molecular sieve (CMS) membranes on 10 cm-long alumina hollow fiber supports for use in the separation of C_3H_6/C_3H_8 gas mixtures. Considering the manufacturing costs and scalability by modulation, low grade alumina powder (< 20 US$/kg) was selected as the inorganic material for the porous support following its extrusion into a hollow fiber structure. An intermediate layer of alumina was initially introduced onto the hollow fiber via a sol-gel method to reduce the effective pore size, and a commercial polyimide (Matrimid 5218 ®) film was then coated onto this alumina layer. Following subsequent pyrolysis, the resulting CMS membrane exhibited a C_3H_6 permeance of 45 GPU and a C_3H_6/C_3H_8 selectivity of 16.5. The separation performance for this gas mixture was lower than that of single-component permeance (i.e., 80 GPU C_3H_6 and 30 C_3H_6/C_3H_8 ideal gas selectivity) due to guest-guest interactions between the permeating C_3H_6 and C_3H_8 molecules. Finally, long-term stability tests for the CMS membrane at 2 bar over 500 h indicated a tendency to reach stabilization, whereas the test carried out at 7 bar exhibited a continuous decrease in gas permeance, which remains an issue for the use of our CMS membrane system in industrial applications.

1. Introduction

Carbon molecular sieve (CMS) membranes are commonly prepared via the pyrolysis of polymer membranes under a controlled atmosphere. Upon comparison to the methods employed for the preparation of microporous membrane materials, such as zeolites, silica, and metal-organic frameworks, this simple fabrication method is of particular interest as it is advantageous in the production of large quantities of membranes [1]. During the pyrolysis of polymer films, volatile compounds (e.g., H_2, CO, CO_2, NH_3, and CH_4) evaporate from the carbon backbone, thereby leading to the formation of turbostratic porous carbon structures in the membrane [2,3]. Both the intrinsic properties of the precursor polymer and the thermal pyrolysis protocols employed are critical in determining the separation performance of the produced CMS membranes, as both can alter the membrane pore structures [4–7]. Thus, the facile control of the porous CMS membrane structure has been examined and developed through tuning a number of experimental parameters, including the final pyrolysis temperature, the atmosphere employed, the use of pre-oxidative treatments and post-treatments, and the selection of suitable polymer precursors [8–11]. This tunability of the CMS membrane pores renders this system potentially suitable for application in both small gas mixture and large organic vapor separations.

To date, the application of CMS membranes in a variety of industrial separation processes has been studied, including in natural gas purification, post-combustion carbon capture, air separation, and organic vapor separations [12–15]. In addition, due to the small kinetic diameter of CO_2 and the high adsorption affinity of CMS membranes to this gas, such membranes have exhibited excellent gas separation performances in the separation of CO_2/N_2 and CO_2/CH_4 gas mixtures [16,17]. Furthermore, CMS membranes are resilient to plasticization under high feed pressures (> 60 bar), thereby rendering them superior to polymeric membranes under such conditions [18]. Moreover, challenging separations of O_2/N_2 and N_2/CH_4 gas mixtures have also been achieved by CMS membranes, despite the small size differences between each gas pair [17,19,20]. However, recent research into CMS membranes has gradually shifted towards the area of organic gas/vapor separations, where an effective pore size of > 0.4 nm is required, and the feeds are

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Abbreviations: CMS, carbon molecular sieve; GPU, gas permeation units

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highly condensable. Such operational conditions are not favorable for polymeric membranes in terms of separation performance and long-term stability whereas the pores of CMS membranes can be tuned for specific organic gas/vapor separations, and such processes can be operated steadily without plasticization under high pressure feeds. Indeed, Koros and coworkers have carried out extensive studies using free-standing CMS membranes for olefin/paraffin separation [21,22]. More specifically, dense CMS films and self-supported CMS hollow fibers were successfully prepared through pyrolysis of commercial polyimides (Matrimid 5218® and 6FDA-DAM), and the resulting CMS membranes exhibited a C_2H_4/C_2H_6 selectivity of > 10, which greatly exceeds the performance of polymeric membranes. This high selectivity was attributed to entropic selection originating from the two-dimensional silt-liked pore structures of the CMS membranes. In addition, they further demonstrated that this unique performance in the separation of olefin/paraffin mixtures gave potential for the replacement of current distillation-based olefin refinery processes using energy-efficient membrane-distillation hybrid systems [23]. Furthermore, Koh and coworkers reported self-supported CMS membranes derived from polyvinylidene difluoride (PVDF) hollow fibers for the separation of xylene isomers [24]. They found that crosslinked PVDF hollow fibers preserved their porous structure without densification during pyrolysis, thereby enriching the pressurized (> 100 bar) equimolar liquid feed mixture with 80 mol% of *p*-xylene at room temperature. Thin CMS membranes supported on robust porous substrates have also been explored. For example, Lin and coworkers prepared CMS membranes on alumina disks and measured their separation properties for propylene/propane mixtures [25]. Indeed, a high C_3H_6 permeance was achieved for these membranes, although increasing the membrane thickness to 500 nm gave a particularly high C_3H_6 permeance of 30 GPU and a C_3H_6/C_3H_8 selectivity of 31. Furthermore, Teixeira and coworkers reported the preparation of CMS membranes on alumina tubes from boehmite-loaded phenolic resin [26]. This membrane exhibited a high C_3H_6 permeance of > 50 GPU with a C_3H_6/C_3H_8 selectivity of 15.

Although it is evident that supported CMS membranes demonstrate a number of advantages in terms of both separation performance and physical strength compared with unsupported membranes, their manufacturing costs and scale-up through modulation remain significant challenges. One potential solution to such issues could involve the use of alumina hollow fiber as a porous support, as such fibers can be prepared from low-cost alumina powder (< 20 US$/kg), and are both robust and easily transformed into membrane modules. Thus, we herein report our investigation into the development of thin CMS membranes on alumina hollow fiber supports for use in olefin/paraffin (C_3H_6/C_3H_8) separation. Following synthesis of the alumina hollow fiber from low-grade alumina powder, this material will be employed as a support for preparation of the CMS membrane, and the diffusion of single gas components and gas mixtures though the membranes will be characterized. In particular, the permeation of C_3H_6/C_3H_8 mixtures through the supported CMS membrane will be examined, and the long-term stability of the membrane at feed pressures of 2 and 7 bar under a continuous C_3H_6/C_3H_8 flow will be explored.

2. Experimental

2.1. Preparation of CMS membranes on porous alumina hollow fibers

Porous α-alumina hollow fibers were prepared via an extrusion spinning process. Polysulfone (PSF, Ultrason S6010, BASF, USA), Polyethylene glycol (PEG200, SAMCHUN, Korea), Magnesium hydroxide ($Mg(OH)_2$, 99.9%, SAMCHUN, Korea), Disperbyk-190 (BYK-Chemie, Germany), and N-methyl-2-pyrrolidone (NMP, SAMCHUN, Korea) were used as binder, pore former, additive, dispersing agent, and solvent, respectively. PSF, PEG 200, $Mg(OH)_2$, and BYK were dissolved in NMP, and stirred for 24 h at 50 °C. Then, alumina power (alpha, 99.9%, Sumitomo, d_{50} = 1.1 μm, < 20 US$/kg) was added into the mixture solution, and stirred for additional 72 h at 50 °C. A final weight ratio of the dope solution was PSF:PEG 200:$Mg(OH)_2$:BYK:α-Alumina:NMP = 6:2:0.5:0.8:70:20.7. The dope was degassed under vacuum for 5 h at 25 °C, and transferred to a reservoir. It was extruded through a spinneret (outer diameter 2.5 mm and inner diameter 0.9 mm) using a single-screw extruder (FM-P20, Miyazaki Iron Works Co., Ltd.). The bore fluid was de-ionized water while tap water was used as the external coagulant. An air gap was set to 100 mm. Extruded fibers were immersed in tap water for 1 h at 25 °C, then further cleaned in fresh tap water at 60 °C for 12 h. After drying for 24 h at 25 °C, the fibers were calcined to yield alumina hollow fibers. The heating protocol was as follows; (1) increase to 600 °C at a rate of 2 °C/min, (2) hold for 1 h at 600 °C, (3) increase to 1450 °C at a rate of 3 °C/min, (4) hold for 1 h at 1450 °C, and (5) naturally cooled to room temperature.

Each hollow fiber measured 10 cm in length, and possessed an outer diameter of 2.0 mm, an inner diameter of 1.2 mm, and an average pore size of 70–80 nm, as determined using a PMI capillary flow porometer (CFP-1200-AEL, Porous Materials, Inc., USA). Prior to use, the alumina supports were cleaned by sonication over 30 min, then dried at 80 °C for 1 h.

The CMS membrane was then constructed via the preparation of an intermediate layer coating, subsequent polymer precursor coating, and a final carbonization/pyrolysis step. Initially, an aqueous alumina sol (for preparation, see [27]) was coated on the alumina support to serve as an intermediate layer and prevent the polymer solution penetrating the pores of the α-alumina support. After covering one end of the α-alumina hollow fiber with Parafilm, it was immersed vertically into the alumina sol for 60 s using a dip-coater (EF-2100, E-FLEX, KOREA). Removal rates of the fiber from the alumina sol ranged from 0.1 to 30 mm/s. Following sol coating, the support was dried in a glove box for 3 h at 25 °C prior to calcination at 700 °C (heating rate: 1 °C/min) over 3 h.

A commercial polyimide (Matrimid 5218®) was employed as the polymer precursor for the CMS membrane. Thus, a polymer precursor solution was prepared by dissolving Matrimid 5218® in *N*-methyl-2-pyrrolidone (NMP, SAMCHUN, Korea) at 60 °C, and the viscosity of this solution was tuned by varying its concentration. The dip-coating procedure described above for coating of the alumina sol was also employed for introduction of the polymer precursor onto the support. The resulting polymer-coated sample was then dried at 25 °C over 24 h prior to annealing at 200 °C for 2 h to evaporate any remaining solvent. The samples were horizontally placed on a mount with vertical wings. The polymeric film was pyrolyzed in a tubular furnace (inner diameter 100 mm and total length 1500 mm) under an atmosphere of ultra-high purity helium gas (99.9999%), which flowed along the length of the tubular furnace. The helium flow rate was maintained at 50 cc/min after purging the reactor with 100 cc/min He for 1 h at 200 °C. A heating rate of 2.8 °C/min was employed to reach the final pyrolysis temperature of 650 °C, and a thermal soak time of 1 h was employed. Finally, the furnace was cooled to < 50 °C by natural convection and the carbonized samples were removed.

2.2. Characterization

2.2.1. Microscopic characterization

Scanning electron microscopy (SEM, Tescan VEGA-II LSU, Czech Republic) was employed to observe the surface and cross-sectional morphologies of the γ-alumina layers and the CMS membranes. A nanoperm porometer (NPP, SEIKA, JAPAN) was employed to determine the pore size distribution (< 0.02 μm) of the alumina intermediate coating layer [28].

2.2.2. Gas permeation tests

For the single gas permeation tests, high purity gases including H_2, Ar, N_2, CH_4, C_3H_6, and C_3H_8 were used. The gases were fed into the shell-side of the membrane in dead-end flow, and the volumetric flow