Carbon-Silica Membranes Derived from Polyimide/Silica Composites for Gas Separation

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1. Introduction

Membrane-based technology has been presently settled down at several industrial processes and application. Particularly, membrane-based gas separation is a relatively young and eye-opening technology and accounts for US$ 230 million per year, but is growing fast with a rate higher than 15% a year. Up to now, polymer membranes are used commercially to separate air, to remove hydrogen from mixtures with nitrogen or hydrocarbons in petrochemical processing applications. Polymer membranes, however, have an obvious tradeoff relation between permeability and selectivity: Polymers that are more permeable are commonly less selective and vice versa. In addition, polymeric membrane do not operate well in corrosive and high temperature environments. Therefore, the development of new membrane materials could play a significant role in the future of membrane-based separation field. Amongst membrane materials being watched with keen interest, carbonaceous materials with ultramicroporosity have been extensively investigated owing to their excellent permeability and permselectivity. Carbon membranes are effective for separating gas mixtures with similar molecular sizes such as O_2/N_2, CO_2/CH_4, and CO_2/N_2, and have greater mechanical strength and are able to withstand higher pressure differences for a given wall thickness. In addition, feed pressure does not greatly affect the permeation properties of carbon membranes and the permeation properties of carbon membranes is not time dependent. Finally, carbon membranes have superior stability in the presence of organic vapor or solvent and non-oxidizing acid or base environments and higher thermal stability. In spite of these many advantages, carbon is very susceptible to

oxidation, which is an obvious drawback to easy and reproducible fabrication of the carbon membranes. Therefore, combining carbon with silica or silicon-containing compounds as attempted in previous and present study seems to be a natural choice for the next step in expanding the modern molecular separation science and technology.

2. Experimental Section

For the preparation of polyimide/silica (PI/SiO_2) composites, a calculated amount of tetraethoxysilane (TEOS; previously diluted in ethanol) was added to the poly(amic acid) (PAA) solution derived from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA), which was diluted to 10 wt.-% with N-methyl-2-pyrrolidinone (NMP). 0.15 M HCl solution, also diluted with NMP, was added to PAA/TEOS solution mixture at room temperature under a nitrogen atmosphere with fast agitation (water/alkoxide mole ratio is 4:1). The compositions of the silica in PI/SiO_2 matrix were 10, 20, and 30 in wt%, respectively. For the preparation of polyimide/modified silica ($PI/m\text{-}SiO_2$), dimethyldiethoxysilane (DMDEOS) was added into PAA/TEOS solution having a constant TEOS amount in order to change silica network in polyimide/silica matrix. The compositions of the DMDEOS/TEOS in $PI/m\text{-}SiO_2$ matrix were 25 and 50 in mol%, respectively. After 24 h of reaction, a homogeneous solution was cast on a Teflon-coated glass slide and dried for 6 h at 40 oC. The resulting PAA/SiO_2 and PAA/m-SiO_2 films were thermally imidized at 100, 200, and 300 °C for 1 h each step. The morphology, thermal, and chemical properties of PI/SiO_2 and $PI/m\text{-}SiO_2$ membranes were studied with FE-SEM, ^{29}Si-NMR, ESCA, and TGA. After that, C/SiO_2 and C/m-SiO_2 membranes were prepared by an inert pyrolysis of PI/SiO_2 and $PI/m\text{-}SiO_2$ membranes up to 600 °C using a predetermined pyrolysis protocol. To evaluate the gas separation capability of the C/SiO_2 and $C/m\text{-}SiO_2$ membranes prepared in this study, gas permeation test was carried out to measure the pure component gas permeability through the membranes selecting He, H_2, CO_2, O_2, and N_2. Gas permeability was measured at 25 °C with a high-vacuum ($<10^5$ Torr) time-lag method under the pressure difference of 76 cmHg. All measurements were conducted at ambient temperature.

3. Results and Discussion

Tables 1 and 2 show the gas permeation data of PI/SiO_2 and PI/*m*-SiO_2 and their pyrolyzed products, C/SiO_2 and C/*m*-SiO_2 membranes. Effect of silica content on the gas permeation properties of polyimide matrix and carbon matrix was summarized in Table 1. Generally, increase of silica content obtained from sol-gel reaction in polyimide matrix led to decline of both gas permeabilities and permselectivities as compared with PI/SiO_2 having the lowest silica content. In this study, any coupling agents, which are usually used to prevent severe phase separation between silica particles and organic polymer matrix, were not considered in the preparation of PI/SiO_2 membranes. Therefore, macroscopic phase separation was observed even in PI/SiO_2 with 10 wt% silica content. The phase separation might cause large interfacial gaps between polyimide and silica domains, which penetrants could permeate through these interfacial gaps rather than silica domains in continuous polyimide matrix. These behaviors continued to the gas permeation properties of C/SiO_2 membranes derived from the PI/SiO_2 membranes. Heat treatment at a high temperature could make the silica network in the carbon matrix denser and also interfacial gaps larger. Interestingly, the gas permeation behaviors of precursors and their C/SiO_2 membranes are very similar, which are due to using thermal stable phases, that is, polyimide and silica phases.

Table 1. Gas Permeation Results of PI/SiO_2 membranes and C/SiO_2 membranes at 25 °C.

Sample code	Permeability (Barrer)					Selectivity			
	He	H_2	CO_2	O_2	N_2	He/N_2	H_2/N_2	CO_2/N_2	O_2/N_2
PS1	35.5	37.7	14.0	3.5	0.63	56.0	59.5	22.1	5.6
PS2	24.6	25.2	9.9	2.5	0.47	52.5	58.0	21.1	5.4
PS3	24.7	28.2	10.4	2.6	0.49	50.3	57.4	21.1	5.3
CS1	3469	9807	2292	573	61.6	56.3	159.2	37.2	9.3
CS2	2669	7039	1897	436	55.0	48.2	127.1	34.2	7.9
CS3	3219	9809	2673	659	103.0	31.3	95.2	26.0	6.4

In the case of PI/*m*-SiO_2 membranes, the gas permeabilities increased with more addition of DMDEOS as a silica network modifier. Introduction of a silica network modifier in PI/SiO_2 matrix would lead to more sparse silica structure. Increase of permeability and decease of selectivity are supported to

this explanation. For C/*m*-SiO_2 membranes, we felt that proper control of silica network embedded in carbon matrix would make possible to improve the gas permeation performances of the pyrolytic carbon-silica membranes. Consequently, incorporation of silica into carbon membranes will help the improvement of gas flux in the carbon membranes without a large sacrifice of gas selectivity.

Table 2. Gas Permeation Results of PI/*m*-SiO_2 membranes and C/*m*-SiO_2 membranes at 25 °C.

Sample Code	Permeability (Barrer)					Selectivity			
	He	H_2	CO_2	O_2	N_2	He/N_2	H_2/N_2	CO_2/N_2	O_2/N_2
PS2	24.6	27.2	10.9	2.5	0.47	58.0	52.5	23.2	5.4
PS2D1	29.4	31.1	12.8	3.0	0.51	61.2	57.9	25.2	5.9
PS2D2	59.3	67.0	29.1	7.7	1.36	49.3	43.7	21.4	5.6
CS2	2669	7039	1897	436	55	48.2	127.1	34.2	7.9
CS2D1	3230	9021	4120	893	125	25.8	72.2	33.0	7.1
CS2D2	3755	10689	6679	1520	220	17.0	48.5	30.3	6.9

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