



Gas separation using tetrahydrofuran clathrate hydrate crystals based on the molecular sieving effect



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ABSTRACT

The molecular sieving effect of tetrahydrofuran (THF) clathrate hydrate was experimentally investigated. The capture and release of seven gases, i.e., helium (He), hydrogen (H₂), neon (Ne), nitrogen (N₂), xenon (Xe), methane (CH₄), and ethane (C₂H₆), in THF clathrate hydrate were investigated. For gases with a diameter smaller than the window diameter, the order of the gas uptake rates in the THF clathrate hydrate was in accordance with the order of their van der Waals diameters, except for He. This result indicates that the gas uptake rate is generally controlled by the size of the gas molecules. The apparent diffusion coefficients for these gases in the THF clathrate hydrate were estimated. The van der Waals diameters of CH₄ and Xe are larger than the window diameter. However, gas uptake by THF clathrate hydrate was observed for both gases. This can be attributed to the formation of the type I clathrate hydrate of these gases. No significant gas uptake of ethane was observed. Based on the results, H₂/N₂ and H₂/C₂H₆ separation experiments were conducted. Gas separation of H₂/N₂ by THF clathrate hydrate was successfully achieved using the difference in their gas uptake rates of the gases, and the separation ratios were in the range 4–16 mol/mol. Gas separation of H₂/C₂H₆ was also achieved utilizing the molecular sieving effect of THF clathrate hydrate.

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1. Introduction

Tetrahydrofuran (THF) forms the type II clathrate hydrate structure, where the large cages are occupied by THF molecules and the small cages are empty [1]. Fig. 1 shows the THF clathrate hydrate structure. The empty small cages can hold hydrogen (H₂) molecules, and THF clathrate hydrate could be used as a hydrogen storage medium [2–8]. The capture of H₂ by THF clathrate hydrate is reversible. With increasing partial pressure of H₂, the occupancy of the small cages increases, and the occupancy decreases with decreasing pressure. This suggests that H₂ can reversibly pass through the surface of the THF clathrate hydrate crystals. The transportation of H₂ would occur through the surface of the small

cages. The effective “window” diameter of the small cages is about 4.2 Å, which is larger than the van der Waals diameter of H₂ (2.72 Å). Thus, it can be considered that a molecular diameter ≤4.2 Å is required for reversible capture and release by THF clathrate hydrate. When THF clathrate hydrate is exposed to a gaseous mixture containing component 1 that can pass through the crystal surface and component 2 that is repelled by the crystal surface, only component 1 will be captured by THF clathrate hydrate. After capture, pure component 1 can then be separated by releasing it from the THF clathrate hydrate. Therefore, THF clathrate hydrate can be used as a molecular-sieving absorbent [9]. In our previous study [9], we prepared composite membranes composed of a thin layer of THF clathrate hydrate formed on a porous alumina support membrane. The thickness of the THF clathrate hydrate layer can be controlled by a combination of dipping and coating methods. Permeation of helium (He) through the composite membrane was observed, while no permeation of sulfur hexafluoride (SF₆) was observed, and thus a molecular sieving effect was achieved.

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Nomenclature

C	gas concentration in gas phase (mol/m ³)	\bar{q}	value of q averaged over all THF clathrate hydrate particles (mol/m ³)
C_0	initial value of C (mol/m ³)	r	radial distance (m)
C_∞	value of C as $t \rightarrow \infty$ (mol/m ³)	r_p	radius of THF particle (m)
D	apparent diffusion coefficient (m ² /s)	R	gas constant (J/(mol K))
$n(t)$	amount of pure gas in gas phase (mol)	t	time (s)
$P(t)$	gas pressure at time t (Pa)	T	temperature (K)
$Q(t)$	gas uptake at time t (mol/g-hydrate)	V_G	gas phase volume (m ³)
$Q_A(t)$	uptake of gas A at time t (mol/g-hydrate)	w	amount of THF clathrate hydrate in the cell (g)
$Q_B(t)$	uptake of gas B at time t (mol/g-hydrate)	x_A	molar fraction of gas A (-)
q	gas concentration in THF clathrate hydrate (mol/m ³)	x_B	molar fraction of gas B (-)
q_0	initial value of q (mol/m ³)		
q_∞	final value of q as $t \rightarrow \infty$ (mol/m ³)		

In this study, we applied the molecular sieving effect to experimentally investigate the capture and release phenomena of He, H₂, neon (Ne), nitrogen (N₂), xenon (Xe), methane (CH₄), and ethane (C₂H₆) in THF clathrate hydrate. Based on the results, H₂/N₂ and H₂/C₂H₆ separation experiments were conducted, which uses the difference in gas uptake behavior of the different gases.

2. Experimental

2.1. THF clathrate hydrate preparation

An aqueous solution of THF without stabilizer was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and used for THF clathrate hydrate preparation. The stoichiometric ratio of THF to water in the type II clathrate hydrate has been reported to be 19 wt% (corresponding to 1:17 M ratio) [1,10–12]. The concentration of THF was fixed, which was slightly higher than the stoichiometric condition to take into account the evaporation of THF. The aqueous solution was poured into a container and cooled in a freezer at 248 K to form THF clathrate hydrate. The reported melting point of THF clathrate hydrate is 277 K [11,12]. The generation of THF clathrate hydrate was confirmed with a laser Raman spectroscopy system (Seki Technotron Corp., Tokyo, Japan) by observing the shifted characteristic peak for the THF ring-breathing band at 919 cm⁻¹ [13]. The generated THF clathrate hydrate was then crushed and classified in a nitrogen atmosphere.

2.2. Capture/release experiments

Seven gases were used for the experiments: helium, hydrogen, neon, and nitrogen, which have diameters smaller than the window size (4.2 Å), and xenon, methane, and ethane, which have diameters larger than the window size. The capture/release experiments were performed with the apparatus schematically shown in Fig. 2.

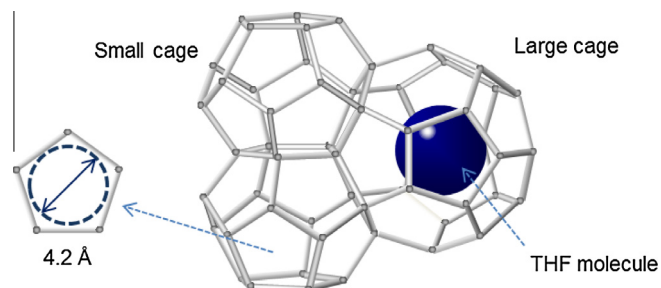


Fig. 1. THF clathrate hydrate structure. The effective “window” diameter of the small cage is about 4.2 Å.

The experimental system was a constant volume system with temperature control. The high-pressure cell was made with SUS 303 stainless steel with an inner volume of 12 mL. Weighted THF clathrate hydrate particles were introduced into the cell, and the cell was immersed in a constant-temperature bath maintained at 268 K. The experimental temperature was set considering the reported melting point of THF clathrate hydrate is 277 K [11,12]. Then, pure gas was introduced into the cell using a cylinder with inner volume of 100 mL at a specific initial pressure. The capture of the pure gas was monitored by the pressure changes accompanied with gas uptake into the THF clathrate hydrate particles. The equilibrium gas uptake by THF clathrate hydrate was then estimated from the gas pressure as follows. The amount of pure gas in gas phase, $n(t)$ (mol), can be calculated by

$$n(t) = \frac{P(t)V_G}{RT} \quad (1)$$

where t (s) is time, $P(t)$ (Pa) is the gas pressure at time t , V_G (m³) is the gas phase volume, R (J/(mol K)) is the gas constant, and T (K) is the temperature under the ideal gas assumptions. The gas uptake at time t , $Q(t)$ (mol/g-hydrate), was then calculated by

$$Q(t) = \frac{[n(0) - n(t)]}{w} \quad (2)$$

where w (g) is the amount of THF clathrate hydrate in the cell.

For the gas release experiment, the inner gas was directly vented from the pressurized cell. The release of the pure gas was

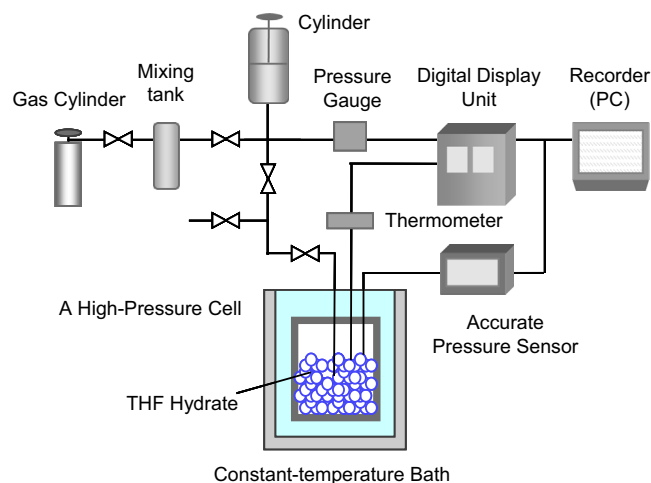


Fig. 2. Schematic diagram of the experimental apparatus for the gas uptake measurements.

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