



Kinetic effects of methane on binary mixture separation on methyltriethoxysilane templated silica membranes



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ABSTRACT

Separation characteristics and dynamic behavior of two binary mixtures, CO₂/CH₄ (50:50, vol%) and CH₄/N₂ (50:50, vol%), on methyltriethoxysilane templated silica (MTES) membrane were studied experimentally and theoretically. The permeation of the binary mixtures was compared with that of pure CO₂, CH₄, and N₂ at 323–473 K and 300–600 kPa. The permeation flux of pure CO₂, which has the strong adsorption affinity, was much higher than that of CH₄. However, the permeation flux of the CO₂/CH₄ mixture was hindered by CH₄ with large kinetic diameter. Although the permeation flux of pure N₂ was higher than that of pure CH₄, the permeation flux of CH₄ in the CH₄/N₂ mixture was greater than that of N₂ owing to the disturbance of N₂ permeation by CH₄ and the relatively weak adsorption affinity of N₂. Because the molecular interactions, adsorption affinity, and kinetic diameter and structure of each component contributed to the separation, compared to the separation factors, the permselectivity was overestimated in the CO₂/CH₄ mixture, but somewhat underestimated in the CH₄/N₂ mixture. Due to its kinetic effects, the diffusion mechanism of CH₄ needs to be investigated thoroughly in pore-controlled silica-based membranes. The transient permeation and separation behaviors of the binary mixtures on MTES membranes were successfully predicted by the generalized Maxwell–Stefan model, which incorporated the dusty gas model and Langmuir isotherm model.

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1. Introduction

Since various industrial effluent gases contain CO₂, N₂, and CH₄, understanding the permeation behaviors of these gases is important for gas separation and purification processes, such as H₂ recovery, CO recovery, CH₄ recovery, and CO₂ capture. Furthermore, the separation of CO₂ and N₂ from CH₄ is crucial in many natural gas wells for energy efficiency and corrosion prevention. Membrane processes are attractive for removing CO₂ and N₂ from various gases because they are inexpensive and involve low energy consumption [1,2].

Polymeric membranes for CO₂ and N₂ separation from natural gas were first used in the 1980s. Studies to improve the process efficiency of such membranes are still ongoing because the high

CO₂ partial pressure in natural gas wells can plasticize polymeric membranes and decrease their separation performance. As an alternative, microporous inorganic membranes with pore sizes of less than 1 nm have been widely studied for gas separation owing to their superior thermal and mechanical stability, good chemical resistance, and high pressure stability [3,4]. In addition, inorganic membranes are expected to be useful in membrane reactors to enhance conversion in dehydrogenation and methane reforming reactions [5].

Microporous silica [6], carbon molecular sieve (CMS) [7,8], metal organic framework (MOF) [9,10], and zeolite membranes [11,12] have been reported for gas (vapor) mixture separation [13,14]. Stability is still an important issue, even in microporous inorganic membranes, as some membranes are decomposed and densified by water, which significantly reduces the permeability [15–17]. On the other hand, methyltriethoxysilane templated silica (MTES) membranes, which incorporate hydrophobic terminal methyl groups (–Si–CH₃), show much greater hydrophobicity than silica membranes (more than 10 times), making MTES membranes an attractive and practical solution for densification [18–20].

Abbreviations: MOF, metal organic framework; MTES, methyltriethoxysilane templating silica; CMS, carbon molecular sieve; GMS, generalized Maxwell–Stefan; DGM, dusty gas model; MFC, mass flow controller; LRC, loading ratio correlation; CFD, centered finite difference method; DAE, differential algebraic equation.

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Nomenclature

Roman letters

b_i	parameter in the Langmuir isotherm model (Pa^{-1})
$b_{0,i}$	parameter of species i in the Langmuir isotherm model at zero loading (Pa^{-1})
B_i^0	Poiseuille structural parameters of species i (m^2)
C_i	molar concentration of species i (mol cm^{-3})
D_i^{Kn}	Knudsen diffusivity of species i ($\text{m}^2 \text{sec}^{-1}$)
$\mathcal{D}_{0,i}$	Maxwell-Stefan surface diffusivity at infinite temperature ($\text{m}^2 \text{sec}^{-1}$)
\mathcal{D}_i	Maxwell-Stefan surface diffusivity ($\text{m}^2 \text{sec}^{-1}$)
E_a	activation energy (J mol^{-1})
ΔH_{ads}	heat of adsorption (J mol^{-1})
k_1	temperature-dependent parameter for saturated adsorption capacity (mol g^{-1})
k_2	temperature-dependent parameter for saturated adsorption capacity (-)
l	effective membrane thickness (m)
l'	membrane thickness measure by SEM image (m)
M_i	molecular weight of species i (mol g^{-1})
N_i	molar flux of species i ($\text{mol m}^{-2} \text{sec}^{-1}$)
N_i^{Kn}	molar flux of Knudsen diffusion of species i ($\text{mol m}^{-2} \text{sec}^{-1}$)
N_i^{P}	molar flux of pore diffusion of species i ($\text{mol m}^{-2} \text{sec}^{-1}$)
N_i^{S}	molar flux of surface diffusion of species i ($\text{mol m}^{-2} \text{sec}^{-1}$)
N_i^{tot}	total molar flux of species of i ($\text{mol m}^{-2} \text{sec}^{-1}$)
N_i^{vis}	molar flux of viscous diffusion of species i ($\text{mol m}^{-2} \text{sec}^{-1}$)

$N_{i,0}$	molar flux of species i at pseudo-steady-state ($\text{mol m}^{-2} \text{sec}^{-1}$)
P_i	partial pressure of species i (Pa)
q_i	adsorbed species concentration within layer pores (mol g^{-1})
q_i^{sat}	saturated capacity of adsorbed species i (mol g^{-1})
R	gas constant, $8.314 \text{ (J mol}^{-1} \text{K}^{-1})$
r_p	pore radius (m)
T	absolute temperature (K)
t	time (sec)

Greek letters

β	penetration modification factor (-)
Γ_{ij}	thermodynamic factor of species i, j (-)
ε	porosity of membrane (-)
η_i	viscosity of species i (Pa s)
θ_i	fractional surface occupancy of species i (-)
μ_i	chemical potential of species i (J mol^{-1})
ρ	membrane density (g m^{-3})
τ	tortuosity factor (-)

Subscripts and superscripts

$i, j, 1, 2$	component $i, j, 1, 2$
vis	viscous flow
Kn	Knudsen flow
tot	total flow
sat	saturated

Microporous inorganic membranes with adsorptive surface diffusion and molecular sieve properties have relatively high gas permeance and good selectivity at elevated temperatures [21–25]. In the case of adsorptive and molecular sieving materials, such as zeolite or CMS membranes, the permeation/separation mechanisms have been studied in extensive detail [6,26–28]. Equilibrium and kinetic effects in inorganic membranes are reported to be important for the development of efficient membrane systems.

Many attempts have been made to improve the selectivity and permeance of inorganic membranes for CH_4 separation by developing new membrane materials or systems [5,6,29–34]. However, the performance of most silica membranes has been evaluated using single gas permeation tests, even though gas mixture measurements are required for practical applications because of the possible effects of both equilibrium and kinetic controls among the different molecules in the pores on separation [22,30,31,35]. Furthermore, the tetrahedral structure of CH_4 is expected to have a significant structural hindrance effect on the permeation of other molecules in the membrane pores [29]. Therefore, understanding the kinetic role of CH_4 in surface diffusion and adsorptive affinity is important for achieving separation of CO_2 and N_2 , as well as other gases from CH_4 .

This study investigated the permeation and separation of CO_2/CH_4 and CH_4/N_2 mixtures through tubular-type methyltriethoxysilane templating silica/ α -alumina composite membrane (MTES membrane) under transient (unsteady) and pseudo-steady-state conditions. Experiments using single gases (CO_2 , CH_4 , and N_2) and binary mixtures (CO_2/CH_4 (50:50, vol%) and CH_4/N_2 (50:50, vol%)) were performed at 323–473 K and 300–600 kPa. Subsequently, the kinetic effects of CH_4 on mixture separation resulting from its structural and adsorptive characteristics were elucidated. To depict the dynamic permeation and separation mechanisms of the mixtures theoretically, the GMS (generalized Maxwell–Stefan)

model, which incorporated the DGM (dusty gas model) and Langmuir isotherm model, was applied to the experimental results.

2. Experimental methods

A $\text{SiO}_2/\alpha\text{-Al}_2\text{O}_3$ composite support (1.6 nm mean pore diameter) was prepared by pressurized coating of a colloidal silica sol inside tubular $\alpha\text{-Al}_2\text{O}_3$ supports (100 mm length and 0.1 μm mean pore diameter). Using MTES (99% purity, Aldrich, USA) sol as a structure-directing agent, the organic-templated silica composite membrane was fabricated by repeatedly dip-coating the $\text{SiO}_2/\alpha\text{-Al}_2\text{O}_3$ composite supports in the templating silica sols. The pore size of the silica composite membrane was controlled by using a TEOS-EtOH solution, and a uniform pore radius of $\sim 3 \text{ \AA}$ was obtained in the amorphous silica membrane. The characteristics of the membrane are described in Table 1. The synthesis of the membrane was described previously in detail [22,29].

A schematic of the experimental membrane system is shown in Fig. 1. The MTES membrane was placed in a stainless steel tubular module consisting of a body, disks, and lids, which is called a modified Wicke–Kallenbach cell. Then, the permeation and separation were evaluated under transient (unsteady) and pseudo-steady-state (constant permeation flux) conditions.

The cell consisted of a sweeping gas inlet line and a three-way permeated outlet line to prevent the stagnation of permeated gases. The inlet gas line, inner cell and outer cell were equipped with thermocouples (RTD-type, Pt 100 Ω) to measure the system temperature. Two electrical heating tapes were wrapped from the front of the inlet gas to the membrane cell. The cell temperature was regulated by a temperature controller with a thermocouple at the outer cell while the experimental temperature was measured by a thermocouple at the inner cell positioned in the

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