이산화탄소 회수용 탄소분자체 복합막 모듈의 기체 분리 특성

한상훈[1], 김승주[1], 박호범[2], 이영무[1,*]
[1]한양대학교 화학공학과
[2]울산대학교 화학공학과

Separation Properties of Carbon Molecular Sieve Composite Membranes for CO_2 Recovery

Sang Hoon Han[1], Seung Joo Kim[1], Ho Bum Park[2], Young Moo Lee[1,*]

[1]School of Chemical Engineering, Hanyang University, Seoul 133-791, Korea
[2]School of Chemical Engineering and Bioengineering, University of Ulsan, Ulsan 680-749, Korea

1. Introduction

Membrane-based gas separation is one of the promising separation technologies due to its high energy efficiency as well as excellent separation properties. During the last several decades, polymer materials like polysulfone, poly(ether sulfone), and polyimide have been used for gas separation membrane. Recently, many researchers have shown interests in carbon membranes rendered from polymeric precursors as good candidate materials for gas separation with their superior separation performances, highly excellent stabilities for vapor and condensable gases, and extraordinary durability in heated and corrosive circumstance. In our previous study, we developed carbon-silica(C/SiO_2) membranes for enhanced permeabilities of small gas molecules. The C/SiO_2 membranes derived from poly(imide siloxane) copolymers were composed of the dispersed silica domains to give higher permeable region as well as the continuous carbon matrix to retain the

selectivities of common carbon membranes. We have modified the C/SiO_2 materials by UV treatment, by changing the ratio of siloxane domain to polyimide region, by adding sol-gel solution of alkoxysilane, or, by partial oxidation of siloxane domain in pyrolysis to obtain the most suitable membrane for CO_2 separation. Furthermore, we have studied to develop the composite membrane coated on porous supports for large areas of inorganic membrane and practical applications. Here, we would like to demonstrate the gas permeation properties of supported carbon composite membrane modules prepared from polyimide and poly(imide siloxane) to fabricate a large inorganic membrane and to test their CO_2/N_2 separation properties for CO_2 sequestration in flue gases.

2. Experimental

For preparing poly(imide siloxane) as polymeric precursors, calculated amounts of pyromellitic dianhydride(PMDA) were dropped to equimolar 4,4'-oxydianiline(ODA) and α,ω-aminopropyl dimethylsiloxane (PDMS, Mw=900) solution in 1-methylpyrrolidinone (NMP) and tetrahydrofuran(THF). The α-alumina support(O.D. = 4.8 mm, I.D. = 3.0 mm, length = 400 mm) purchased from Nanoporous materials™ were slip-casted by boehmite sol and calcinated at 700°C to prepare mesoporous intermediate layer.

The prepared polymeric precursors were coated on the alumina supports modified by γ-alumina layer, and the composite membranes were carbonized at 600°C in a tubular furnace. Finally, a carbon membrane module was fabricated by sustainable stainless (SUS 316) housing and Viton™ O-ring for permeation test at high temperature. The effective area of each carbon membrane was 50.2 cm^2.

Gas permeation properties of pure gases were recorded to GPU unit by MFCs(mass flow controller) and Baratron™ manometers at 1 to 5 atm. Mixed gas separation experiments were conducted by using binary gas mixtures(21% O_2/79% N_2, 15% CO_2/85% N_2, 50% CO_2/50% CH_4), and the compositions of permeateand retentate flow were measured with different stage-cuts by gas chromatography (GC-2010 ATF, Shimadzu Co. Ltd., Japan) at room temperature to 150°C.

3. Result and Discussion

The cross-sectional morphologies of each composite membrane were investigated by FE-SEM. The uniform intermediate layer were
The uniform mesoporous γ-alumina layer and defect-free carbon layer coated on the alumina support were 1~2 μm and 2-3 μm thick, respectively.

Gas permeances of He, H_2, CO_2, O_2, N_2, CH_4 were 207, 310, 169, 39, 6.1, and 2.7 GPU(1GPU=$10^{-6}cm^3 \cdot cm^{-2} \cdot sec \cdot cmHg$), respectively. Ideal gas selectivities of the composite membrane were 7 and 27 to O_2/N_2 and CO_2/N_2 at 298K, similarly with the factors calculated from gas permeabilities of flat carbon membranes by time-lag method in our previous study. The gas permeances increased at higher temperature, whereas the selectivities slightly decreased.

$$\cdot\ stage-cut(\Theta) = \frac{V_p}{V_i} = \frac{V_p}{V_p + V_r}$$

$$\cdot\ recovery\ ratio = \frac{V_{p,CO_2}}{V_{i,CO_2}} = \frac{V_p \times y_{CO_2}}{V_i \times y^0_{CO_2}} = \Theta \times \frac{y_{CO_2}}{y^0_{CO_2}}$$

For binary gas mixtures, composition (y^0 : conc. at inlet, y : conc.at permeate, y_r : conc. at retentate) and flux (V_i : flux at inlet, V_p : flux at permeate, V_r : flux at retentate) were recorded to calculate the stage-cut and recovery ratio. Stage-cut, the ratio of permeate flux(V_p) divided by inlet flux(V_i), provides information related to the capacity of a membrane module. The larger stage-cut indicates that large amount of feed gas can be supplied at a constant pressure, while the enrichment of the permeate stream should drop proportionally to the increasing stage-cut. Recovery ratio, the ratio of the recovered gas flux per supplied gas flux at inlet stream, is the value of stage-cut multiplied by the permeate concentration. Therefore, the recovery ratio approaches to 1 at higher stage-cut. In CO_2/N_2 separation test, the enriched CO_2 concentration dropped from 85 to 15% at the stage-cut of 0 to 1, while the recovery ratio of CO_2 approached from 0 to 1. At the optimized stage-cut of 0.25, the recovery ratio and the permeate composition were 0.9 and 60% CO_2.

4. Conclusions

Carbon/alumina composite membranes were obtained from poly(imide siloxane) by coating on surface modified supports, and CMSM module was manufactured successfully for the high temperature application. The gas transport properties of CMSM module were measured by MFC, pressure gauge and GC. Operation factors like pressure ratio, stage-cut, and recovery ratio were considered to obtain the optimization condition for CO_2 recovery from CO_2/N_2 mixture. At about 0.3 of stage-cut, recovery ratio went over 98% and the composition of permeate was 60% of CO_2 and 40% of N_2.

Reference

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