

수소 스테이션용 템플레이팅 실리카/알루미나 복합막을 이용한 콤팩트형 수소 분리

문중호, 배운상, 이상진, 이창하*

연세대학교 화학공학과

(leech@yonsei.ac.kr*)

Compact Type Hydrogen Separation Using Templating Silica/Alumina Composite Membrane for a Hydrogen StationJong-Ho Moon, Youn-Sang Bae, Sang-Jin Lee, Chang-Ha Lee*

Department of Chemical Engineering, Yonsei University

(leech@yonsei.ac.kr*)

Introduction

With the steady depletion of fossil fuel reserves, hydrogen based energy sources become increasingly attractive. Therefore hydrogen production or separation technologies, such as gas separation membrane based on adsorption technology, have received enormous attention in the industrial and academic fields. In this study, the transport mechanisms of the MTES (methyltriethoxysilane) templating silica/ α -alumina composite membrane were evaluated by using unary, binary and quaternary hydrogen gas mixtures permeation experiments at unsteady- and steady-states [1]. Since the permeation flux in the MTES membrane, through the experimental and theoretical study, was affected by molecular sieving effects as well as surface diffusion properties, the kinetic and equilibrium separation should be considered simultaneously in the membrane according to molecular properties. In order to depict the transient multi-component permeation on the templating silica membrane, the GMS (generalized Maxwell-Stefan) and DGM (dust gas model) were adapted to unsteady-state material balance [2-3].

Theory

The mass balance of a component i in an infinitesimal volume can be presented as follows [1-2].

$$\frac{\varepsilon}{RT} \frac{\partial P_i}{\partial t} + (1 - \varepsilon) \frac{\partial q_i}{\partial t} = - \frac{1}{r} \frac{\partial (rN_i^{tot})}{\partial r} \quad (i = 1, \Lambda, n) \quad (1)$$

The total permeate flux is composed of pore diffusion and surface diffusion ($N_i^{tot} = N_i^p + N_i^s$). The multi-component pore diffusion composed of Knudsen diffusion and Poilseulle diffusion can be expressed by DGM.

$$N_i^p = - \frac{\varepsilon}{\tau RT} \left(D_i^{Kn} + \frac{B_i^0}{\eta_i} P_i \right) \cdot \frac{\partial P_i}{\partial r} \quad (2)$$

The surface flux through a multi component system can be expressed by GMS [3]:

$$N_1^S = -\rho \cdot (1-\varepsilon) \cdot q_1^{sat} \cdot \frac{D_1^S}{1-\theta_1-\theta_2} \cdot \frac{\left[(1-\theta_2) + \theta_1 \frac{D_2^S}{D_{12}^S} \right] \nabla \theta_1 + \left[\theta_1 + \theta_1 \frac{D_2^S}{D_{12}^S} \right] \nabla \theta_2}{\theta_2 \frac{D_1^S}{D_{12}^S} + \theta_1 \frac{D_2^S}{D_{12}^S} + 1} \quad (3)$$

Where surface coverage, θ_i , is calculated by Langmuir isotherm model.

$$\theta_i = \frac{q_i}{q_i^{sat}} = \frac{b_i P_i}{1 + \sum b_j P_j} \quad (4)$$

Experimental

1. Membrane synthesis

Organic templating membranes were prepared by a dip coating on tubular α -Al₂O₃ support or γ -Al₂O₃ /SiO₂ composite support (outside diameter, 10mm; thickness, 1.0 mm, length 100 mm; and mean pore diameter 0.1 μ m) by MTES (methyltriethoxysilane) sols. After several times of dip coating, MTES templating silica membranes (mean pore diameter \approx 3 Å) without pinhole and crack products were prepared [1].

2. Measurement of permeation and separation

Measurements of gas permeation of H₂, CH₄, N₂, CO and CO₂ on inorganic membrane were performed in the 323-473 K temperature range, 100-700 kPa pressure range. The permeation of single gas was measured in dead-end mode without the retentate stream. However, permeation of H₂ binary and quaternary gas mixtures were measured by a through-flow type in order to control stage-cut. The flow rate and composition of separated gas in the binary and quaternary mixtures were analyzed by an online mass spectrometer (QMG 422, Balzers Co., Germany).

Results and discussion

1. Single gas permeation

Fig. 1(a) shows the steady-state permeations of H₂, CH₄, N₂, CO and CO₂ through the MTES membrane. H₂ was found to have almost linear permeation fluxes that were proportional to feed pressure. In addition, permeate fluxes of other molecules were non-linearly proportional to feed pressure. CO₂ permeation exhibited particularly strong favorable curvature in the permeation flux, which resulted from a high adsorption affinity. In addition, as can be seen in Fig. 1(b), it is noteworthy that the observed temperature dependency of each molecule is different. The permeate flux of CO₂ was high at low temperature, but decreased with increasing temperature. On the other hand, the permeate fluxes of H₂, He, CH₄, and N₂, increased with increasing temperature. Especially H₂ showed strong temperature dependencies; as temperature increased, its permeation flux also increased due to increased movement of molecules. Fig. 1(c) shows the transient permeations of H₂, CO₂, CO, N₂, and

CH₄ on the MTES membrane at 323 K and 500 kPa. Where, N_i/N_i^0 is the proportion between a steady-state permeation flux and the transient permeation flux at a feed pressure. H₂ reached steady-state within about 30 sec, significantly earlier than the other components. CO₂ reached steady-state at about 200 sec, while CO, N₂ and CH₄ took longer than 700 sec to reach steady-state.

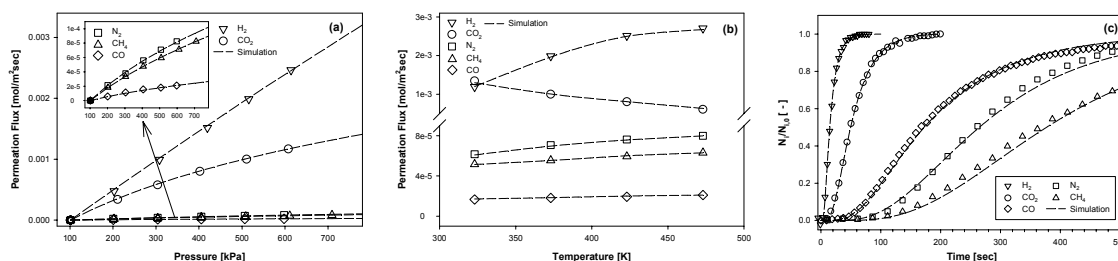


Fig. 1. Single gas Permeation flux of H₂, CO₂, N₂, CH₄ and CO on a MTES membrane : (a) pressure effect at 373 K, (b) temperature effect at 500 kPa and (c) transient permeation at 373 K and 500 kPa

2. Separation of H₂ in gas mixtures : steady-state permeation of binary system

Fig. 2 shows the steady-state permeations and ideal separation factors of (a) H₂/CH₄, (b) H₂/CO₂ and (c) H₂/N₂ mixtures through the MTES membrane. As can be seen in Fig. 2, H₂ selectivity was very high in binary systems. H₂ molecules were not affected by steric hindrance of the MTES templating silica layer with complex amorphous pore structure. This is due to its structure, small kinetic diameter (2.92 Å), and weak adsorption affinity. However, in Fig. 2(a), the permeation of CH₄ was very low because the tetrahedral structure and relatively large kinetic diameter (3.82 Å) of CH₄ led to steric hindrance or molecular sieving on the MTES templating silica layer. In addition, as shown in Fig. 2(b), the permeation of N₂ was low due to its large kinetic diameter (3.64 Å), even though it has a linear structure. In case of H₂/CO₂ mixture, in Fig. 2(c), owing to strong surface diffusion effect, relatively low H₂ selectivity was observed. The flux of H₂ was significantly hindered by the strongly adsorbed CO₂ molecules. As a result, the CO₂ selectivity led to blockage of the H₂, one of the major properties of a nano- or micro-porous membrane relying on surface diffusion. It is remarkable that separation factors of CO₂ and CH₄, molecules with strong adsorption affinity, decreased with increasing pressure. On the other hand, N₂, with comparatively lower adsorption affinity, showed opposite tendency.

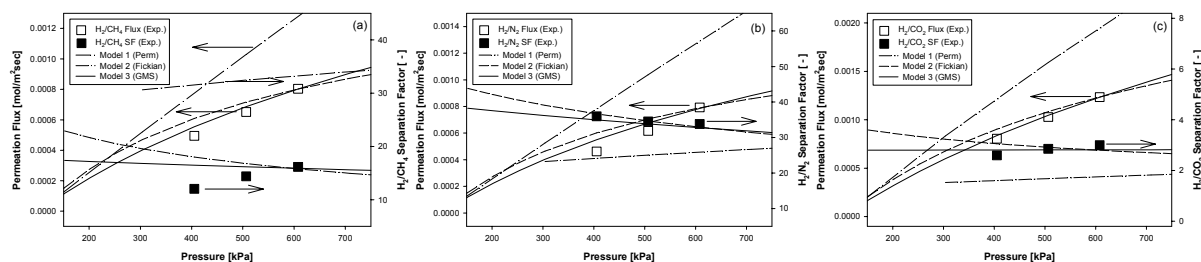


Fig. 2. Permeation fluxes and separation factors of binary mixtures on a MTES membrane at 373K : (a) H₂/CH₄ (50:50 vol %), (b) H₂/N₂ (50:50 vol %) and (c) H₂/CO₂ (50:50 vol %)

3. Separation of H₂ in gas mixtures : transient permeation of binary and quaternary system

Fig. 3 shows the transient permeations and separations of (a) binary system H₂/CH₄ (50:50 vol %) at 323 K and 500 kPa, (b) quaternary system H₂/CH₄/CO/CO₂ (67:3:2:26 vol %) at 373 K and 500 kPa. As can be seen in Fig. 3 (a), permeation rate of H₂ became slower owing to blocking effect of strongly adsorbed CH₄ on MTES pore wall. On the contrary, permeation rate of CH₄ became somewhat faster comparing to single gas permeation in Fig. 1(c). Permeation of quaternary system in Fig. 3(b) also shows similar behavior of binary system in Fig. 3(a). H₂ enhance the permeation rate of other molecules, but permeation rate of H₂ was hindered by other slow molecules. However, due to the sieving effect, concentration of H₂ increased and those of other molecules were decreased. As can be seen in Fig. 3(b), mole fractions of CO (2 % → 0.39 %), CO₂ (26 % → 5.2%) and CH₄ (3 % → 0.9%) were decreased considerably. Since elimination of CO, CO₂ and CH₄ improves efficiency of reformer greatly in H₂ station, adaptation of the MTES membrane as compact type H₂ purifier might be an effective solution.

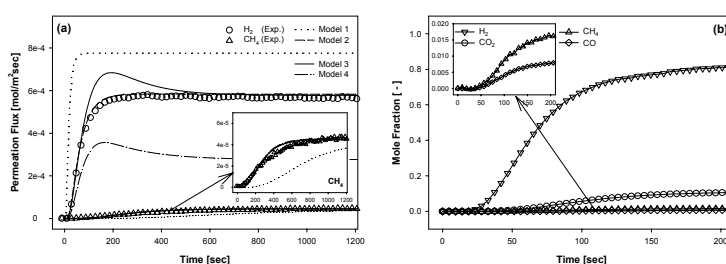


Fig. 3. Transient permeation fluxes on MTES membrane : (a) binary system H₂/CH₄ (50:50vol %) at 323 K and 500 kPa and (b) quaternary system H₂/CH₄/CO/CO₂ (67:3:2:26 vol %) at 373 K and 500 kPa

Conclusion

Since the permeation flux in the MTES membrane was affected by molecular sieving effect, as well as surface diffusion property, the kinetic and equilibrium separation should be considered simultaneously in the membrane according to molecular properties.

Reference

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