Journal of Membrane Science 368 (2011) 41–47

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Ammonia-activated mesoporous carbon membranes for gas separations

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ARTICLE INFO

Article history:
Received 3 August 2010
Received in revised form 26 October 2010
Accepted 2 November 2010
Available online 9 November 2010

Keywords:
Mesoporous carbon
Membrane
Gas Separations

ABSTRACT

Porous carbon membranes, which generally show improved chemical and thermal stability compared to polymer membranes, have been used in gas separations for many years. In this work, we show that the post-synthesis ammonia treatment of porous carbon at elevated temperature can improve the permeance and selectivity of these membranes for the separation of carbon dioxide and hydrocarbons from permanent gases. Hierarchically structured porous carbon membranes were exposed to ammonia gas at temperatures ranging from 850 °C to 950 °C for up to 10 min and the N_2, CO_2, and C_3H_6 permeances were measured for these different membranes. Higher treatment temperatures and longer exposure times resulted in higher gas permeance values. In addition, CO_2/N_2 and C_3H_6/N_2 selectivities increased by a factor of 2 as the treatment temperature and time increased up to a temperature and time of 900 °C, 10 min. Higher temperatures showed increased permeance but decreased selectivity indicating excess pore activation. Nitrogen adsorption measurements show that the ammonia treatment increased the porosity of the membrane while elemental analysis revealed the presence of nitrogen-containing surface functionalities in the treated carbon membranes. Thus, ammonia treatment at high temperature provides a controlled method to introduce both added microporosity and surface functionality to enhance gas separations performance of porous carbon membranes.

1. Introduction

The separation of target gases from mixtures occupies an integral part of many industrial and energy-generation processes. The removal of carbon dioxide from combustion products in flue gas is particularly relevant given the potential environmental ramifications of these emissions. In addition, the separation of hydrocarbons such as propylene from nitrogen is important in the recovery of olefins from carrier gases in polyolefin manufacturing [1]. There has been an increasing interest in replacing conventional separations techniques such as cryogenic distillation, swing adsorption, and condensation that are energy intensive with more efficient separation methods. Within this context, membrane technology has garnered attention as a more environmentally sustainable separation method that offers an order of magnitude reduction in energy use compared to more traditional techniques [2]. Though a variety of membrane compositions and architectures have been proposed and developed, non-porous polymer membranes in a hollow fiber configuration dominate because of relatively simple processability and lower cost. Polymer membranes, however, are prone to degradation and swelling with prolonged exposure to gas streams. In addition, polymer membranes are bound by the Robeson limit, which reflects the inherent trade-off relationship between the two key parameters of membrane performance, the permeance of the target gas and the separation factor, or selectivity [3–5]. Consequently, porous inorganic materials such as silica, zeolites, and carbon as well as hybrid, or mixed matrix, membranes have attracted attention because of improved chemical and thermal stability and the potential to move beyond the Robeson limit to enhance separations performance [6].

Long-standing interest in carbon-based membranes, dating back to the pioneering work of Barrer and Strachan [7], is a consequence of the high thermal and chemical stability as well as the high corrosion resistance of the material. Moreover, these membranes typically possess inherent porosity that is uniform and can be well-controlled enabling the potential for designed separation performance and the possibility of overcoming the Robeson limit [8]. This is particularly relevant in light of recent advances in the synthesis of porous carbon materials reported by several groups [9–12]. Depending on the pore size, the separation mechanism in porous carbon membranes can be either molecular sieving or adsorption/diffusion. Molecular sieve membranes, where the separation is simply a molecular size effect, generally have pore sizes less than 0.5 nm. In contrast, adsorption/diffusion carbon membranes, where molecules essentially adsorb and diffuse along the surface of the pores, typically have pore sizes between 0.5 nm and

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doi:10.1016/j.memsci.2010.11.007

1 nm. As an example, Fuertes utilized a post-synthesis air oxidation treatment to prepare supported porous carbon membranes that incorporated an absorption/diffusion transport mechanism to enhance the gas permeance compared to pristine membranes [13,14]. Additionally, we recently reported a free-standing porous carbon membrane synthesized by pyrolysis of phenolic resin and block co-polymer composite films that exhibited selective transport of propylene over nitrogen via the adsorption/diffusion mechanism [15].

The performance of adsorption/diffusion carbon membranes is critically dependent on the properties of the surface which can facilitate gas adsorption and diffusion, and define selectivity. The importance of the surface properties has encouraged the incorporation of specific functional groups on the carbon surface to enhance attachment of target gas molecules to the pore walls and promote diffusivity through the membrane. Various functionalities such as nitrogen or oxygen-containing groups can be integrated into the carbon through diverse methodologies ranging from direct synthesis using nitrogen-containing precursors to post-synthesis oxidation processes [16]. Some functionalization methods, however, can generate excessive pore blocking or pore clogging by the chemicals, leading to loss of gas permeance and/or gas adsorption capacity. As an alternative to many of these impregnation processes, the incorporation of nitrogen functional groups has been achieved via exposure of carbon materials to anhydrous ammonia at elevated temperature. For example, Mangun et al. reported the treatment of activated carbon fibers with ammonia at high temperature and showed that this treatment served a dual role. First, there was an increase in the surface area and pore size of the activated carbon depending on the treatment temperature demonstrating that the ammonia acted as an etchant [17]. In addition, they reported the enhanced adsorption of an acidic gas, which confirmed the presence of a basic nitrogen functional group introduced by the ammonia treatment. The mechanism of incorporating nitrogen functionality into the carbon involves decomposition of ammonia at high temperature into radicals such as $^{\bullet}NH_2$, $^{\bullet}NH$, and $^{\bullet}H$ [18]. These radicals can etch carbon fragments leading to increased porosity and they can replace oxygen-containing species on the carbon to form surface groups such as $-NH_2$, –CN, pyrrolic and quaternary nitrogen thus producing surface functionalization [19].

Some work has been reported using ammonia exposure to improve the CO_2 absorption capacity of various porous carbon materials. For example, Plaza et al. showed that ammonia exposure at 800 °C led to the formation of narrow microporosity in a carbon char formed from almond shells [20]. The ammonia exposure served the dual function of creating porosity and introducing nitrogen surface functionality into the carbon leading to enhanced CO_2 adsorption and selectivity. Pevida et al. treated two commercial activated carbon materials with ammonia at different temperatures. They found that CO_2 capture capacity at room temperature increased from 7 wt.% for the pristine carbon to 8.4% for carbon treated at 800 °C for 2 h [21]. The importance of specific nitrogen-containing functionalities as opposed to total nitrogen content was also emphasized. In addition to activation of carbon for CO_2 capture, a recent report described the performance of an ammonia-activated ordered mesoporous carbon for an oxygen reduction reaction for polymer electrolyte membrane fuel cells [22].

Though the ammonia activation method has been used to functionalize porous carbon materials for CO_2 capture, to our knowledge, the ammonia treatment has not been applied to gas separations membranes. In this work, we use ammonia activation to enhance the permeance and selectivity for CO_2/N_2 and C_3H_6/N_2 separation through the introduction of additional porosity and the incorporation of stable nitrogen functionality into a mesoporous carbon membrane. The effects of exposure temperature and soak time on the CO_2, C_3H_6, and N_2 permeance values as well as on the selectivity were investigated. By exposing the carbon at 900 °C for less than 10 min, the permeance and selectivity could be improved compared to untreated carbon membranes. In addition, the selectivity is improved compared to our previously reported results in which the non-porous layer was removed via plasma etching [15]. Potential applications for the ammonia-treated carbon membrane include CO_2 removal from flue gas and C_3H_6 recovery in polyolefin manufacturing.

2. Experimental

2.1. Membrane synthesis

Mesoporous carbon disks were synthesized using a soft templating method previously described [15]. Briefly, an ethanolic solution containing phloroglucinol, formaldehyde, and a block co-polymer (F127) was cast onto a hydrophilic Mylar support to produce a uniform polymer film. After drying and curing at 80 °C for 24 h, the free-standing polymer film was detached from the Mylar support and cut into approximately 1 cm × 1 cm square membranes. The membranes were then pyrolyzed at 400 °C for 2 h under N_2 atmosphere followed by additional heating at 850 °C for 2 h under N_2 atmosphere. This synthesis method produced flat, free-standing carbon membranes with well-defined pore structure. Ammonia activation was accomplished by first placing the carbon membranes in a tube furnace with a flow of nitrogen. Once the carbon reached the treatment temperature, ammonia gas flowed through the tube at a rate of 100 mL/min for a pre-set exposure time ranging from 1 to 10 min. Three different treatment temperatures (850 °C, 900 °C, and 950 °C) were used to activate the carbon membrane.

2.2. Permeance measurements

Permeance measurements were performed on the carbon membrane using a custom test chamber [23]. The test system, which consists of feed and permeate chambers separated by the membrane, measures the non-steady state permeation through the membrane. Because the carbon membranes were much smaller than the support, it was necessary to mount the membrane using 5-min epoxy (Devcon) on a 47 mm non-porous film with a hole cut in the center. The supported carbon membrane was then carefully placed on a highly porous stainless steel support that provided mechanical stability and negligible resistance to gases. Two Viton o-rings were used to separate the feed chamber from the permeate chamber to eliminate leaking. In addition, a Viton gasket was positioned on top of the membrane to provide an additional seal. With this arrangement, the only path from the feed chamber to the permeate chamber occurs through the open area of the carbon, which was typically a diameter of 4–6 mm depending on the size of the center hole and the amount of epoxy used to seal the carbon. After loading the carbon membrane, the chamber was evacuated with a mechanical pump to a base pressure of 40 mTorr. The membrane was allowed to remain in the test chamber for at least 2 h to reach a steady base pressure.

All measurements described here are single-gas permeation values in which each gas was individually introduced to the feed side at a pre-determined pressure. A ballast volume of approximately 300 mL was used to minimize pressure loss during the experiment. After establishing the gas pressure on the feed side, the pressure on the permeate side was measured as a function of time using a Baratron pressure gauge (MKS Instruments) connected to a data acquisition board (Vernier). The pressure measurement from the Baratron gauge is independent of gas composition and has a range up to 100 Torr. The pressure on the permeate side was typically measured for 30 min and all measurements were acquired at 25 °C.