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New Insights on a μm -Scale into the Transformation Process of CH_4 Hydrates to CO_2 -Rich Mixed Hydrates

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Abstract: The global occurrences of natural gas hydrates lead to the conclusion that tremendous amounts of hydrocarbons are bonded in these hydrate-bearing sediments, serving as a potential energy resource. For the release of the hydrate-bonded CH_4 from these reservoirs, different production methods have been developed during the last decades. Among them, the chemical stimulation via injection of CO_2 is considered as carbon neutral on the basis of the assumption that the hydrate-bonded CH_4 is replaced by CO_2 . For the investigation of the replacement process of hydrate-bonded CH_4 with CO_2 on a μm -scale, we performed time-resolved in situ Raman spectroscopic measurements combined with microscopic observations, exposing the CH_4 hydrates to a CO_2 gas phase at 3.2 MPa and 274 K. Single-point Raman measurements, line scans and Raman maps were taken from the hydrate phase. Measurements were performed continuously at defined depths from the surface into the core of several hydrate crystals. Additionally, the changes in composition in the gas phase were recorded. The results clearly indicated the incorporation of CO_2 into the hydrate phase with a concentration gradient from the surface to the core of the hydrate particle, supporting the shrinking core model. Microscopic observations, however, indicated that all the crystals changed their surface morphology when exposed to the CO_2 gas. Some crystals of the initial CH_4 hydrate phase grew or were maintained while at the same time other crystals decreased in sizes and even disappeared over time. This observation suggested a reformation process similar to Ostwald ripening rather than an exchange of molecules in already existing hydrate structures. The experimental results from this work are presented and discussed in consideration of the existing models, providing new insights on a μm -scale into the transformation process of CH_4 hydrates to CO_2 -rich mixed hydrates.

Keywords: gas hydrates; in situ Raman spectroscopy; CH_4 - CO_2 transformation process; shrinking core model

1. Introduction

Natural gas hydrates are non-stoichiometric crystalline inclusion compounds where the hydrogen-bonded water molecules form a three-dimensional framework of water cavities. The cavities are stabilized by hosting guest molecules (e.g., methane, ethane, carbon dioxide, hydrogen sulfide or other hydrocarbons) of suitable sizes and shapes [1]. Natural gas hydrates occur at all active and passive continental margins, permafrost regions and also in deep lakes such as Lake Baikal [2]. The widespread global occurrence and the high energy density of natural gas hydrates lead to the assumption that large amounts of natural gas, predominantly CH_4 , are stored in natural gas hydrate deposits/reservoirs [3–5]. Motivated by their potential as a future energy source, exploration and production of CH_4 from natural gas hydrates are attracting considerable attention.

The main technologies tested during the last decades for the productions of gas from hydrate-bearing sediments were (1) depressurization [6–9], (2) thermal stimulation [10–12], and (3) chemical stimulation via injection of chemical inhibitors (such as salts or alcohols) [13,14], or a combination of these techniques [15,16]. For the conventional methods, natural gas hydrates dissociate in response to the pressure–temperature conditions being shifted outside of the hydrate stability zone [17]. Although these methods have been successfully employed to produce gas from marine or permafrost hydrates, there are still some concerns of decomposing natural gas hydrates based on these stimulations. One important aspect that needs to be accounted for is the change in the mechanical properties of the hydrate-bearing sediments as a result of hydrate dissociation, which may trigger slope instability and subsidence [18,19].

Another technology for the production of gas from natural gas hydrates is a variant of chemical stimulation, namely, the injection of CO₂. In this scheme, the chemical disequilibrium between the initial CH₄ hydrate and the CO₂ gas phase induces the transformation of the original CH₄ hydrate into a CO₂-rich hydrate. Ideally, this process may not result in a dissociation of the hydrate phase, but a replacement of the hydrate-bonded CH₄ with CO₂ molecules and thus resulting in the production of CH₄ and simultaneously the capturing of CO₂ in the hydrate phase. In addition, CO₂ is thermodynamically favored in the hydrate phase compared to CH₄ at relevant conditions and they both form a structure I hydrate [2], as do mixtures of these gases [20]. Hence, this gas replacement strategy may be considered as an emission-free approach, with higher stability of the hydrate-bearing sediments and reduced geo-hazards [21,22].

During the past decades, efforts have been made on experimental studies to investigate the kinetics of CH₄–CO₂ swapping. Lee et al. [23] investigated hydrate samples prepared from powdered ice (the particle size of the ice and resulting hydrates were 5–50 µm) in porous silica gel (pore size 15 nm). They injected gaseous CO₂ into the CH₄ hydrate phase and observed the establishment of a steady state after 5 h with a CH₄ recovery rate of about 50%, which indicated a mixed hydrate phase with a 50/50 ratio of CO₂/CH₄. Similar results were observed by Schicks et al. [24], who also formed a CH₄ hydrate from powdered ice with a particle size of <10 µm in a small pressure cell (~400 µL) and exposing the CH₄ hydrate phase to a continuous CO₂ gas flow. Raman spectroscopic measurements indicated the transformation of the initial CH₄ hydrate phase into a mixed hydrate phase with the large 5¹²6² cavities partly filled with CO₂ and CH₄ and the small 5¹² cavities filled with CH₄. After 116 h, the gas incorporated into the mixed hydrate phase was composed of 50% CO₂ and 50% CH₄, indicating that 50% of the CH₄ was released from the initial CH₄ hydrate phase. These are two examples carried out with gaseous CO₂, but in the first example a porous medium was used, which may have had an effect on the kinetics of the transformation process. This indication is also given when researchers applied liquid CO₂ to prove the feasibility of replacing CH₄ in hydrates, as the following examples might show. Hirohama et al. [25] filled about 560 mL of water (31 mol) into a pressure vessel, pressurized the cell with CH₄ and converted 24 mol of the water into a bulk CH₄ hydrate phase. Thereafter, the CH₄ gas phase was replaced by liquid CO₂, which induced the conversion of the remaining free water phase (7 mol) into CO₂ hydrate. In addition, they observed the transformation of about 15% of the initial CH₄ hydrate into CO₂ hydrate after 800 h. A higher conversion rate was observed by Ota et al. (2005) [26], who conducted similar experiments but on a smaller scale. They formed CH₄ hydrates from 1.05–1.38 mol water and the CH₄ hydrate phase was exposed to liquid CO₂. The results indicated that after 307 h the mole fraction of CH₄ in the hydrate phase reached 0.65. The authors assumed that the CH₄ hydrate decomposed and they observed that the amount of decomposed CH₄ hydrate was almost the same as that of the formed CO₂ hydrate. They suggested that the released CH₄ transferred into the liquid CO₂ phase was re-occupied into the small cavities again, whereas the CO₂ molecules were incorporated into the large cavities. Zhou et al. [27] conducted the replacement of CH₄ by use of liquid CO₂ under the same conditions as in Ota's experiment. The recovery ratio was about 18.6% after 96 h. However, when porous media were added, the recovery ratio of CH₄ could be increased to approximately 45% after 288 h under otherwise identical conditions as reported by Xiong et al. [28]. The effect was even more pronounced when sandstone cores were

used: Ersland et al. [19] investigated the swapping process on hydrates in the pores of sandstone cores. After the CH₄ hydrate formation, the core was exposed to liquid CO₂. Within 300 h up to 60% of the CH₄ was recovered from the hydrate phase. Besides the effects from sediments, additional heat supply can help overcome the mass transfer limitations and thus improve the efficiency of the transformation process, as observed by Deusner et al. [29]. They investigated the production of CH₄ hydrates in quartz sand with pure ice by injecting hot supersaturated CO₂ at 368.15 K in a flow-through apparatus instead of a typical batch, fixed-bed reactor. This unique method permitted a higher CH₄ recovery rate of 40.7% in a relatively short duration of 44 h. To further improvement the slow transformation process, Park et al. [21] investigated the effect of additional N₂ on the transformation kinetics. They synthesized CH₄ hydrate from powdered ice and CH₄ gas in a stirred reactor before exposing about 1 mL of the pure CH₄ hydrate sample to a N₂–CO₂ gas mixture (80% N₂, 20% CO₂). After about 24 h, 85% of the CH₄ from the hydrate phase was recovered. It is noteworthy that the production of CH₄ via CO₂ + N₂ injection was already tested in 2012 at the Alaskan North Slope in the Ignik Sikumi Field Trial [30]. A mixture of 23 mol% CO₂ and 77 mol% N₂ was injected into the target sediments. According to its final report, 70% of the injected N₂ and 40% of the injected CO₂ were recovered along with 24,210 m³ of CH₄ during the flowback phase. However, 1421 m³ of N₂ and 82 m³ of CO₂ remained in the formation, which indicated the occurrence of CH₄–CO₂ replacement in the solid phase or dissolution of the gases into the brine [30,31].

The above mentioned examples are chosen to show how much the efficiency of the transformation process and thus the CH₄ recovery rate differ depending on the chosen scale and experimental conditions. In addition to those studies focusing on the optimization of the process with regard to the recovery rate of CH₄, there are other studies that deal with the transformation process on a μm-scale, to understand the mechanisms on a molecular scale. Due to the high complexity of the experimental systems, only some common assumptions may be allowed from previous research: (1) the exchange process is incomplete and reversible to a certain degree [24,32]; (2) the kinetics of the replacement process appears to follow a variant of the shrinking-core model, involving two stages that are similar but not identical to the formation of methane hydrate from ice [33,34]; (3) the initial exchange takes place at the interface of the CH₄ hydrate, which is rapid and heterogeneous [24,35]; and (4) the subsequent reaction, requiring the penetration of gas molecules through the previously formed mixed hydrates, is found to be generally slow [36–38]. However, although it is now generally accepted that the driving force for the CH₄–CO₂ swapping process is the difference in the chemical potential between the coexisting CH₄ hydrate phase and surrounding gas phase when exposed to a CO₂ gas [24], the transformation mechanism on a molecular scale is still under discussion. The replacement process is neither simply the dissociation of the initial CH₄ hydrate followed by the CO₂ hydrate formation, nor the one-to-one replacement of a CH₄ molecule with a CO₂ molecule. A recent study on the CH₄–CO₂ replacement by Mok et al. [39] provides time-dependent information on the guest exchange behaviors and cage occupancies during the replacement process applying in situ Raman spectroscopy together with NMR and PXRD. They quantitatively analyzed the CO₂ enclathrated in each cage of the structure I hydrate throughout the whole replacement process. However, it is still not yet clarified if this replacement process is correlated with a diffusion of the CO₂ molecules in the hydrate phase through “holes-in-the-cages”, as suggested by Falenty et al. 2016 [40], a recrystallization and re-arrangement of the water molecules or a (partial) dissociation and reformation, as suggested by, e.g., Ota et al. and others [24,36].

The uncertainty of the mechanism originated in the use of different analytical methods, such as in situ Raman spectroscopy [24,26,32,38,41], PXRD [42,43], NMR [23,44], in situ Neutron Diffraction [40,45] and MRI [19,37], to study the in situ dynamic replacement reactions or visualize the transformation process on a μm scale. Among these methods, Raman spectroscopy is the most widely used method for determining the composition and cage occupancies of the hydrate. Since it allows an analysis of the compositions of each phase and the changes in molecules in the corresponding hydrate cavities, promising results can be given for the guest replacement experiments. For instance,

Yoon et al. [38] investigated the guest replacement reaction applying in situ Raman spectroscopy. They monitored the changes in the relative intensities of the Raman peaks corresponding to CH₄ and CO₂ in large and small cages of sI hydrate. A sharp increase in the Raman peaks of CO₂ in the hydrate phase was observed in the first 100 min, but the increase in intensity slowed down after 100 min, which may indicate an effect from the surface shielding of the CO₂ hydrate formed in the outer layer. Another example is from Zhou et al. [41], who also studied the swapping process. Real-time Raman spectra monitoring the changes in composition for CO₂ and CH₄ in the hydrate phase depicted no significant fluctuations throughout the transformation process. The observation suggested that the transformation was simply not a dissociation process followed by a reformation process. Up to now, most researches applying Raman spectroscopy only provided spectroscopic evidence but did not provide enough real-time visualization information for the transformation process.

Against such a background, the ultimate goal of our research was to advance our understanding on the transformation process of the hydrate-bonded CH₄ with CO₂ on a μm -scale, applying in situ Raman spectroscopy and microscopic observations. Time-resolved Raman measurements were performed on pure CH₄ hydrates exposed to a continuous CO₂ gas flow, recording changes in compositions and cage occupancies during the whole transformation process. In addition to the single-point measurements, line scans and Raman maps were also taken from the hydrate phase. With the help of a confocal microscope and a motorized sample stage, hydrate crystals were analyzed in all three dimensions with a high spatial resolution. In this paper, the transformation kinetics of the CH₄ hydrates to CO₂-rich mixed hydrates are discussed in detail based on the experimental data. For a better understanding, the μm -scale investigation results from this research are compared and discussed in consideration of the previous kinetic models that were originally developed for other solid-state reactions. The microscopic investigations on specific hydrate crystals at defined depths expand our understanding on the transformation process and reveal more detailed information.

2. Materials and Methods

2.1. Experimental Setup

Experiments were performed with a specialized experimental setup. The main part of this setup is a high-pressure cell made of Hastelloy with a volume of 550 μL for the sample chamber. A quartz window (diameter 18 mm/thickness 10 mm) on the top of the cell allows for microscopic observations of the process in the sample area and the in situ Raman spectroscopic investigations. The pressure in the sample cell was adjusted by a pressure regulator (ER3000, Tescom); it can be used at pressures up to 10 MPa. A thermostat controlled the temperature of the sample cell with a precision of 0.1 K by means of a Peltier cooling device, which provides a quick temperature change. Another unique feature of the pressure cell is that it operates with a continuous gas flow as two valves outside the sample chamber control the inlet and outlet of the gas phase. The gas flow was measured and regulated with a commercial flowmeter (Bronkhorst HI-TEC digital mass flow controller F230M-AAD-11-K). A supply line with a diameter of max 1.6 mm and a length of 45 mm for the feed gas was drilled into the cell body so as to cool the incoming gas and avoid any heating effects. The pressure cell was mounted on a motorized, software-controlled, Märzhäuser Scan+ sample stage attached to the microscope. For the in situ Raman measurements, a confocal Raman spectrometer (LABRAM HR Evolution, Horiba Jobin Yvon) with a 1800 grooves/mm grating and 20 $\times$ microscope objective was used. The Raman spectrometer was equipped with a frequency-doubled Nd:YAG solid-state laser with an output power of 100 mW working at 532 nm. The laser power at the sample reaches a maximum of ~ 48 mW at the sample surface and can be reduced by use of various filters. With a focal length of 800 mm, this spectrometer achieves a maximum spectral resolution of 0.5 cm^{-1} . In order to determine the spectral resolution under the chosen experimental conditions, a Raman spectrum of neon light was recorded and the full width at half maximum of the neon band at 1706 cm^{-1} was determined, from which a spectral resolution of 0.6 cm^{-1} resulted. A motorized confocal pinhole enabled to increase the spatial resolution

of the laser-spot measurements, which in the x–y direction is $\sim 0.5\ \mu\text{m}$ in maximum and $\sim 1.5\ \mu\text{m}$ in the z direction. In this study, by using a long-working distance objective and selecting a pinhole number of 30 μm , an optimum spatial resolution of $1.6\ \mu\text{m}$ in the planar and $6.2\ \mu\text{m}$ in the z direction was reached. The Raman spectral positions were calibrated employing the silicon peak ($521\ \text{cm}^{-1}$). Further details regarding the experimental setup and the confocal Raman spectroscopic method can be found in Schicks et al. [46].

2.2. Experimental Procedures

The experiment started with the formation of pure CH_4 hydrate by following the same procedures as described in Schicks and Ripmeester [47]. The empty pressure cell was first flushed with the CH_4 gas for about one hour with a gas flow of $1\ \text{mL/min}$. Next, $150\ \mu\text{L}$ of deionized and degassed water was filled into the sample cell. The cell was carefully sealed and flushed again with the CH_4 gas at room temperature. After the system was pressurized to the experimental value of $3.2\ \text{MPa}$ in $60\ \text{s}$, the cell was cooled down to $253\ \text{K}$ with ca. $2\ \text{K/min}$ to induce the spontaneous crystallization of hydrate and ice. Since the spontaneous formation of the hydrates came along with the formation of ice at this condition, the cell was slowly warmed up to be above the ice melting point to ensure all the ice was melted, and then the temperature was increased slightly above the CH_4 hydrate equilibrium curve to melt most of the hydrate crystals. After only a few hydrate crystals remained, the system temperature was lowered to $274\ \text{K}$. At this point, euhedral crystals of CH_4 hydrate started to grow. The experimental p–T condition allowed the formation of CH_4 hydrates and CO_2 hydrates (see Figure 1) without the presence of liquid CO_2 . All the phase data were calculated using CSMGem [2]. At least 15 of the formed hydrate crystals were selected for continuous in situ Raman measurements to record the changes in the clathrate structure, composition and cage occupancy. Morphology changes of the hydrate surface were also monitored regularly. It took 5–6 days until the pure CH_4 hydrate reached a steady state where no further changes in the hydrate compositions with regard to the cage occupancy were recorded (see also Section 3.1, CH_4 Hydrate Formation). It should be noted that a steady state is not synonymous with an equilibrium state [48]. The steady state is a stationary non-equilibrium state that is characterized by the fact that the chemical potential in the system is not constant, but the changes are so minimal that they cannot be detected in the framework of the experiment [49]. In this context, a steady state means that the hydrate composition did not change significantly within hours. Nevertheless, the composition of the steady state does not necessarily correspond to the composition of the equilibrium state.

To initiate the hydrate transformation process, the feed gas composition was changed from the initial CH_4 gas to CO_2 gas, conducting similar steps as described in the publication of Beeskow-Strauch and Schicks [32] at a constant pressure and temperature. First, the CH_4 gas flow was stopped by closing the gas inlet valve at the sample cell. The gas line was then flushed with CO_2 gas to ensure that the gas flowing into the sample cell from this step onwards was pure CO_2 gas. However, the very last part of the gas line could not be flushed, which resulted in a certain delay until CO_2 entered the sample cell. Afterwards, the gas inlet valve was reopened to a continuous stream of CO_2 gas into the sample cell at a flow rate of $1\ \text{mL/min}$. Raman measurements were performed both on the gas phase and at different depths in the hydrate phase from the surface to the core of each crystal (surface, $15\ \mu\text{m}$, $30\ \mu\text{m}$, $60\ \mu\text{m}$ and $90\ \mu\text{m}$) with a confocal pinhole of $30\ \mu\text{m}$ to record the progression of the gas replacement process in the crystal in terms of the relative guest molecular composition. In order to obtain more information on the spatial composition of the guest molecules in the hydrate phases, a specific area of a well-structured crystal with large flat surfaces was selected for mapping. The selected area was automatically scanned step-by-step in one direction for the line scans and both the x and y directions for the area maps. The whole experiment was repeated three times and similar results were achieved as discussed in the following section.

Figure 1. Phase boundaries of the hydrates formed from pure CH₄ (red line), and pure CO₂ (blue line) calculated using CSMGem [2]. Also shown is the CO₂ vapor–liquid boundary (green dashed line) and experimental p–T condition (triangle symbol) at 3.2 MPa and 274 K that is maintained throughout the entire process, including CH₄ formation and the gas replacement process.

2.3. Data Processing

In this study, the whole process of CH₄ hydrate formation and CH₄–CO₂ transformation was analyzed using in situ confocal Raman spectroscopy. The Raman spectra were obtained from several points, starting from the surface to the core of the selected hydrate crystals. The measured Raman band positions were in good agreement with the literature data, as summarized in Table 1.

Table 1. Spectroscopic information for the CH₄ and CO₂ molecules in the gas phase and for different cavities in the hydrate phase.

Component	Vibrational Mode	Cavity Type/Gas Phase	ν_{measured} (cm ^{−1})	$\nu_{\text{literature}}$ (cm ^{−1})	References
CH ₄	ν_1 C–H symmetric stretching	Gas phase	2917	2917	[50]
		sI 5 ¹²	2915	2915	[51]
		sI 5 ¹² 6 ²	2905	2905	[51]
CO ₂	ν_1 C–O symmetric stretching	Gas phase	1285	1285	[50]
		sI 5 ¹² 6 ²	1277	1276	[32]
	$2\nu_2$ overtone of bending	Gas phase	1388	1388	[50]
		sI 5 ¹² 6 ²	1382	1381	[32]

The molar compositions in the gas and hydrate phase were determined on a semi-quantitative basis following the same calculation routine as described in Beeskow-Strauch et al. [52]. The Raman peak areas of the components in a mixed system are proportional to the number of molecules present in the sample; thus, the molar fraction of a component *a* (X_a) can be calculated using the following equation:

$$X_a = \frac{[A_a / (\sigma_a \xi_a)]}{\sum [A_i / (\sigma_i \xi_i)]}$$

where A_a represents the area of the Raman band of component *a*, σ_a is the Raman scattering cross-section factor of component *a* and ξ_a represents instrumental efficiency. The index *i* represents the values for all species present in the sample and Σ is their sum.

The Raman band areas were corrected with wavelength-independent cross-section factors for each specific molecule type, assuming that the cross-section factors do not vary with pressure, inclusion of the component into different cage types of the hydrate phase or the presence of other components in the different phases [50,53,54]. In this work, the molar compositions of the CH₄ and CO₂ in the gas and hydrate phase were given as relative percentages, assuming the total Raman bands for the guest molecules were set to 100%.

Since we consider and discuss the relative changes in the hydrate compositions over time in this work, this method for the determination of the semi-quantitative composition of the hydrate phase is sufficient. If a more precise determination of the hydrate composition is necessary, the method developed by Qin and Kuhs [55] should be considered.

3. Results

3.1. CH₄ Hydrate Formation

During the formation of CH₄ hydrate, the initial Raman measurements detected the appearance of Raman bands at 2905 cm⁻¹ and 2915 cm⁻¹, as shown in Figure 2, which illustrated the C–H stretching mode of the CH₄ molecules in the hydrate phase. This figure indicated the enclathration of CH₄ molecules into the hydrate cavities, with the Raman bands of 2905 cm⁻¹ and 2915 cm⁻¹ assigned as the CH₄ encased into the large 5¹²6² and small 5¹² cavities of the structure I hydrate, respectively, as tabulated in Table 1. The ratios for the integrated intensities of the Raman bands at 2905 cm⁻¹ and 2915 cm⁻¹ were calculated to ensure that the CH₄ hydrate followed the structure I equilibrium 3:1 ratio of large to small cavities. The equilibrium ratio was achieved after 24 h for some of the well-developed crystals, whereas it took longer than 24 h for the less-developed crystals to reach the expected equilibrium ratio. After 6 days, the cage occupancy ratio for most of the CH₄ hydrate crystals reached 3.1 (±0.2):1, which indicated that the system was close to an equilibrium state. It should be noted that the presence of the CH₄ gas peak in the Raman spectra at 2917 cm⁻¹ may have an effect on the calculation of the cage occupancy ratio. In this case, we considered the CH₄ gas peak in the Raman spectra. However, after careful calculation, it turned out that the impact from the CH₄ gas peak was lower than 2%rel on average whether it was considered or not.

Figure 2. Raman spectra for the C–H stretching mode of the CH₄ molecules enclathrated into the large 5¹²6² (2905 cm⁻¹) and small 5¹² (2915 cm⁻¹) cavities of the structure I hydrate. The spectral resolution achieves 0.6 cm⁻¹ as described in Section 2.1.

Microscopic observations indicated no remaining free water phase after that time. In addition, the shape of the Raman bands of the water indicated that at least most water molecules were bonded into the hydrate structure: according to the literature, the left shoulder of the band shape ($2800\text{--}3350\text{ cm}^{-1}$) is attributable to the strongly hydrogen-bonded water molecules in the hydrate or ice structure, whereas the right shoulder ($3350\text{--}3800\text{ cm}^{-1}$) is attributable to weakly hydrogen-bonded water molecules such as in liquid water [56,57]. Please note that in this context the terms “strong” and “weak” refer to the number of hydrogen bonds a water molecule forms with its neighboring water molecules.

3.2. Changes in Composition of the Initial Gas and Hydrate Phase When Exposed to CO_2

After there were no further changes in the CH_4 hydrate composition with regard to the ratio of large to small cavities occupied with CH_4 that signify a steady-state condition has been reached, the gas flow was changed from CH_4 to CO_2 to induce the transformation process at a temperature of 274 K and pressure of 3.2 MPa. Both CH_4 hydrate and CO_2 hydrate were considered to be stable under these conditions following the phase diagram shown in Figure 1. The time when the gas flow was changed is defined as time zero ($t = 0\text{ min}$). Single point Raman measurements of the gas phase and on different hydrate crystals were continuously taken over time.

It took more than 50 min before the CO_2 could be detected in the gas phase besides CH_4 . CO_2 gas was represented by the Raman bands at 1285 cm^{-1} and 1388 cm^{-1} , which could be assigned to the ν_1 C–O symmetric stretching and $2\nu_2$ overtone of bending for the CO_2 molecules, respectively. The delay in detecting CO_2 in the gas phase may result from several reasons. There might be CH_4 gas left in the pipe line between the gas bottle and pressure cell. The very last part of the gas line also could not be flushed. It is also possible that the CO_2 concentration in the cell is too low at the beginning to be clearly detected with Raman spectroscopy. As for CH_4 gas, the Raman band occurs at 2917 cm^{-1} . With longer time, the intensities for the CH_4 gas band in the Raman spectra reduced, while the intensities for the CO_2 gas bands in the Raman spectra continued to increase, as shown in Figure 3a. Figure 3b shows the changes in gas composition versus time in two separate tests. The blue diamonds and red circles in Figure 3b represent the gas composition in Test 1 while the pink and light blue symbols show the results from Test 2. Within the first 100 min after the feed gas was changed, the CO_2 proportion (given as molar composition in %) increased dramatically. Thereafter, the gas exchange process slowed down until almost 100% CH_4 in the gas phase was replaced by CO_2 after 4000 min. Even though the respective times of measurements varied slightly in these two tests, similar trends for the gas phase composition were observed when repeating the transformation process, indicating a high reproducibility of the measurements.

Figure 3. Cont.

Figure 3. Changes in the gas phase composition as a result of the continuous gas flow after the exchange from CH_4 gas to CO_2 gas: (a) real-time Raman spectra monitoring, and (b) the relative molar composition of the gas phase over time in two separate tests. For a better overview, the time axis in Figure 3a is displayed value-independent.

Raman measurements on the hydrate crystal surfaces revealed the enclathration of the CO_2 molecules in the hydrate phase by detecting the first appearance of the Raman bands at 1277 cm^{-1} and 1382 cm^{-1} after around 500 min (8.3 h). The CO_2 gas peaks were still detectable due to the effects of the surrounding gas phase on the hydrate surface during measurements. As shown in Figure 4, the intensities for the CO_2 hydrate bands increased with time, while the intensities of the Raman bands representing CH_4 in the hydrate phase decreased.

Figure 4. Real-time Raman spectra monitoring of the (a) CO_2 hydrate and (b) CH_4 hydrate for changes in the solid phase as a result of the shift in gas phase from CH_4 gas to CO_2 gas. Blue arrows in Figure 4a point out the first appearance of Raman bands at 1277 cm^{-1} and 1382 cm^{-1} for the CO_2 hydrate after around 500 min. The time axes are displayed value-independent.

At least 15 different hydrate crystals within the sample were closely monitored and measured for their transformation behavior. By referring to the plot of changes in composition over time for these selected hydrate crystals in Figure 5, it was found that the relative compositions for all the selected hydrate crystals scattered over a wide range. By repeating the Raman measurements on one crystal three times, a good reproducibility of the measurements was confirmed with a standard deviation of 0.2 mol% for the measuring points. Therefore, the scattered composition of hydrate crystals indicated the heterogeneity of the hydrate phase with regard to the content of CH₄ and CO₂. Using these data, the average molar composition for CH₄ and CO₂ in the hydrate phase was determined, and plotted on the same graph. The experiment was repeated three times and the standard deviation of the average molar composition was calculated for all the depths and all days. It turned out that the standard deviation ranged from 0.6 mol% to 5.3 mol% over the 8 days for the hydrate surface whereas the range was 0.1 mol% to 9.4 mol% for deeper depths. The steep slope from the plot of average molar compositions at the surface of the crystals shown in Figure 5 represented a faster reaction for the transformation of the pure CH₄ hydrate into mixed CH₄–CO₂ hydrate during the first 2 days (around 2880 h) after the gas flow was changed compared to a much slower conversion that was recorded afterwards. The integrated Raman intensity of CH₄ in the 5¹²6² cavities and the 5¹² cavities also changed from nearly 3:1 to a ratio of 2.0 (± 0.2):1, which signified that a mixed hydrate has formed during the exchange process containing CO₂ and CH₄ in the 5¹²6² cavities and CH₄ in the 5¹² cavities. It should be noted that no CH₄ gas peaks were observed at that time in the Raman spectra taken from the hydrate phase due to a low concentration of CH₄ in the gas phase. Therefore, CH₄ gas peak did not impact the calculation of the cage occupancy ratio. After more than 7000 min (116.7 h), the average composition of the resulting hydrate phase contained ~80% CO₂ and 20% CH₄, which was defined as CO₂-rich mixed hydrates. However, it should be noted that for some of the hydrate crystals the CO₂ concentration is still much less.

Figure 5. Results of the Raman spectroscopic measurements on the surfaces of 15 selected hydrate crystals, illustrating the exchange process of pure CH₄ hydrates to CO₂-rich mixed hydrates when exposed to CO₂ gas. The dashed lines show the average molar composition changes in CH₄ (red) and CO₂ (blue) in the hydrate phase fitted by smooth curves. The standard deviation of the average molar composition ranged from 0.6 mol% to 5.3 mol% according to the data from three repeated experiments.

With the use of confocal Raman spectroscopy and a motorized sample stage, Raman spectra were acquired not only on the surface of the hydrate crystals, but also at different penetration depths inside the crystals by focusing the laser beam at a defined depth. For this purpose, the laser beam was initially focused on the surface of the hydrate crystal and the position of the sample stage was recorded as zero at

the Z-axis. With the help of the software Labspec 6.5, this position of the motorized stage was changed vertically in such a way that the focus of the laser beam moved into the hydrate crystal. With a spatial resolution of $6.2\ \mu\text{m}$ in the z direction, measurements were therefore made at penetration depths of $15\ \mu\text{m}$, $30\ \mu\text{m}$, $60\ \mu\text{m}$ and $90\ \mu\text{m}$ into the hydrate crystals to ensure that the measurements had covered the whole range of depths. A curve fit was created in Figure 6 for the individual measurement points in order to better illustrate the trend of the transformation process. Each curve represents the average composition changes for 15 different hydrate crystals at a specific depth. The standard deviations of the average composition at specific depths from the three experiments serve as the error bars in Figure 6. The measurements on different hydrate crystals and different depths for each crystal serve as a better representation for the whole system. The results clearly indicated the incorporation of CO_2 into the hydrate phase with a concentration gradient from the surface to the core of the hydrate particle. It was shown from Figure 6 that after the pure CH_4 hydrate crystals were exposed to a CO_2 gas for around 1.5 days, the average conversion to a mixed CH_4 – CO_2 hydrate composition was 50 mol% CH_4 /50 mol% CO_2 on the surface of the hydrate crystals. However, at $60\ \mu\text{m}$ depth into the hydrate crystals, the average conversion to mixed CH_4 – CO_2 hydrate composition was 80 mol% CH_4 /20 mol% CO_2 after 1.5 days. With time, a higher conversion to CO_2 hydrate was recorded for all depths. However, after Day 6, small fluctuations to the hydrate compositions were observed at all depths (see Supplementary Information).

Figure 6. Changes in the average composition in mol% of the hydrate phase at defined depths over time after the initial CH_4 hydrate was exposed to a CO_2 gas phase. The standard deviation of the average composition in three repeated CH_4 – CO_2 exchange experiments were used for the descriptive error bars.

It was confirmed that the transformation process from pure CH_4 hydrates to CO_2 -rich mixed hydrates took place initially at the interface of CH_4 hydrate and CO_2 gas as the results showed the faster composition changes at the surface. Since there was no direct contact between the inner layers of the hydrate crystal and the CO_2 gas, the reaction into the hydrate crystals became diffusion-limited with depths. The driving force of the concentration gradient also decreases with depth. Over longer time, the results from the Raman spectroscopy indicated that the CO_2 molecules penetrated from the surface to the deeper depths through the hydrate layer. It started with the enclathration of the CO_2 molecules on the surface and was then followed by the enclathration of the CO_2 molecules into the hydrate structure in the deeper layers. Therefore, these observations support in general the

hypothesis of the “shrinking-core model” and are similar to the findings by Lee et al. (2014) [34] and Falenty et al. (2016) [40].

Apart from the single-point Raman measurements on the hydrate crystals during the transformation process, line scans and Raman maps were also performed at the surface of the hydrate crystals after 5 days. Figure 7a depicts the line scan on one of the well-developed hydrate crystals, where 50 measuring points along 37 μm across the surface were scanned step-by-step in one direction. This process took over 60 min for the 50 points. One has to assume that the transformation process will continue during this time. It is therefore not possible to repeat the line scan in order to prove the reproducibility of the measurements. As such, the reproducibility of the Raman line scans was tested before the experiment on a hydrate crystal with only a few measuring points. The standard deviation was 0.2 mol% for 12 measuring points on a crystal surface over three repeated tests. Therefore, the results presented in Figure 7b indicate the measured variations in local composition of the hydrate crystal. Interestingly, the concentration recorded for CO_2 in the mixed hydrate crystal was higher at the edges of the crystal, compared to the CO_2 concentration towards the center of the crystal. Since the edge of this hydrate crystal had a wider contact surface with the gas phase, CO_2 molecules could attack the hydrate crystal from different sides and were available to be incorporated into the hydrate phase. Similar trends were observed while repeating the experiment on different hydrate crystals.

Figure 7. (a) Raman line scan across hydrate crystal surface was scanned step-by-step in one direction. (b) Composition variations for the CH_4 and CO_2 encased into the hydrate phase at 50 measuring points across the formed hydrate crystal. The standard deviation for the line mapping was 0.2 mol%.

Raman mapping conducted on a specific rectangle area ($42 \mu\text{m} \times 61 \mu\text{m}$), scanning both in the x and y directions on the surface of the hydrate crystal (see Figure 8), demonstrated the inhomogeneous nature of the formed CH_4 – CO_2 mixed hydrates. There was also overall a higher CH_4/CO_2 ratio towards the center of the measured crystal, as shown in Figure 8b, indicating more CH_4 remained in the hydrate phase. It should be noted that pixels in Figure 8b only show results of each measuring point. The X axis in Figure 8b corresponded to the direction parallel to the short side of the rectangle in Figure 8a, while the Y axis indicated the direction parallel to the long side of the rectangle.

Figure 8. (a) Raman mapping on a hydrate crystal surface. A total of 49 (7×7) measuring points were chosen to be analyzed to determine the composition of the hydrate crystal. (b) The calculated CH_4/CO_2 ratio in the mapped area based on the integrated Raman band areas of CH_4 and CO_2 , respectively, without a correction with the Raman scattering cross section factor or instrumental efficiency. Increasing darkness reflects a higher CH_4/CO_2 ratio, whereas lighter points represent a lower CH_4/CO_2 ratio.

3.3. Changes in Morphology of Hydrate Crystals When Exposed to CO_2

For the microscopic observations during the transformation of the initial CH_4 hydrate to mixed gas hydrates, a series of snapshots were acquired periodically using a digital camera mounted on the confocal microscope. These snapshots were used to systematically study the morphology of the pure CH_4 hydrate crystals when the gas phase was changed to CO_2 . In this observation, at least ten crystals of pure CH_4 hydrate were initially selected. The ratio of large to small cavities for the structure I hydrate has reached 3:1 for these crystals. They were also categorized as well-developed crystals that exhibited a polyhedral shape with sharp edges and flat surfaces when they were first exposed to the CO_2 gas. However, when the transformation process started, the crystals' appearance changed significantly over time.

Figure 9 presents two crystals as examples, showing the evolution of the hydrate crystals from the initial pure CH_4 hydrates to CO_2 -rich mixed hydrates. As shown in Figure 9a, the initial flat rectangular shape surface of the crystal shrank on Day 1 and Day 2. On Day 3, it started to grow again until Day 6. However, on the last day of the experiment, the hydrate crystal surface was found to be smaller. The calculation of the diameter for the entire crystal showed that it decreased by 57.8% on Day 7 (39.8 μm) compared to the diameter before it was exposed to CO_2 gas (94.2 μm). As for the crystal in Figure 9b, it experienced a continuous dwindling within the 7 days of the experiment. Already on Day 2, the sharp edges of the crystal were invisible. The complete shape of the crystal disappeared at the end. For this reason, a comparison for the diameter of the crystal could not be conducted. Other crystals changed their surface morphology over time without showing a clear trend in decrease or increase regarding their sizes. It should be noted that the dwindling of the hydrate crystals was not considered as an effect from the irradiated laser beam during the Raman measurements. No physical damage was observed on the hydrate crystal surfaces where the laser beam was hitting. Besides, no significant changes were recorded in the Raman spectra regarding the shapes and sizes of the O–H stretching bands, which indicated that the hydrate crystals were fully intact.

Figure 9. Changes in surface morphology on two CH_4 hydrate crystals (shown in (a) and (b), separately) after the shift of gas phase to CO_2 gas at experiment conditions of $p = 3.2$ MPa and $T = 274$ K. The CH_4 hydrate crystal in Figure 9a was found to grow in the first few days followed by a shrinking on the last day. However, the crystal in Figure 9b experienced a continuous dwindling and disappeared on Day 7. The green point with crossed lines was the exact measuring spot site on the hydrate crystal.

It is noteworthy that the crystals that experienced a continuous dwindling according to the microscopic observations showed a different transformation profile compared to those crystals that grew or maintained their sizes. Two types of transformation curves can be observed from Figure 10, which presents the changes in CH_4 concentration on the surfaces of the hydrate crystals over time. Different symbols represented the plots from different crystals. Blue full symbols represented the dwindling crystals that decreased continuously regarding their sizes while the red empty ones were the crystals that grew or at least maintained similar sizes. It becomes clear that the dwindling crystals (blue symbols) tend to have a higher CH_4 composition in the hydrate phase, which means a slower transformation rate especially at the very beginning when the CH_4 hydrates were exposed to a CO_2 gas. The reaction rate was almost constant throughout the whole experimental period. For the crystals that grew or maintained their size (red symbols), a faster transformation was observed at the beginning of the reaction, which slowed down with time. It should be noted that the growing of the hydrate crystals' size was not due to the growth of a CO_2 hydrate layer on the initial CH_4 hydrate crystal. This could be proved by the results from the Raman measurements. With the present setup, we were also not able to detect the formation of an aqueous phase in which the CO_2 could dissolve during the decomposition of the hydrates. However, the existence of free water molecules could still be possible during the transformation process. Since the cage structure has to open to a certain extent for the

replacement of guest molecules, the observed dwindling phenomena after the exposure of the pure CH₄ hydrate crystal to the CO₂ gas may be an indication for at least a rearrangement of the molecules.

Figure 10. Changes in CH₄ concentration on the surface of the hydrate crystals over time. Crystals marked in blue experienced a clear decrease regarding their size while those marked in red either grew or maintained their size.

4. Discussion

There are several theories proposed to explain the mechanism behind the CH₄–CO₂ replacement process. However, whether the transformation refers to a substitution of guest molecules, a re-arrangement of the hydrate cavities or a recrystallization still remains uncertain. To gain more insight into the transformation kinetics, the experimental data obtained in this work were applied to the Avrami equation and the shrinking-core model, which have been widely used for describing the nucleation and growth process of the solid-state reaction [58,59]. Although not developed for the description of hydrate kinetics, they have been successfully applied before to fit data from hydrate formation [60–62] and also the CH₄–CO₂ swapping process [63].

Random nucleation followed by the growth of the nuclei is often modelled using the Avrami rate law. The Avrami rate law is in principle also applicable for the initial stage of the CH₄–CO₂ exchange reaction [34]. It assumes that an initial layer of mixed CH₄–CO₂ hydrate is formed with a quick exchange with CH₄ hydrate on the surface after the CH₄ hydrate is exposed to the CO₂ gas. A general expression for the Avrami rate law [58] can be presented as

$$\alpha = 1 - \exp(-kt^n) \quad (1)$$

where α is the degree of hydrate conversion at time t , k is the rate constant for the enclathration-controlled reaction step of hydrate formation and n is the Avrami exponent that accounts for the dimensions of crystal growth. Once the initial layer of mixed CH₄–CO₂ hydrate was formed, which can be mathematically described by the Avrami model (the first stage), the growth of the mixed hydrates slowed down, as shown in Figures 5 and 6, which corresponds to a diffusion-controlled process (the second stage). The presence of mixed CH₄–CO₂ hydrate on the surface limited the mass transfer for the subsequent hydrate growth. The shrinking-core model was employed in this stage, when the diffusion of the gas and water molecules through a continuously growing mixed hydrate layer controlled the rate of the reaction. Three different equations for the simple shrinking-core model, expressed as follows, were applied, and their results were compared:

Jander [64]:

$$\frac{2k_1 t}{r^2} = \left(1 - (1 - \alpha)^{\frac{1}{3}}\right)^2 \quad (2)$$

Levenspiel [65]:

$$k_2 t = 1 - 3(1 - \alpha)^{\frac{2}{3}} + 2(1 - \alpha) \quad (3)$$

Fujii-Kondo [66]:

$$(1 - \alpha)^{\frac{1}{3}} = \frac{-(2k_3)^{\frac{1}{2}}}{r} (t - t^*)^{\frac{1}{2}} + (1 - \alpha^*)^{\frac{1}{2}} \quad (4)$$

where t is referred to as time, and α is the hydrate conversion ratio after the first stage reaction has taken place, at time t . r in both the Jander and Fujii-Kondo equations is the radius of the hydrate particle. k_1 in Jander's model is the formation rate constant composed of the diffusion coefficient D and the concentration of the diffusing component (CO_2) c_0 at the contact surface. While in the model of Levenspiel, $k_2 = r^2 \rho / 6bDeC_A$, whereby r is the particle radius, De is the diffusion coefficient of the CO_2 gas in the mixed hydrate layers, C_A is the concentration of CO_2 in the gas phase, ρ is the molar density of the hydrate and b is the stoichiometric ratio of the CH_4 hydrate. In the Fujii-Kondo model, k_3 is referred to as the diffusion rate constant. These three rate constants are obtained from the slope of the curves when plotting the t against the relevant terms according to the equations. The amount of hydrate formed during the first step is deducted in the Jander and Levenspiel models and the corrected reaction time t was introduced starting with $t = 0$ min. In addition to time t , a measurable amount of time t^* is also introduced into the equation after which the hydrate formation is diffusion-controlled. The corresponding hydrate conversion ratio at time t^* was defined as α^* .

In general, all the three equations mentioned above provide mathematical descriptions for the general shrinking-core model, which was developed for heterogeneous reactions between a gas phase or a liquid phase and a spherical solid particle. The model of Jander [64] was one of the first models that described solid-state reactions. The model describes the contact of two non-ideal crystal faces with an immediate formation of a product layer on the surface of one crystal. A concentration gradient is created for the educt molecules from the unreacted crystal through the product layer, leading to a diffusion-controlled reaction. It has to be noted that the Jander equation implicitly assumes that both of the two reacting spherical crystals do not change their sizes during the whole reaction and only the product layer and the diffusion way change. It is also assumed that only the unreacted crystal diffuses through the product layer. In this way, Jander's model is also applicable for the reaction from a gas and a solid phase. However, it completely neglects the decrease in the reaction surface due to the shrinking of the unreacted core. The model of Levenspiel [65] was developed for gas–solid reactions with a product in the gas phase while considering the shrinking core effect. In this model, the concentration gradient of the gas is considered as a constant based on the assumption that the shrinking of the unreacted core is far slower than the flow rate of the reactant through the product layer. Moreover, the stoichiometry of the reaction is also assumed to be constant so that the ratio of the consumed number of gas reactant particles and the solid particles are constant, too. However, care has to be taken when applying the model for gas hydrate formation as they are non-stoichiometry compounds. The Fujii-Kondo model [66] was originally modified from the Jander model and has been used to fit the diffusion-controlled step during the process of hydration of cement grains. When the surface of the initial hydrate crystal is entirely covered by the product layer, the nucleation stage stops and the reaction proceeds only by diffusion of the molecules inward to the unreacted cores. In consideration of the time taken for the surface nucleation, a critical measurable time t^* with a corresponding conversion rate α^* is introduced into the equation when the reaction starts to be diffusion-controlled. It is apparent that the model does not apply to the vicinity of the assumed transition time t^* as it predicts the formation rate constant k_3 to approach infinity (Equation (4)). This is due to a simplification of the model, which assumes that the transition from the nucleation stage to the diffusion-controlled stage occurs instantaneously for a single particle while in reality this should occur over a period of time.

In addition, the best way to model the reaction would be to apply the equation to an individual particle with a given size to avoid the effect of particle size distribution on the reaction kinetics.

With all the calculations performed using these three different equations, the compositions for mixed $\text{CH}_4\text{-CO}_2$ hydrates in mol% were back-calculated, and the values were compared with the experimental data to find which equation best described the kinetics of the $\text{CH}_4\text{-CO}_2$ transformation process. Figure 11 shows the results of these calculations for two crystals with different transformation patterns: (a) a “survived” crystal with a remaining or growing size and (b) a dwindling crystal that experienced a continuous decrease regarding the size. For most of the remaining crystals, the results clearly indicated the incorporation of CO_2 into the hydrate phase with two stages involved: (1) a fast surface reaction on the gas–solid interface, and (2) a gradual slow process due to the resistance to diffusion of gas through the formed mixed hydrate layer. The experimental data satisfactorily fitted with the Avrami rate law in the first stage of the exchange process. As for the second stage, all the three equations fitted the data to certain extents. Among them, the Fujii-Kondo equation suited best compared to Levenspiel and Jander (see Figure 11a). Similar findings were also recorded by Lee et al. [34], where they showed the well-fitted trend of the Avrami and Fujii-Kondo models with their experimental data. It is also possible that the transformation process is only weakly influenced by the diffusion. Therefore, the Avrami rate law fitted the complete transformation process for some crystals. However, for the dwindling crystal, the experimental data still fitted with the Avrami rate law at the beginning of the process. After about 100 h the experimental data no longer followed the trend calculated with the Avrami rate law; also, none of the three kinetic models matched well for the dwindling crystal (as shown in Figure 11b) since they were all based on the assumption that the solid crystal did not change its size but only the unreacted core shrank. Instead, a linear regression was achieved between the time and the measured CO_2 composition in the hydrate phase with an R-value of 0.994. This indicated a constant reaction rate during the complete transformation process rather than a two-stage process. The dwindling process of the hydrate crystals as a result of hydrate dissociation may prevent the establishment of a stable CO_2 -rich mixed hydrate phase as a diffusion layer at the surface of the hydrate crystal. Therefore, the chemical disequilibrium between the crystals and the gas phase was maintained. This may explain why there is no significant change in the reaction rate shown in Figure 11b.

Figure 11. Comparison of the Avrami (solid line) and shrinking core models (dashed lines) with experimental data for the formation reaction of two different mixed $\text{CH}_4\text{-CO}_2$ hydrate crystals: (a) a “survived” crystal with a remaining or growing size and (b) a continuously dwindling crystal. Blue dots show the experimental results taken at the surface of each crystal. The black dotted line in Figure 11b represents a linear regression for the experimental data and R is the coefficient of correlation.

The parameters for the models are listed in Tables 2 and 3, respectively. Table 2 shows the formation rate constants and the Avrami exponents for the enclathration-controlled step for three runs, using two crystals each time. The values for the formation rate constant range over two orders of magnitude. This indicates that the speed of the enclathration-controlled step significantly varies from crystal to crystal. This is applicable for the single experiment as well as for the different runs, which is a further indication of the heterogeneous nature of the transformation process. In addition to the k-values, the Avrami model also provides information about the dimension of the crystal growth. For the experiments shown here, the values vary between 1 and 2, indicating that the growth of the mixed crystals is one- to two-dimensional. Table 3 shows the rate constants for the diffusion-controlled step, which were determined according to the Fujii-Kondo model, as well as the radius of the examined crystal. The fitting with this model gives the best results. Although the rate constants are of the same order of magnitude for the three runs, they vary significantly for the individual crystals.

Table 2. Formation rate constants and Avrami exponents obtained from the enclathration-controlled step for six crystals.

Crystal Number	k/min ⁻ⁿ	n	Experiment
1	9.11×10^{-6}	1.5829	Run 1
2	9.31×10^{-5}	1.2674	Run 1
3	3.23×10^{-5}	1.3221	Run 2
4	5.28×10^{-7}	1.8317	Run 2
5	5.16×10^{-5}	1.2594	Run 3
6	3.55×10^{-7}	2.0291	Run 3

Table 3. Formation rate constants of the Fujii and Kondo equation obtained from the diffusion-controlled step for six crystals (the radius of the crystals was obtained from the microscopic images of crystals and determined with the software “ImageJ”).

Crystal Number	k/min ⁻ⁿ	Radius/ μ m	Experiment
1	4.20×10^{-3}	46.2	Run 1
2	1.59×10^{-2}	45.5	Run 1
3	7.63×10^{-3}	30.2	Run 2
4	2.50×10^{-2}	43.4	Run 2
5	2.08×10^{-2}	51.0	Run 3
6	1.69×10^{-2}	44.9	Run 3

In addition to these kinetic data, microscopic observations on the hydrate phase revealed alterations in hydrate morphology, which were an indication for potentially different transformation behaviors of hydrate crystals. Changes in the morphology directly affected the sizes of the hydrate crystals. As a consequence, the crystal would either expand, shrink or completely disintegrate.

One assumption for the morphology change would be the dissociation of pure CH₄ hydrates and a parallel growth of mixed hydrates. This effect was observed by Schicks et al. [31], who studied the exchange process of CO₂/N₂-CH₄ in gas hydrates, simulating the Ignik Sikumi field trial. The coexistence of initial pure CH₄ hydrates and secondary mixed gas hydrates containing CH₄, CO₂ and N₂ was detected in the solid phase. While continuously measuring the decomposing CH₄ hydrate crystals, the Raman spectra of the solid phase clearly indicated only the CH₄ molecules in the hydrate phase and the composition did not change until the dissociation process ended after about 20 h at the given pressure and temperature conditions. In contrast, coexistence of pure CH₄ hydrate and mixed hydrate was not observed in the solid phase for this study. Within the first few hours (around 8.3 h), when the enclathration of the CO₂ molecules were not detected in the hydrate phase, the morphological changes of the hydrate crystals may be attributed to the decomposition of the pure CH₄ hydrates. However, after 8.3 h, only the CH₄-CO₂ mixed hydrates were confirmed from the depth

profile analysis by applying Raman spectroscopy. All Raman spectra taken from the hydrate crystals after this time showed Raman bands at 1277 cm^{-1} and 1382 cm^{-1} , assigned as CO_2 in the hydrate phase, besides Raman bands at 2905 cm^{-1} and 2915 cm^{-1} for CH_4 in the hydrate cavities. The observed shrinking of the crystals for the remaining time was therefore clearly the dissociation of the mixed hydrates. This kind of dissociation process of some mixed hydrate crystals while other mixed hydrate crystals grow or maintain their size is reminiscent of a process similar to Ostwald ripening.

Ostwald ripening, known as a grain coarsening process, has been observed by previous researchers with different visualization techniques such as X-ray computed tomography [67], optical microscopy [68,69] and X-ray diffraction [70]. The process has been studied not only in simple materials like metals ceramics but also in more complexed crystalline hydrates [71]. It differs from the normal hydrate grain growth process and has a strong effect on hydrate pore-scale habit and spatial distribution, in which larger crystals grow at the expense of the dissolution of smaller crystals [67]. The thermodynamic basis of the ripening is the size-dependence of the stability of a crystal. According to the Gibbs–Thomson effect, the solubility limit is inversely proportional to the radius of the spherical particle [72], which means a molecular concentration gradient may develop in the surroundings between a small crystal and a nearby large one [69]. This leads to a diffusive transport from the higher concentrations around smaller crystals toward larger crystals. Eventually, smaller crystals that are energetically less stable are consumed by larger ones to minimize surface area and lower the free energy. In this case, we could also speculate a CO_2 gas concentration gradient surrounding the existing mixed hydrate crystals. Thus, a thermodynamically driven spontaneous process occurs, resulting in a net flux of molecules flowing to larger crystals that can be described as a rearrangement of molecules (see Figure 12). This shrinking process may take place simultaneously with the diffusion process as described in the shrinking core model, which partly explained the observed compositions and morphology changes of the crystals in our experiment. It may also lead to small fluctuations in the hydrate compositions in the surrounding area.

Figure 12. Schematic illustration of the growth of CH_4 – CO_2 mixed hydrate at the expense of smaller hydrate crystals considering the Ostwald ripening effect. The left panel indicates a CO_2 molecular concentration gradient between the large and small hydrate crystals based on the Gibbs–Thomson effect. Therefore, the diffusion of CO_2 molecules due to the concentration gradient is initiated from the small crystal towards the large crystal together with CH_4 molecules and water molecules so as to minimize the surface area and lower the free energy. Finally, the large crystal grows and the small crystal disappears, as shown in the right panel.

5. Summary and Conclusions

The transformation process of pure CH₄ hydrates into CO₂-rich mixed hydrates was unveiled in this study on a μm scale by use of time-resolved in situ Raman spectroscopic measurements and microscopic observations. The results from the Raman spectroscopic measurements clearly indicated the incorporation of CO₂ into the hydrate phase with a concentration gradient at different penetration depths rather than the growth of a CO₂ layer on the existing CH₄ hydrate crystal. The heterogeneity of the hydrate composition at defined depths was confirmed. It was shown from the line scans and Raman maps that the transformation process was more advanced at the edge of a crystal than that in the center. The analysis of the results suggested that most of the crystals displayed a two-stage reaction, supporting, in general, the hypothesis of the shrinking-core model. It involved a fast formation of the mixed hydrates on the surface of the initial CH₄ hydrate crystals, which was rate-limiting, followed by a slow diffusion-controlled process that was dominated by the molecules penetrating inwards for the formation of mixed hydrates at deeper depths. This behavior was found for the crystals that kept their size or even started to grow after their exposure to CO₂ gas. The formation rate constants for the kinetic models varied from crystal to crystal, indicating again the heterogeneity of the transformation process.

Microscopic observations indicated that all crystals of the initial CH₄ hydrate phase changed their surface morphology when exposed to a CO₂ gas. Some crystals of the initial CH₄ hydrate phase decreased in size and some completely disappeared over time. In contrast to the two-stage reaction mechanism described above, these crystals showed an almost constant reaction rate for the complete transformation process. This observation supports the assumption of a rearrangement of the molecules and a (partial) dissociation followed by the formation of a mixed hydrate phase and not a replacement of the guest molecules in the existing hydrate cavities. A possible explanation for the morphology changes would be the Ostwald ripening effect as the large crystals grow at the expense of small ones, resulting in changing sizes and shapes of the mixed hydrate crystals.

In summary, our research provides time-resolved and quantified information for the whole CH₄–CO₂ exchange process on a μm level. The reaction mechanism of the CH₄/CO₂ transformation process seems to be influenced by how the hydrate morphology changes after the crystals are exposed to CO₂ gas. On a long-term perspective, more work should be done to clarify the reaction mechanisms in consideration of a CO₂ injection as an attractive gas production method from the natural hydrate reservoirs.

Supplementary Materials: The following are available online at <http://www.mdpi.com/1996-1073/13/22/5908/s1>, Figure S1: Composition of the selected hydrate crystals as a function of time at penetration depths of (a) surface, (b) 15 μm , (c) 30 μm , (d) 60 μm , and (e) 90 μm , after the exchange from CH₄ gas to CO₂ gas.

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