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Gas transport properties of alumina composite membranes

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Abstract

The composite mesoporous ceramic membranes were prepared with γ-alumina and poly (2,6-dimethyl-1,4-pyphenylene oxide) (PPO) on the surface of the macroporous α-alumina ceramic membranes and the permeation results were compared with those of the α-alumina membrane for large-scale applications. In the results of the transport experiments, the ceramic membranes gave high gas permeances mainly due to Knudsen diffusion and surface diffusion as an additional mechanism. And, the polymer modification increased the permeances of the strongly adsorbing gas components. In this study the modifications of alumina ceramic membranes could increase the gas permeation performances especially for the strongly absorbing gas components.

Keywords: alumina ceramic membrane; transport; gas permeance

1. Introduction

Interest on membrane processes for gas separation using ceramic membranes has considerably increased in many application areas since ceramic membranes have high gas permeances and represent thermal, chemical and mechanical stabilities [1,2]. Of applications, the importance for the separation of CO_2 and CH_4 has been increasing especially in the landfill gas system and natural gas system, which consist of CH_4, CO_2 and N_2 as major components and hydrocarbons and water vapor as minor components [3-5]. The mechanisms for gas transport through a porous membrane are primarily varied with pore size distribution and to some extent with chemical interaction between the diffusing species and the membrane material [6]. The Knudsen diffusion occurs in a membrane whose pore size is approximately less than 1/10 that of the mean free path of the diffusing species. When adsorption of a species occurs on to the surface of the membrane pore structure, the performance of gas transport can be enhanced due to surface diffusion [7]. Finally, capillary condensation can occur in the pores of the membranes and transport through the membrane in the presence of condensable gas components.

Ceramic membranes with a wide range of pore sizes can be prepared using various methods for many different applications. The ceramic membranes having mesoporous γ-alumina layer on a macroporous α-alumina are considered as one of the effective preparation methods to reduce the pore size or to improve the specific surface properties for high gas permeances [7,8]. In addition, development and characterization of new polymers for gas separation is one of the important considerations as an alternative gas separation technology. Of polymers, poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) is considered as a promising candidate due to high glass temperature and high permeability [9-11]. In this study, the alumina ceramic membranes were modified with γ-alumina and PPO polymer on the surface of the α-alumina layer. And, the transport mechanisms were considered for gas components and the membrane performances were compared.

2. Experimental

The membranes investigated in this study are asymmetric and composite ceramic

membranes (Noritake, Japan). The support is an extruded α-alumina with an average pore diameter of 0.7 μm and a porosity of 39 %, whose layer is 1.45 mm thick. A second layer (α-alumina layer) with the thickness of 80 μm is slip-cast on the surface of the support and an average pore diameter 0.06 μm and a porosity of 40 %. The γ-alumina ceramic membrane on the α-alumina layer was slip-cast, having the thickness of 4 μm, whose porosity is 40 % and a nominal average pore size of 4 nm. Also, the α-alumina layer was coated with PPO polymer (15 wt%) in order to increase the gas permeation performances. The gas permeations were measured using a permeation apparatus having a film flow meter (MKS, Japan) at an ambient temperature and pressure ranges. The transport of gas components were investigated using weakly adsorbing components (He, N_2, and CH_4) and strongly adsorbing components (CO_2 and C_2H_6).

3. Results and discussion

A characteristic feature of gas transport by the Knudsen mechanism is that the permeance shows an inverse square root dependence on temperature and molecular weight of the diffusing gas molecules, assuming that there is no involvement of adsorption. The gas permeance, P, can be obtained as follows [12]:

$$P = \frac{\varepsilon d_p}{\tau L}\left(\frac{8}{9\pi MRT}\right)^{1/2}.$$

Here, ε represents the porosity, τ the tortuosity, d_p the pore diameter, L the membrane thickness, relating to the membrane properties. Therefore, every diffusing gas molecule should have the same of $P(MT)^{1/2}=(\varepsilon d_p/\tau L)(8/9\pi R)^{1/2}$ independent of temperature if gas transport through the membrane is affected by Knudsen diffusion. Gas permeation data on the γ-alumina ceramic membrane were analyzed in the relationship between $P(MT)^{1/2}$ and temperature (See Fig. 1). Relatively constant values of $P(MT)^{1/2}$ were observed for the weakly adsorbing gas species (N_2 and CH_4) over the applied temperature range in this study, indicating that the transport of these gases takes place mainly due to Knudsen diffusion. Meanwhile, the strongly adsorbing gas species (CO_2 and C_2H_6) showed different aspects from those for the weakly adsorbing gas species. The results for those gas species can be explained by the occurrence of the surface diffusion at low temperature [12]. As temperature decreases the contribution of surface diffusion increases due to adsorption on the pore surface. It is interesting that the value of $P(MT)^{1/2}$ for C_2H_6 represented higher than that of CO_2, implying that the adsorption capacity of C_2H_6 is higher than that of CO_2 on the pore surface in the γ-alumina ceramic membrane.

The results for the gas permeation experiments with the γ-alumina ceramic membranes were summarized in Table 1 in terms of permeance, selectivity, and the estimated activation energy. The permeance data at 35 °C and their selectivities with CO_2 showed that the gas transport properties were mainly affected by Knudsen diffusion. However, it is considered that the permeance of the most strongly adsorbing gas species (C_2H_6) showed 2.1 x 10^{-6} mol/m^2 s Pa, much higher value compared with that of nitrogen having similar molecular weight. The higher permeance of C_2H_6 is assumed to be related to high adsorption capacity on the pore surface, as discussed before. In the influence of temperature on the gas permeation, it is generally accepted that the lower value of the activation energy presents the lower resistance to transport through membranes. The results of the estimated activation energy showed that C_2H_6 represented the lowest value except He, implying that adsorption on the pore surface could increase gas permeance performance through mesoporous γ-alumina ceramic membranes. Based on the estimated activation energy, C_2H_6 has the highest adsorption capacity on the pore surface of γ-alumina membrane, and the order from higher to lower value was $CO_2 > CH_4 > N_2$.

Table 2 shows the results of the permeation experiments with the PPO coated α-alumina

ceramic membrane. The gas permeances showed the order of 10^{-8} mol/m^2 s Pa, irrespective of gas components, about 1/100 of the value of the γ-alumina membrane shown in Table 1. The permeances of the strongly adsorbing gases, however, showed much higher value than N_2. It is interesting that the permeance of C_2H_6 showed the highest except He, assuming that C_2H_6 has the highest adsorption to PPO polymer.

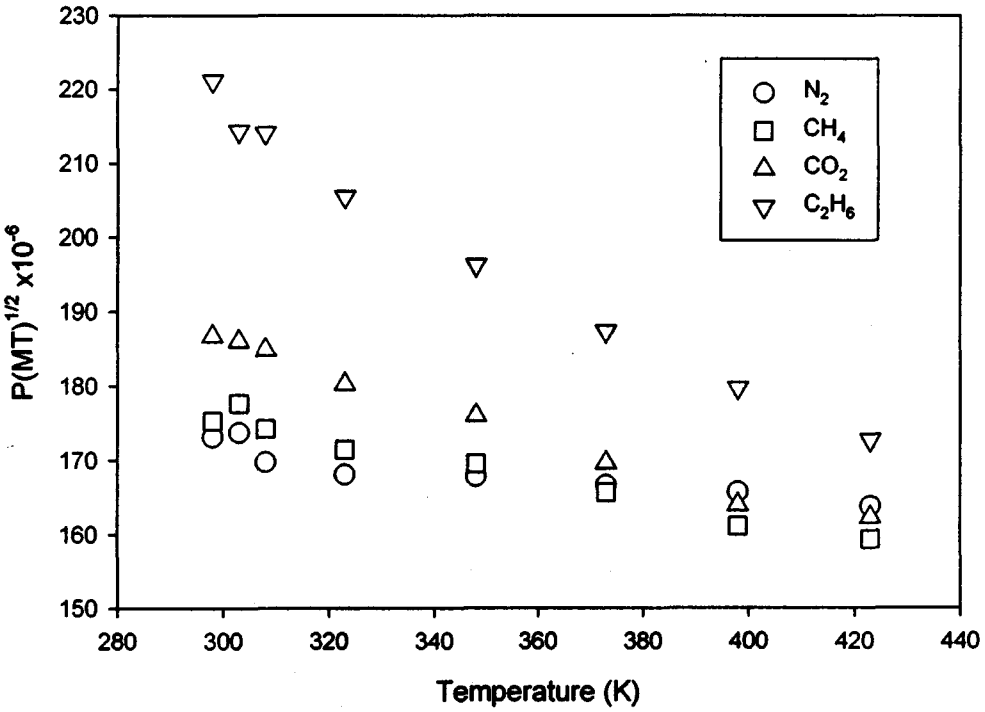

Fig. 1. Relationship between $P(MT)^{1/2}$ and temperature for γ-alumina membrane.

Table 1 Results of the permeation experiments with the γ-alumina membrane

Gas	Permeance x10^{-6}(mol/m^2 s Pa)	Selectivity with CO_2		Activation energy (KJ/mol)
		Experimental	Knudsen diffusion	
He	5.7	3.8	3.3	-1.3
CH_4	2.2	1.5	1.7	-1.0
N_2	1.6	1.1	1.3	-0.8
C_2H_6	2.1	1.4	1.2	-1.5
CO_2	1.5	1.0	1.0	-1.2

Table 2 Effect of the polymer modification on gas permeances

Gas	Permeance x10^{-8}(mol/m^2 s Pa)	Selectivity with CO_2	Selectivity with N_2
He	5.5	1.8	1.9
C_2H_6	4.1	1.3	1.4
CH_4	3.8	1.2	1.3
CO_2	3.1	1.0	1.1
N_2	2.8	0.9	1.0

4. Conclusions

In the emerging large scale applications, interests on ceramic membranes have increased

due to high permeances and their thermal, chemical and mechanical stabilities. In this study, the mesoporous γ-alumina ceramic membranes were prepared on the surface of the macroporous α-alumina ceramic membranes for large-scale applications. Also, the surface of the α-alumina ceramic membranes were modified with poly (2,6-dimethyl-1,4-pyphenylene oxide) (PPO) to increase gas permeance performances. The results were shown that the ceramic membranes gave high gas permeances due to Knudsen diffusion and surface diffusion especially for the strongly adsorbing gas components. The modification of the surface of alumina ceramic membranes with the polymer could significantly increase the permeances of the strongly adsorbing gas components. It was shown through the gas transport experiments that the adsorption on the surface of the membrane pore structures affected the gas permeation performance and that the permeances especially for the strongly absorbing gas components were increased by the surface diffusion mechanism.

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