

Conference Paper

Guest-exchange Behaviors of Different Hydrocarbons with CO₂ + N₂ Occurring in SII Mixed Hydrates

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Abstract

The replacement of SII CH₄-C₂H₆-C₃H₈ hydrates in sandy sediments by CO₂/N₂ is studied to investigate the gas recovery from SII gas hydrate reservoirs. It was found that CH₄ was the easiest one to be replaced in all experiments, and CO₂/N₂ played different roles during replacement in different CO₂ concentrations. Particularly, the addition of N₂ in replacement gas can cause the decrease in the replacement efficiency, which was related with the difference in swapping patterns. The increase of the N₂ concentration may strengthen the structural stability of SII hydrates and lead to reducing the portion of SII hydrates transformed into SI hydrates.

Keywords: gas hydrate, CO₂+N₂, structure II, replacement efficiency

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1. Introduction

Gas hydrates are ice-like crystalline compounds composed of hydrogen-bonded water molecules encapsulating gas molecules [1]. Natural gas hydrates have recently received considerable attention as a promising future energy source because of the large amounts of massive hydrate reservoirs [2]. A series of methods for gas hydrate production have been proposed based on the special characteristics of the hydrate, such as depressurization, thermal stimulation, and inhibitor injection [3], which are all based on decomposition of clathrate crystals through external stimulation. However, when the solid hydrate dissolves, it may lead to destabilization of sediments and subsequent seafloor subsidence [4]. Therefore, the CO₂ replacement method has recently emerged as a promising method of recovering hydrocarbons (HC) without hydrate dissociation and sequestering CO₂ into natural gas hydrate reservoirs, simultaneously [5].

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Since the idea of swapping CO₂ for CH₄ in gas hydrates was first advanced by Ohgaki et al. [6], extensive research of the replacement behaviors of SI hydrates has been conducted [5] owing to their abundance in nature. Beside SI natural gas hydrates predominantly consisting of CH₄ molecules, natural occurrence of SII hydrates has been discovered in some deposits, such as the Gulf of Mexico outside the Caspian Sea [7], Lake Baikal [8], the Qilian Mountain permafrost of China [9], and the Pearl River Mouth Basin of the South China Sea [10]. To date, only few data are available for the swapping process of HC in structure II mixed hydrates [11–15]. The previous reports indicate that structural transformation and isostructural conversion may occur in the replacement of SII hydrates [15]. Compared with CH₄ hydrates, multiple guests engaged into small and large cages of SII natural gas hydrates may cause the unique pattern of the replacement occurring in SII hydrates. Larger HC entrapped in large cages, such as C₂H₆, C₃H₈, and C₄H₁₀, play an important role in the stability of the hydrate structure. Therefore, the release of larger HC from SII hydrates can cause the structural transformation. However, studies on the replacement kinetics of SII hydrates with CO₂/ N₂ are still insufficient.

In this work, the replacement of CH₄ + C₂H₆ + C₃H₈ mixed hydrates using CO₂/N₂ is experimentally studied. The guest-exchange behavior of different HC with CO₂ and N₂ occurring in SII natural gas hydrates was examined through the composition analysis of the fluid phase during replacement. The heterogeneous composition of the final replaced hydrates caused by solid state diffusion was indirectly obtained by coupling gas production measurements with compositional analysis. Furthermore, the replacement efficiencies of different HC were calculated based on the final compositions of the replaced hydrates and the composition of the vapor phases measured by a gas chromatography.

2. Experimental Section

CO₂ (99.99%) and gas mixtures of CH₄ (81.10%) + C₂H₆ (9.53%) + C₃H₈(9.37%), CO₂ (21.10%) + N₂ (78.9%), and CO₂ (53.87%) + N₂ (46.13%) were supplied by Beifang Special Gas Industry Corporation.

Figure 1 shows a schematic diagram of the apparatus and its components. The high-pressure cell has an effective volume of 240 ml, which was immersed in the circulating and cooling glycol bath to keep stable temperature during the experiments. The temperature and pressure of the system are recorded on a PC using a Monitor and Control Generated System through a data acquisition device at regular time intervals.

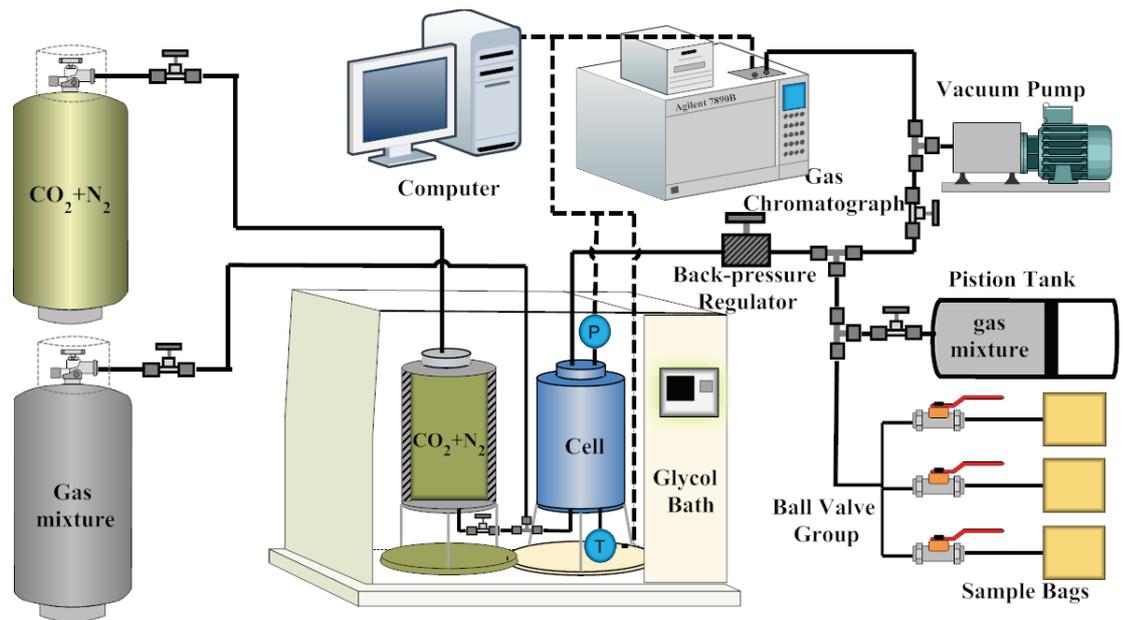


Figure 1: Schematic of the experimental apparatus.

The experimental procedure for the initial CH₄ + C₂H₆ + C₃H₈ hydrate formation was similar to that in our previous work [16]. The cell was initially charged with a known amount of water-saturated porous quartz sands and submerged in the glycol bath to control the temperature. The gas mixture of CH₄ + C₂H₆ + C₃H₈ was injected into the pressure cell to the desired value after vacuuming the whole apparatus, and then the temperature of the cell was gradually lowered to 277.2 K to form mixed hydrates.

After completion of mixed hydrate formation, the pre-cooled replacement gas was rapidly injected into the reactor to purge the remaining gas mixture of HC. When the HC composition of the discharged gas appeared to be less than 0.5 mol %, the outlet valve was closed and the replacement gas was continuously injected into the pressure cell. The replacement process started once the desired pressure was reached and was monitored by taking a series of gas samples at specified time intervals; the gas samples were analyzed using a gas chromatograph. In this study, the experimental parameters of 3 runs for replacement are listed in Table 1.

The replaced hydrates dissociation experiment was performed at the end of the replacement stage. The cell was depressurized rapidly to the atmospheric pressure. At the same time, the gas released from hydrates dissociation was collected in gas sample bags one by one through the ball valve group. The compositions of the gas phase in the sample bags were measured by a gas chromatograph.

TABLE 1: Experimental conditions for CH₄-C₂H₆-C₃H₈ hydrates replacement by CO₂/N₂.

Runs	T/K	CO ₂ /N ₂	Replacement Pressure /MPa	Gas Compositions (Mole Fraction, CH ₄ /C ₂ H ₆ /C ₃ H ₈)		Hydrate Saturation /%	Water Saturation /%	Replacement Time/Hour
				Feed gas	Hydrate			
1	277.2	100/0	2.90	81.10/9.53/9.37	70.44/14.61/14.95	17.85	1.95	210
2	277.2	53.87/46.13	5.37	81.10/9.53/9.37	70.44/14.07/15.48	19.23	0.89	286
3	277.2	21.10/78.90	14.84	81.10/9.53/9.37	69.49/14.94/15.57	18.06	1.82	286

3. Results and Discussion

3.1. Composition analysis of fluid phase

In order to examine the exchange behaviors of multiguests CH₄, C₂H₆, and C₃H₈ in hydrate cavities with CO₂ and N₂, the compositions of the fluid phase under different experimental conditions were measured during replacement. As seen in Figure 2, the fluid composition became gradually decrease in CO₂/N₂ and rich in HC as the HC in hydrates were continuously released to the fluid phase during replacement. This indicated that CO₂ and N₂ molecules could substitute CH₄, C₂H₆, and C₃H₈ molecules entrapped in the cages of mixed hydrates in initial stage of swapping, which was also confirmed in the previous reports.

In particular, the C₃H₈ concentration was found to remain nearly constant after a rapid increase, implying that a small amount of C₃H₈ in the mixed hydrates was displaced especially in the initial stage of swapping. This phenomenon is in accordance with the C₃H₈-CO₂ exchange behavior during the CH₄+C₃H₈-CO₂ replacement in earlier investigation [15]. Earlier studies reported that the driving force of replacement was the gradient of the chemical potential between the hydrate phase and the surrounding phase [12]. The phenomenon in exchange features of C₃H₈ is likely attributed to the difference in chemical potential of the C₃H₈ molecules between the hydrate phase and the surrounding fluid after the rapid initial reaction.

To further investigate the roles of N₂ and CO₂ in the replacement reaction of SII hydrates, the time evolutions of N₂ and CO₂ consumed for the replacement are shown in Figure 3. As shown in Figure 3(a), when the mixed hydrates reacted with 53.87 mol % CO₂ and balanced N₂ gas mixture, the consumption of CO₂ for replacement was large in the early stage of replacement, while the consumption rate of N₂ nearly kept the constant. This indicated that CO₂ had a great replacement driving force at the initial stage of replacement, which could have a great contribution to the production of HC

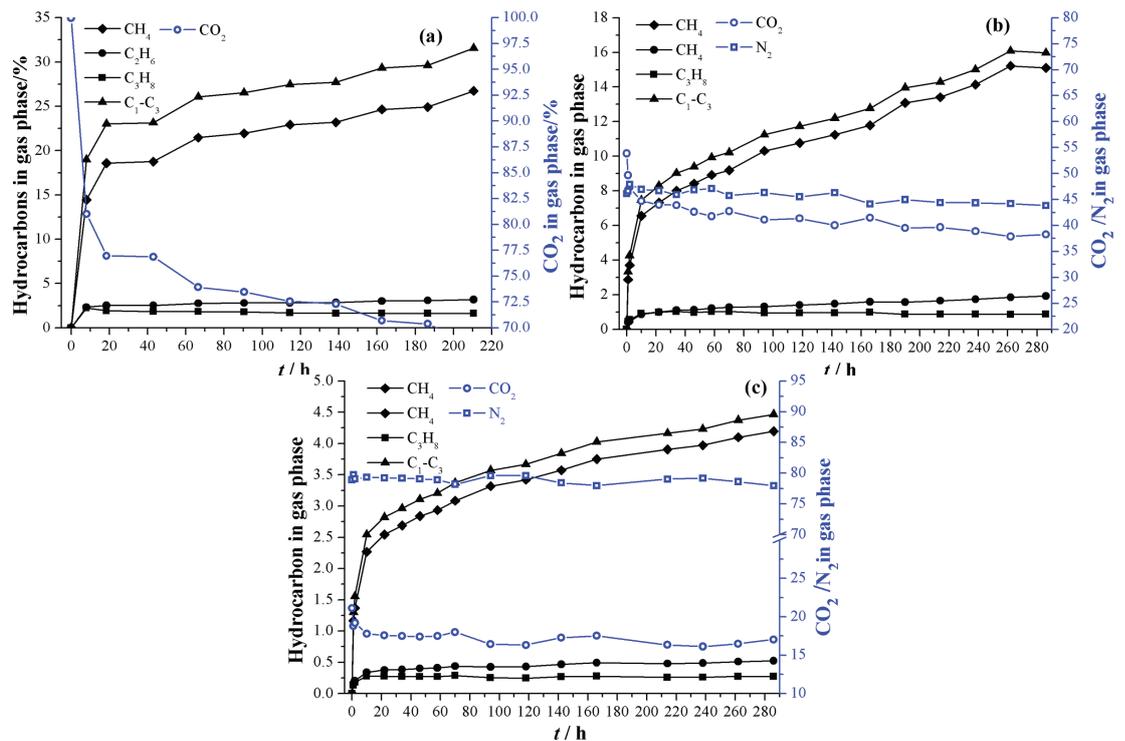


Figure 2: Composition changes in the vapor phase/ liquid phase during replacement at (a) run 1, (b) run 2, (c) run 3.

gases. As the replacement proceeded, the replacement driving force of CO₂ became smaller, and it was more difficult to participate in replacement reaction in the later period. As shown in Figure 3(b), when the mixed hydrates reacted with 21.10 mol % CO₂ and balanced N₂ gas mixture, unlike run 2, the consumption of CO₂ and N₂ for replacement was large in the early stage of replacement. This indicated that both CO₂ and N₂ had a great replacement driving force at the initial stage of replacement, and the thermodynamic effect of CO₂ and N₂ played an important role in the whole process of replacement, because N₂ had a higher partial pressure during run 3 than that during run 2.

3.2. Heterogeneous composition of the replaced hydrates

During the replacement, the parent- and ambient-gas molecules are diffusively transported across the mixed gas hydrate structure [17–21], resulting in the heterogeneous composition of the replaced gas hydrate particles with the continuous concentration changes of guest species along the radius of the replaced gas hydrate particles. As

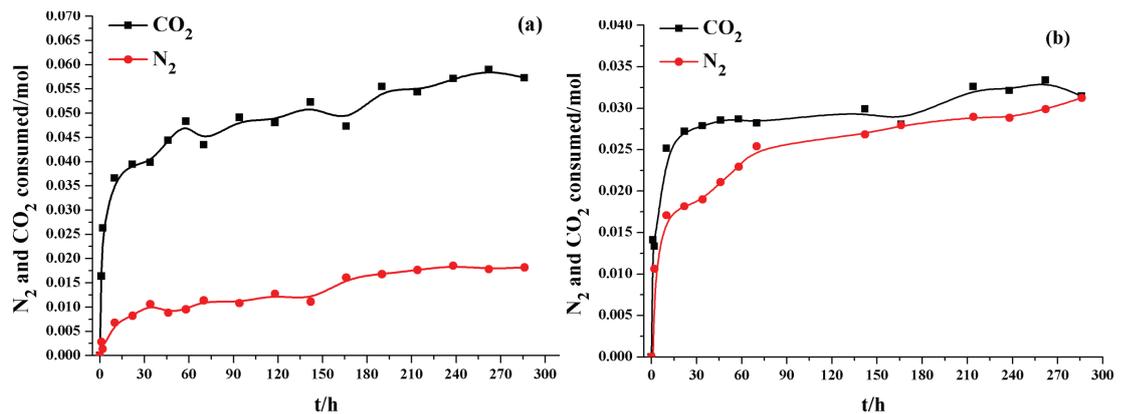


Figure 3: Amount of CO₂ and N₂ consumed for hydrate replacement at 277.2 K: (a) run 2 and (b) run 3.

reported, hydrate decomposition occurs at the solid surface and follows a shrinking-core type pattern [22–24]. Therefore, in this study, the method of coupling gas production measurements with compositional analysis was put forward to investigate the heterogeneous composition of the replaced hydrates.

Figure 4 shows the evolution of the composition of different layers within the replaced gas hydrate particles. It can be observed that the fractions of HC components increased gradually along the radius of the replaced hydrate particles, accompanying a decrease of the CO₂ and N₂ fraction. This indicated that more HC molecules were substituted by CO₂ and N₂ molecules at the surface of replaced hydrates and the replacement efficiency of each hydrate layer decreased gradually from the surface to the core, which was attributed to the outer mixed-hydrate layers hindering the inbound and outbound transport of guest species. The different roles of the CO₂/N₂ gas molecules in the replacement reaction could be more clearly observed in the composition changes across the replaced gas hydrate particle. As shown in Figure 4, the CO₂ concentration of each hydrate layer decreased faster from the surface to the core, while N₂ concentrations of different hydrate layers changed little. This meant that the surface mixed hydrates might hinder the diffusion of CO₂ molecules across the mixed gas hydrate structure and had almost no effects on N₂ molecules. The initial mole ratio of N₂ to CO₂ in gas phase of run 3 was about 4, but after replacement reaction it decreased to about 1 in different hydrates layers. A similar fractionation effect occurred also in run 3. This gives us an important information about the replacement reaction, implying that there is preferential occupancy of CO₂ in the hydrate cavities.

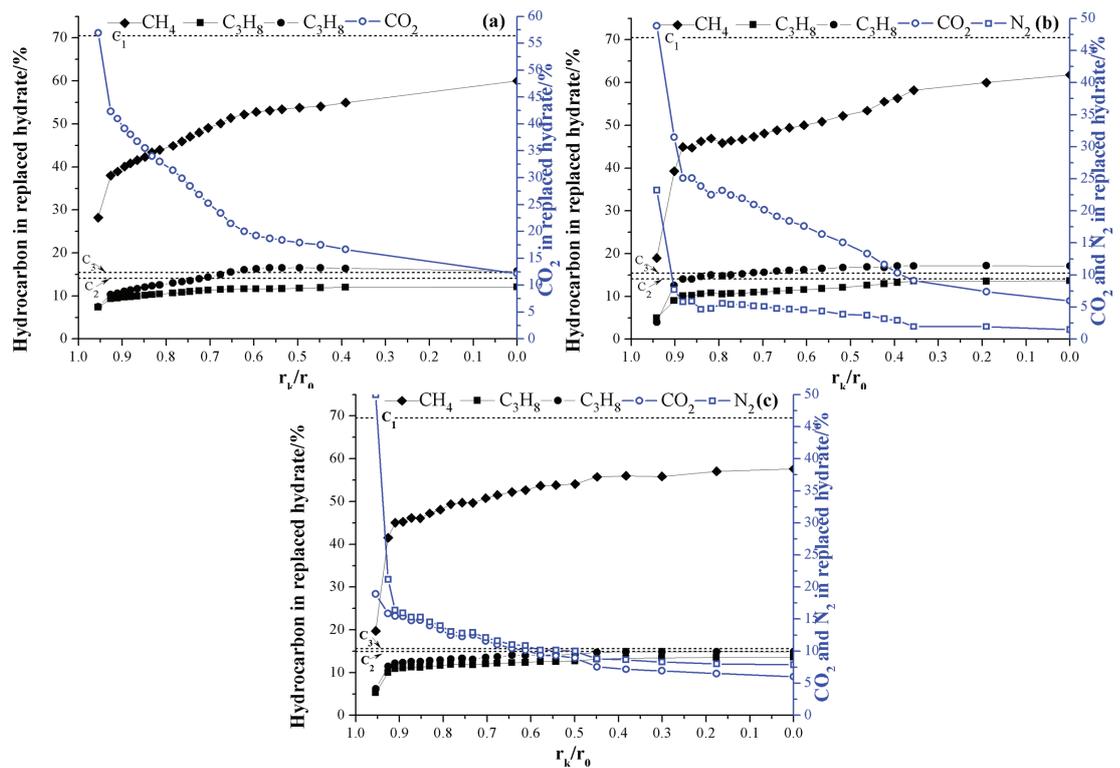


Figure 4: Composition changes of HC, CO₂, and N₂ across the replaced gas hydrate particle: (a) run 1, (b) run 2, and (c) run 3.

3.3. Replacement efficiencies of CH₄-C₂H₆-C₃H₈ hydrates

The guest-to-cavity size ratios of C₁, CO₂, C₂, and C₃ in SI and SII hydrates indicating the preferential occupation of different cages by different guests [1] are listed in Table 2. C₃H₈ molecules possess a sufficient enclathration power to be entrapped in SII-L, because the order of the guest-to-cavity size ratios for SII-L was C₃ > C₂ > CO₂ > C₁ > N₂. Therefore, it is reasonably expected that during the replacement, the exchange of C₃ with CO₂ and N₂ in large cavities of SII hydrates could be accomplished more difficult than that of C₂ and C₁ in large cavities, when the SII hydrates go through SII-isostructural replacement.

In this study, we defined the replacement efficiency of each component as the ratio of the mole of each component in gas phase to the initial mole of each component in hydrate. The final replacement ratios of different HC in all experiments were measured by gas chromatograph (Figure 5). As shown in all experiments, the order of the replacement efficiencies of different HC was C₁ > C₂ > C₃. The overall preferential exchange of C₂H₆ than C₃H₈ indicating SII-isostructural replacement played a major role, although the structural transformation into SI hydrate might occur during the

TABLE 2: Ratios of molecular diameters to cavity diameters for some guest molecules [1].

Molecule	Guest diameter/Å	Structure I		Structure II	
		5 ¹²	5 ¹² 6 ²	5 ¹²	5 ¹² 6 ⁴
N ₂	4.1	0.804	0.700	0.817	0.616
CH ₄	4.36	0.855	0.744	0.868	0.652
CO ₂	5.12	1.00	0.834	1.02	0.769
C ₂ H ₆	5.5	1.08	0.939	1.10	0.826
C ₃ H ₈	6.28	1.23	1.07	1.25	0.943

replacement. In particular, all runs had the similar partial pressure of CO₂, the replacement efficiency gradually decreased with the increase of N₂ concentration. Compared to previous reports on the replacement of CH₄ hydrate with external CO₂/N₂ gas, the addition of N₂ in replacement gas could bring replacement efficiency down instead up, which might be attributable to differences in swapping patterns. The swapping pattern of the mixed hydrates by CO₂/N₂ is shown in Figure 6. In run 1, the SII mixed hydrates at surface may transform into SI hydrates after the injection of CO₂ followed by a SII isostructural replacement occurred inside the particle. In runs 3 and 4, the SII mixed hydrates may mainly go through isostructural replacement. The hydrate structural transition from SII into SI that led to a markedly decrease of small cage fraction [11] would result in the release of HC to a large extent and enhance the extent of replacement. Since pure N₂ gas could react with water and form SII hydrates, the addition of N₂ in replacement gas might strengthen the stability of SII hydrate structure and lead to reduce the portion of SII hydrates transformed to SI hydrates.

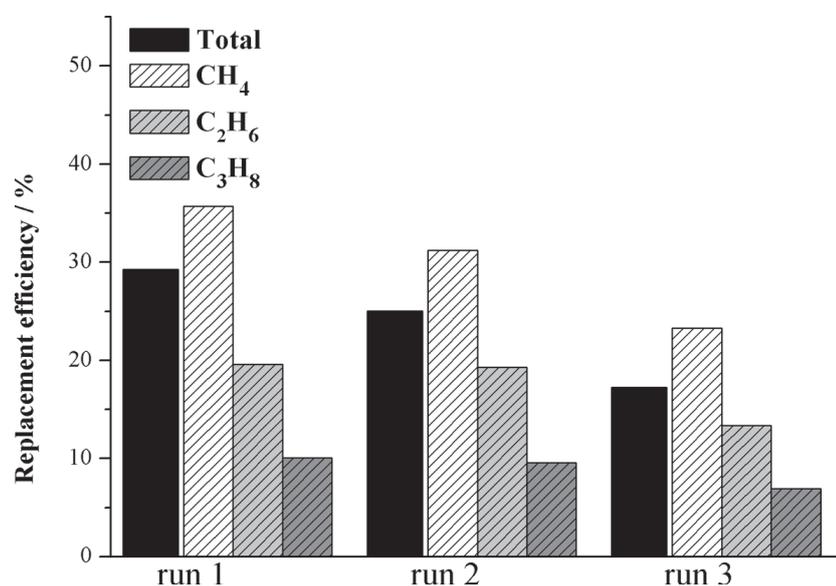


Figure 5: Final replacement ratios for different conditions.

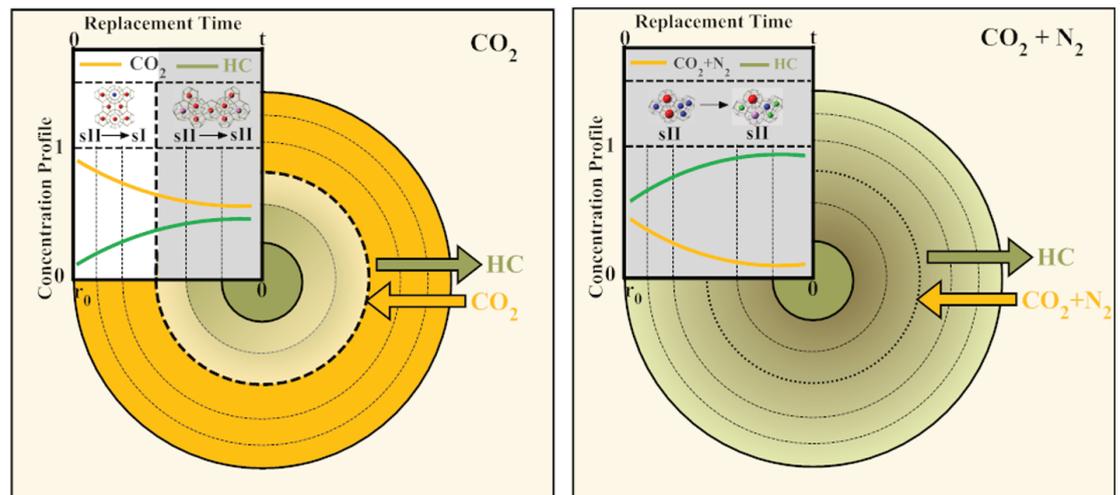


Figure 6: Schematic illustration of the swapping pattern of $\text{CH}_4\text{-C}_2\text{H}_6\text{-C}_3\text{H}_8$ hydrates by CO_2 and CO_2+N_2 .

4. Conclusion

The replacement reaction occurred in mixed gas hydrates containing three guests CH_4 , C_2H_6 , and C_3H_8 in the presence of CO_2/N_2 . The composition changes of gas phase indicated that CO_2 molecules preferably attacked CH_4 molecules compared to C_2H_6 and C_3H_8 molecules in hydrate phase, and only a small amount of C_3H_8 in the mixed hydrates were displaced especially in the initial stage of swapping. Moreover, it can be concluded from the CO_2 and N_2 consumption for replacement and heterogeneous composition of the final replaced hydrates that CO_2/N_2 played the different roles during the replacement reaction in different CO_2 concentrations. In particular, analysis of replacement efficiencies revealed that the addition of N_2 in replacement gas could cause the decrease in the replacement efficiency, which might be attributable to differences in swapping patterns.

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