



Separations of F-gases from nitrogen through thin carbon membranes



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ARTICLE INFO

Article history:

Received 24 September 2015

Received in revised form 2 December 2015

Accepted 7 December 2015

Available online 8 December 2015

Keywords:

CMS membrane

F-gas

NF₃

SF₆

CF₄

Thin film

Supported membrane

ABSTRACT

F-gases, such as NF₃, CF₄, and SF₆, are strong greenhouse gases, and their emissions to the atmosphere should be prevented. We investigated F-gas separations by carbon molecular sieve (CMS) as a strong candidate for reduction of greenhouse gas. The viscosity of the precursor solution (Matrimid5218[®]) was controlled from 10 cP to 40 cP for fabricating defect-free thin polymer films on porous supports, and thermal pyrolysis protocols were subsequently optimized in order to produce high-performance membranes. CMS membranes pyrolyzed at 650 °C in high-purity He (99.9999%) exhibited the best performance for N₂/NF₃ separation (650 N₂ GPU, N₂/NF₃ = 26.6). As compared with polymeric membranes, the CMS membranes performed far outperformed especially because of their high N₂ permeance, which originated from the thickness of the thin film along with the rationally controlled micropores. Therefore, these high-flux CMS membranes are expected to provide high productivity when implemented in large-scale processes for F-gas separation and recovery.

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1. Introduction

F-gases (NF₃, CF₄, and SF₆) are currently popular as major etching and cleaning gases in the production of liquid-crystal displays and silicon-based thin-films. Their demand is expected to rise in response to the growth of associated industries. In Korea, 7000 tons of NF₃ gas were produced and consumed in 2014 with a 10% annual growth rate. For the display industries, spent N₂-based gases contain several thousand ppms of F-gases, which are currently decomposed by heat and plasma [1]. In some fields, however, these gases are emitted without a careful purification and recovery progress. F-gases are powerful greenhouse gases, where NF₃ has a global warming potential (GWP) that is 17,400 times greater than that of CO₂ [2]. Thus, the emission of F-gases to the atmosphere must be minimized. Moreover, their reuse through the use of appropriate recovery systems is also highly recommended due to the high price of F-gases [3].

Membrane-based separation provides a facile route for the separation and recovery of F-gases. The kinetic diameters of F-gases (0.45 nm for NF₃, 0.48 nm for CF₄, and 0.55 nm for SF₆) are larger than that of N₂ (0.36 nm), and hence molecular sieve membranes can discriminate F-gases from F-gas/N₂ mixtures. Polymeric membranes are frequently selected for gas separation membranes because of their cost and large-scalability. In order to discriminate F-gases, membranes should allow for the permeation of N₂ because

of its small size. Unfortunately, the intrinsic gas permeability of N₂ through glassy polymeric membranes such as polyimide and polysulfone is low (less than 1 barrer), and rubbery polymers is not effective for the separation of N₂ and F-gases despite their high permeance [4,5]. On the other hand, "High free-volume polymers" such as PTMSP, AF polymer, and Hyflon could be considered as an option, but they are very expensive and sometimes commercially unavailable [6,7].

In this sense, micro-porous membranes appear attractive for F-gas separation and recovery because of their high gas permeance for N₂ combined with their pore tuning capability. These membranes include zeolites, metal oxide framework (MOF), alumina, silica, and carbon molecular sieve (CMS) membranes [8–12]. Among these, CMS membranes possess slit-shaped pores consisting of a relatively wide opening (micropore) that contributes to fast gas diffusion and narrow pores (ultramicro-pore) that allow for molecular separation. In terms of the preparation of inorganic membranes, CMS membranes have a great advantage over other inorganic materials such as MOF and zeolite. Hydrothermal synthesis needs to be carried out for crystalline membranes, which restricts their large-scale production and also increases their manufacturing cost. On the other hand, CMS membranes can be fabricated as either self-supported forms or supported structures through simple pyrolysis of polymeric precursors, which enables easy and cheap manufacturing.

Pyrolysis of a polymeric film, capillary tube, and hollow fiber leads to the production of self-supported CMS membranes [13]. The self-supported CMS membranes have shown excellent gas

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separation for CO₂/N₂, CO₂/CH₄, and O₂/N₂ as well as for olefin/paraffin separation [14–16]. However, the inherent brittleness of the self-supported CMS membranes is still a major restriction to their widespread application. As an alternative, supported CMS membranes are able to compensate for the drawbacks of self-supported CMS membranes. A robust substrate can provide enough stability to the CMS film under practical stress and turbulence, although the manufacturing cost increases [17–20]. The features that are offered by supported CMS membranes allow for the fabrication of thin CMS films. T.A. Centeno and A.B. Fuertes have prepared CMS films on carbon disks, alumina tubes, and alumina disks after the controlled pyrolysis of phenolic resin [21–23]. Shiflett and Foley used a stainless steel support and poly furfuryl alcohol to make CMS films [24–26]. Recent research from Xiaoli Ma and Y. S. Lin reported the fabrication of CMS films for propylene/propane separation [18]. Such approaches suggest that there is a strong correlation between the formation of non-selective defects and membrane thickness, and that the rational control of thickness is crucial for attaining high-flux membranes as well as good gas selectivity.

We studied the fabrication of thin CMS membranes on porous alumina supports for F-gas separation. Most literatures on CMS membranes have reported that N₂ gas permeates slowly through CMS membranes compared to CO₂ and O₂ because of its large size and weak adsorption. Such features reduce the separation efficiency of current CMS membranes for N₂/F-gases. Thus, new pyrolysis protocols need to be developed. In order to optimize their thickness and, hence, improve their N₂ permeability, the thickness of the polymer film was precisely controlled from 1 μm to 5 μm by adjusting the viscosity of the precursor solution (Matrimid5218, Huntsman International LLC, U.S.). Afterwards, the separation performances of the CMS membranes prepared by varying the pyrolysis temperature were studied. Finally, the optimized CMS membranes were compared with polymeric membranes and their potential for F-gas separation was investigated.

2. Experimental

2.1. Preparation of the CMS membrane

Commercial polyimide (Matrimid5218, Huntsman International LLC, U.S.) was used as a polymer precursor. It was dissolved in a N-Methyl-2-Pyrrolidone (NMP, BASF, Germany) solution. 2 g of the Matrimid powder was added to 50 g of NMP and stirred at 60 °C in an oil bath until it was completely dissolved. The initial viscosity of the polymer solution was measured to be around 30 centipoise (cP) at 25 °C using a BROOKFIELD Viscometer (LV DV-11+ PW, USA). If needed, more NMP solution was added to adjust the viscosity.

Custom-made, rounded alumina disks were used as the porous supports for the CMS membranes. They were polished using sandpaper and then washed in tap water. The polished alumina disks were dried at 150 °C in a convection oven (JEIO-TECH, Korea) for at least 2 h. Before dip-coating in the polymer precursor solution, alumina powder (0.01–0.02 micron powder, α and γ phase) was rubbed on the alumina disks. The polymer films were coated on the alumina disks by slip coating, where the top surface of the alumina disk was dipped into the precursor solution for 30 s. Afterwards, the disk was placed vertically to drain out the excess polymer solution. It was then further exposed to dry air at 25 °C for 2 h and dried at 150 °C in a convection oven for 4 h.

The pyrolysis of the polymeric film on the alumina disk was performed in a parallel tubular furnace (custom-made) with a typical pyrolysis protocol as shown in Fig. 1. N₂ was flowed into the empty furnace at 300 °C for 5 h, and the furnace was cooled down

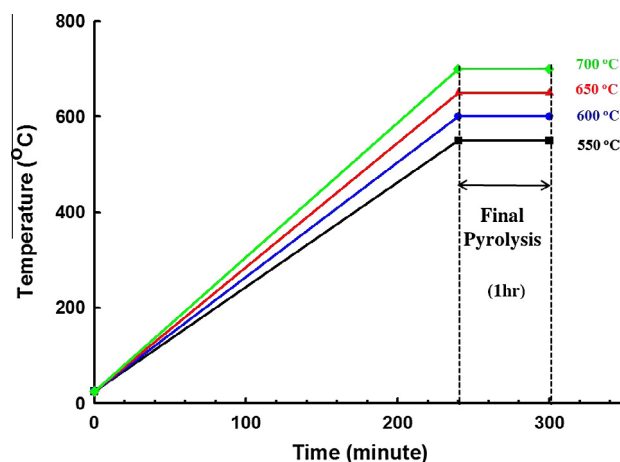


Fig. 1. Typical thermal pyrolysis protocols for the CMS membranes used in this study. After final pyrolysis for 1 h, samples were naturally cooled down.

to room temperature (25 °C) before the samples were placed in it. The final pyrolysis temperature was varied from 550 °C to 700 °C along with the ramping rate that was used to obtain the final pyrolysis temperature. Pyrolysis was carried out either under He (99.9999%) or a N₂/O₂ mixture (99.95% N₂ and 0.05% O₂). After pyrolysis, the alumina disks were naturally cooled down in the furnace to room temperature (25 °C).

2.2. Characterization of the CMS membrane

Pure gas permeation was measured using a conventional test system at room temperature (25 °C). The physical properties of F-gases and N₂ are summarized in Table 1. The CMS membranes were sealed using an O-ring and loaded in custom-made permeation cells. The feed pressure ranged from 2 to 5 bar, and the permeated side was exposed to ambient atmosphere. The volumetric flow rates of the gases passing through the CMS membranes were measured at least three times using a soap bubble meter. For mixture gas separation, mass flow controllers were used to mix pure N₂ and NF₃ gas. Feed concentrations of N₂ were changed from 99.9% to 50%. The feed side was pressured by a mixture gas of N₂ and NF₃, and the permeate side was exposed to atmosphere. The pressure drop was maintained at 2 bar. The compositions of the feed, permeate, and permeate were measured using a gas chromatograph (DS Science, IGC 7200, Korea) equipped with a thermal conductivity detector. All measures were performed at 25 °C.

The permeance of each gas was calculated in gas permeation units (GPU):

$$1 \text{ GPU} = 10^{-6} \text{ cm}^3/\text{cm}^2 \text{ s cm Hg}$$

The ideal separation factor $\alpha_{A/B}$ was calculated based on the gas permeance of the pure gases:

Table 1
Physical properties of N₂ and F-gases.

Property	Value			
	N ₂	NF ₃	CF ₄	SF ₆
Boiling point at 101.325 kPa (°C)	−195.8	−129.0	−128.0	−64
Heat of vaporization (kJ/mol)	5.56	11.6	–	23.7
Heat of formation (kJ/mol)	–	−131.5	–	−1221.6
Critical temperature (°C)	−147.0	−39.3	−45.6	45.6
Critical pressure (kPa)	3396	4530	3739	3759
Critical volume (cm ³ /mol)	89.8	123.8	139.9	197.8
Molecular size (Å)	3.64	4.50	4.80	5.50
Dipole moment	0	0.234D	0	0

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