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To cite this article: Xiao-Hui Yu *et al* 2020 *Chinese Phys. Lett.* **37** 048201

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CH₄ Gas Extraction by CO₂: Substitution in Clathrate Hydrate through Bimolecular Iteration *

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1009-2020

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(Received 30 September 2019)

Methane clathrate hydrate (MCH) is a promising energy resource, but controllable extraction of CH₄ from MCH remains a challenge. Gradually replacing CH₄ in MCH with CO₂ is an attractive scheme, as it is cost efficient and mitigates the environmentally harmful effects of CO₂ by sequestration. However, the practicable implementation of this method has not yet been achieved. In this study, using *in situ* neutron diffraction, we confirm that CH₄ in the 5¹²6² cages of bulk structure-I (sI) MCH can be substituted by gaseous CO₂ under high pressure and low temperature with a high substitution ratio (~44%) while conserving the structure of the hydrate framework. First-principles calculations indicate that CO₂ binds more strongly to the 5¹²6² cages than methane does, and that the diffusion barrier for CH₄ is significantly lowered by an intermediate state in which one hydrate cage is doubly occupied by CH₄ and CO₂. Therefore, exchange of CO₂ for CH₄ in MCH is not only energetically favorable but also kinetically feasible. Experimental and theoretical studies of CH₄/CO₂ substitution elucidate a method to harness energy from these combustible ice resources.

PACS: 82.30.Hk, 82.40.Fp, 82.40.-g, 29.30.Hs

DOI: 10.1088/0256-307X/37/4/048201

Methane clathrate hydrate (MCH), or combustible ice, is a potential clean energy solution to the problem of worldwide fossil fuel shortages: the estimated energy contained in the form of methane clathrate hydrate is probably more than twice that of all natural gas, petroleum, and coal deposits combined.^[1–3] However, liberating CH₄ from combustible ice is a challenge with the existing technology because at high pressure and low temperature, CH₄ is trapped in delicate hydrate structures that can rapidly decompose into gaseous CH₄ and water under small perturbations, such as depressurization and/or warming. CH₄ released in this explosive fashion is difficult to collect and harmful to environment, as it will exacerbate the greenhouse effect.^[4] An attractive alternative is to employ guest molecules to replace CH₄ in MCH without damaging the hydrate lattice. For example, it was determined that another greenhouse gas, CO₂, can occupy both the large (5¹²6²) and small (5¹²)

cages of structure-I (sI) MCH with even larger binding energies,^[5] indicating that substituting CH₄ with CO₂ in MCH is thermodynamically favorable. Thus, if it is kinetically feasible as well, the replacement reaction could allow for the controllable extraction of CH₄ from the clathrate and the reduction of global warming by storing equivalent amounts of CO₂.^[6–8]

Since the first report on natural MCH by Ohgaki *et al.*,^[6] great efforts have been made to explore the possibility of CH₄/CO₂ substitution in MCH. For example, solid-state nuclear magnetic resonance (NMR) was widely utilized to demonstrate that the replacement of CH₄ by CO₂ in hydrate is favored in both laboratory setting and porous media.^[9–11] Park *et al.* employed Raman spectroscopy to reveal that ~64% of CH₄ in the MCH can be replaced by pure CO₂.^[12] The studies on the materials in the presence of impurities such as N₂, SO₂, and C₂H₆ indicated that the key factor of gas exchange is the

*Supported by the National Key R&D Program of China under Grant Nos 2016YFA0401503 and 2018YFA0305700, the National Natural Science Foundation of China under Grant Nos 11575288, 11775011, 21703006, 21773005, and the Youth Innovation Promotion Association of Chinese Academy of Sciences under Grant No 2016006. J. Zhu was supported by the National Thousand-Young-Talents Program and the National Science Associated Funding Grant U1530402. The experimental work has benefited from the use of the neutron source at Los Alamos Neutron Science Center (LANSCE), which is funded by the U.S. Department of Energy's Office of Basic Energy Sciences.

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chemical equilibrium between hydrate phase and the surrounding phases.^[13,14] The CH₄/CO₂ replacement was also proved by the investigation that CO₂ can induce the convention from structure-II (sII) hydrate to the less stable structure-I (sI) hydrate.^[15] Based on these observations, some kinetic models have been established.^[16,17] It is worth noting that the synthesized MCHs under experimental and natural conditions are always complex mixtures containing different forms of hydrates and large amount of pure ice, thus the poor spatial resolution of NMR and high surface sensitivity of Raman spectrum make the result of CH₄/CO₂ substitution in bulk form quite ambiguous. Furthermore, neither *in situ* detailed structural information of the substituted MCH nor the microscopic substituting mechanism are clearly known from these experiments. Meanwhile, the first principles studies have given opposite conclusions. For example, the density functional theory (DFT) calculations demonstrated that an extremely high diffusion barrier (>1.0 eV) through the hydrate cages can obstruct CH₄ diffusion in MCH.^[18,19] CH₄/CO₂ substitution was also characterized to be infeasible by molecular dynamics (MD) simulations,^[20] in which CH₄/CO₂ replacement follows a two-step process: the CH₄ hydrate first melts at the interface, and then an amorphous CO₂ hydrate layer forms, impeding further exchange of guest molecules. Thereby, as the experimental and simulation studies have given contradictory results, to date, the efficiency and microscopic mechanism of CO₂/CH₄ replacement in clathrate hydrates are still under debate.

Due to relatively higher sensitivity to light elements (e.g., C, H(D), and O), neutron diffraction is the most reliable technique to provide both refined structural characteristics in atomic resolution and the statistic information of MCH in centimeter level.^[21,22] In the present work, for the first time, we employ the *in situ* neutron diffraction to study the evolution of MCH crystalline structure in the CO₂ atmosphere, which clearly demonstrates that CO₂ can efficiently substitute for CH₄ in large cavities of bulk-sI MCH with a high substitution ratio of ~44%. Based on the first-principles calculations, we reveal that the replacement reaction is not only energetically favorable, but also kinetically feasible. Through a metastable intermediate state in which one 5¹²6²cage is co-occupied by CO₂ and CH₄, the energy barrier for CH₄ diffusion is significantly reduced by ~50%, so that CH₄ passes by CO₂ from the interior to the surface of the MCH without breaking the hydrate framework. Neutron diffraction and first-principles calculations conclusively confirm this proposed mechanism for CH₄/CO₂ substitution in bulk MCH, which is of great importance for using combustible ice resources.

Figure 1 shows the instrumental setup for MCH synthesis. In order to avoid incoherent scattering of H from H₂O, we used deuterated pure water (D₂O) for synthesis. D₂O was frozen for three days to make bulk

ice. Bulk ice was then pulverized with a coffee grinder and quenched in liquid nitrogen to obtain fine ice powder (to avoid the preferred orientation present in large pieces of ice) and thereafter formed the clathrate, as shown in Figs. 1(a) and 1(b). Next, fine powder ice was loaded into a vanadium cell cooled in a circulating bath. The sealed cell was flushed with methane gas multiple times before pumping to the desired initial pressure. As shown in Fig. 1(c), after two weeks in the cooling bath, the synthesized MCH was ready for neutron diffraction and CO₂ replacement experiments. Using this method, synthesized MCH was in the form of the loose powder, as shown in Fig. 1(d).

The structure of CH₄/CO₂ clathrate was investigated using high-pressure neutron diffraction at the Los Alamos Neutron Science Center (LANSCE), Los Alamos National Laboratory. Figure 1(e) shows the schematic layout of the high-pressure preferred orientation (HIPPO) time-of-flight neutron diffractometer^[23,24] and the setup for hydrate diffraction at low temperature and high pressure. Forward scattering covers large *d* spacing, ranging from 1.0 to ~10.6 Å, which provides accurate lattice parameters for the clathrate; back scattering gives higher resolution of the *d* spacing, ranging from 0.5 to 2.0 Å, which allows us to determine the accurate atomic positions. Using the detector geometry and combined refinement of multi-bank data, we were able to obtain reliable and refined structural parameters for MCH, such as cage occupancy and CO₂/CH₄ substitution ratios. D₂O ice was studied in a high-pressure vanadium gas cell, which withstands a maximum pressure of 50 MPa.

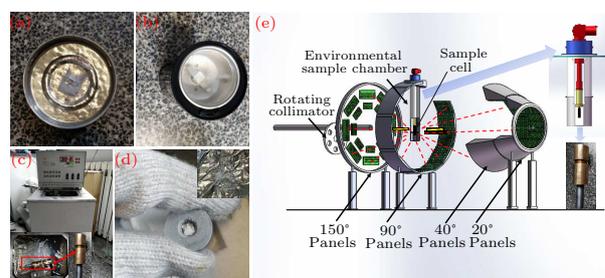


Fig. 1. MCH synthesis in a stainless cell for neutron diffraction measurement: (a) D₂O is frozen in liquid nitrogen; (b) D₂O ice is pulverized with a grinder; (c) D₂O powder is added to a vanadium cell, which is cooled in a circulating bath and flushed with methane gas four times, and then pressurized to 20 MPa; (d) after several days, methane hydrates form; (e) high-pressure preferred orientation (HIPPO) time-of-flight neutron diffraction setup (left panel) with an enlarged view of the sample chamber under vacuum (right upper panel) and the cell used (right lower panel).

Synthesized polycrystalline sample of MCH was characterized by *in situ* high-pressure (20 MPa) and low-temperature (70–270 K) neutron diffractions, and the diffraction patterns were analyzed by the Rietveld method using the General Structure Analysis System (GSAS).^[25–27] As shown in Fig. 2(a), the refined data indicate that the sI MCH crystal adopts the *Pm* $\bar{3}$ *n* space group with a lattice constant around 11.9 Å

for the entire temperature range of 70–270 K. Based on the relationship between the lattice constant and temperature (Fig. S1 in the Supplementary Materials), the thermal expansion coefficient satisfies the equation $a = a_0 \exp \int \alpha(T) dT$, where $\alpha(T) = \beta + \gamma/T$. Here we derived $a_0 = 11.783 \text{ \AA}$, $\beta_a = 5.62 \times 10^{-5} \text{ K}^{-1}$, and $\gamma_a = 1.39 \times 10^{-7} \text{ K}^{-2}$, consistent with the values previously reported for natural gas clathrate.^[28,29] Diffraction patterns were further refined to produce difference Fourier nuclear density maps (without CH₄ in the refined models), which clearly indicate the scattering density with center rotation of CH₄. The refined atomic structure (20 MPa, 270 K) of synthesized sI MCH, as shown in Fig. 2(b) (atomic positions are listed in Table S2 in the Supplementary Materials), indicates that the hydrate framework of the sI clathrate is composed of two kinds of polyhedrons, the 5¹² (dodecahedron with 12 identical pentagonal faces) and 5¹²6² (tetradecahedron with 12 pentagonal and 2 hexagonal faces), in a 1 : 3 ratio. The 5¹² cages share pentagons with the 5¹²6² cages to form linear chains along the [110] direction, while each 5¹²6² cage shares two hexagons with neighboring 5¹²6² cages to form an ice channel along the [100] direction. As shown in Fig. 2(c), the 5¹²6² hexagonal ring channels run through the whole clathrate, which is essential for the diffusion of guest molecules. CH₄ occupancies for both the 5¹²6² and 5¹² cages are ~ 1.0 , thus the formula for synthesized MCH is CH₄·5.75D₂O. In addition to coating the clathrate shell on the surface, unreacted D₂O also forms an inner ice core. As a result, the molar ratio between the clathrate and the ice phases from the refinement is approximately 1 : 4.

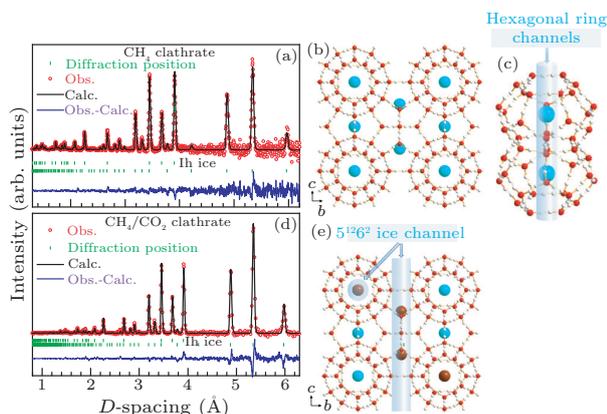


Fig. 2. Characterization of synthesized MCH: (a) time-dependent neutron diffraction patterns for the CH₄ clathrate; (d) neutron diffraction patterns substitution of CH₄ with CO₂ in MCH over 48 h; (b) atomic structure of sI clathrate with CH₄ (balls in cyan); (c) proposed molecular pathway through the hexagonal rings shared by the large 5¹²6² cages; (e) structure of sI clathrate with partial CO₂ (balls in wine) substitution. Red and white balls represent oxygen and disordered deuterium in the D₂O framework, respectively.

After exposure to CO₂ (35 bar, 270 K) for 48 h, substituted MCH was examined again by high-pressure and low-temperature neutron diffraction. A

large CH₄/CO₂ substitution rate of $\sim 44\%$ was found in the 5¹²6² cages, while the framework of clathrate was perfectly conserved, as confirmed by identical GSAS diffraction patterns for the unsubstituted and substituted MCHs, as shown in Fig. 2(d) (detailed structural parameters listed in Table S3 in the Supplementary Materials). Refinement data also indicate that CH₄/CO₂ replacement is assisted by the extensive channel network formed by the hexagonal ice rings of the 5¹²6² large cages, as exhibited in Fig. 2(e). The measured substitution rate in the smaller 5¹² cages is negligible according to the refinement. Considering the tremendous grain boundaries in the sample and the limited kinetics of gas replacement reactions under high-*P*/low-*T* conditions, a substitution rate of $\sim 44\%$ within finite reaction time is reasonable and consistent with the results of Park *et al.*^[12] Furthermore, diffraction data also demonstrate that the ratio of ice phase does not increase in gaseous CO₂; and the unreacted ice core in the original MCH sample is reduced by 25%. This suggests the formation of extra clathrate without melting of the clathrate host lattice during the replacement process. Due to the existence of unreacted ice cores at the end of the synthesis, the system is in a quasi-equilibrium state, where the concentration gradient leads to diffusion of CH₄ towards interior region of synthesized MCH. As the result, the size of ice core is reduced after 48 hours of replacement.

Natural MCH can be porous or confined in pore structures or in bulk and powder forms. Different configurations of natural clathrates and their surrounding hydrogeological conditions can significantly affect their substitution pressures, temperatures, and heat-transfer rates, but do not change the fundamental mechanism for gas exchange at the molecular level. Although neutron diffraction evidence demonstrates that CO₂ can substitute efficiently for CH₄ in the clathrate hydrate without damaging the host framework, experimental investigation of the microscopic substitution process is extremely difficult. Therefore, we employed the first-principles calculations (see the method details in the Supplementary Materials) to evaluate a possible mechanism for the replacement reaction.

The calculated binding energy of CO₂ to the hydrate framework (-0.52 eV) is 0.1 eV larger than that of CH₄ (-0.42 eV), indicating increased stability for the CO₂ clathrate compared to that of guest CH₄, according to the previous reports.^[30,31] We also confirmed that the binding energies for CH₄ and CO₂ increase slightly with increasing distance from the air-hydrate interface (0–15 Å), converging at $>15 \text{ \AA}$. This implies that gas molecules captured in clathrate hydrate are stabilized in the inner bulk phase of the clathrate. The rapidly converging binding energies also suggest that the bulk size of the clathrate affects the substitution process, which further demonstrates that our powder MCH sample is suitable for elucidat-

ing the substitution mechanism.

Diffusion of guest molecules in MCH is a key factor determining substitution kinetics. First, we considered the simplest mechanism: CH₄ spreads out through the 5¹²6² hexagonal ring channels and CO₂ enters the clathrate lattice. According to the DFT calculations, both CO₂ and CH₄ can pass through the large 5¹²6² cages by slightly stretching the hydrogen bonding network of the hexagonal ring without breaking it (Table S1 in the Supplementary Materials). Although the CO₂ binds more strongly to the clathrate hydrate, its linear geometry allows it to pass through the ice channel more readily than tetrahedral CH₄ molecules. The predicted diffusion barriers for CH₄ and CO₂ are 1.29 and 0.52 eV, respectively (Fig. S2 in the Supplementary Materials), consistent with the values 1.17 and 0.42 eV reported by Román-Pérez *et al.*^[18] According to the Arrhenius equation, the barrier difference makes the diffusion rate of CO₂ ~10¹³ times larger than that of CH₄, allowing CO₂ to diffuse easily through the sI clathrate lattice, while CH₄ can hardly pass through the water cages. In addition, CH₄ in the deep bulk phase must travel from the interior to the exterior, during which it experiences numerous high diffusion barriers. This reduces the probability of substitution exponentially. Therefore, the model based on the diffusion of freely spreading individual guest molecules is not feasible.

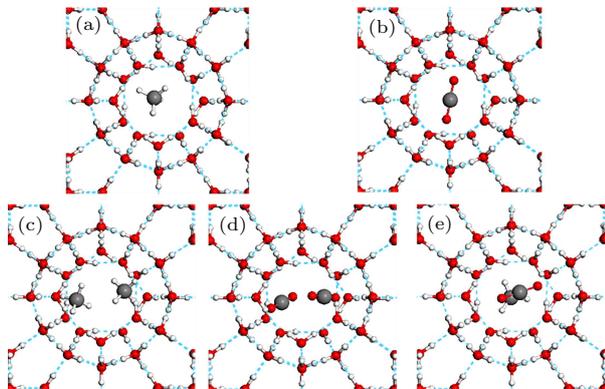


Fig. 3. Optimized structures of 5¹²6² cages singly occupied by (a) CH₄ and (b) CO₂, as well as the structure of 5¹²6² cages doubly occupied by (c) CH₄-CH₄, (d) CO₂-CO₂, and (e) CH₄-CO₂, based on the DFT calculations. Detailed parameters can be found in Table S1 for sI.

Since the free-spreading model is kinetically unfeasible, we explored an alternative pathway for the substitution, where CO₂ displaces CH₄ by experiencing a doubly occupied intermediate state. This was also previously observed in molecular dynamics simulations reported by Tung *et al.*^[32] We found that the sI clathrate lattice is conserved well when the 5¹²6² cage is doubly occupied by guest molecules, as shown in Fig. 3. The relative energies of CH₄-CH₄, CH₄-CO₂, and CO₂-CO₂ co-occupation in the 5¹²6² cage are -0.20, -0.23, and -0.35 eV, respectively, compared to the energy of the empty lattice, illustrating that 5¹²6²

doubly occupied cages (DOC) are less stable than the singly occupied cages, but slightly more stable than empty cages. The order of relative energies confirms our experimental observations that single occupation of clathrate cavities is preferred. In addition, CH₄-CO₂ and CO₂-CO₂ double occupation are more stable than CH₄-CH₄ co-occupation, which illustrates that CH₄ replaced by CO₂ is thermodynamically preferred.

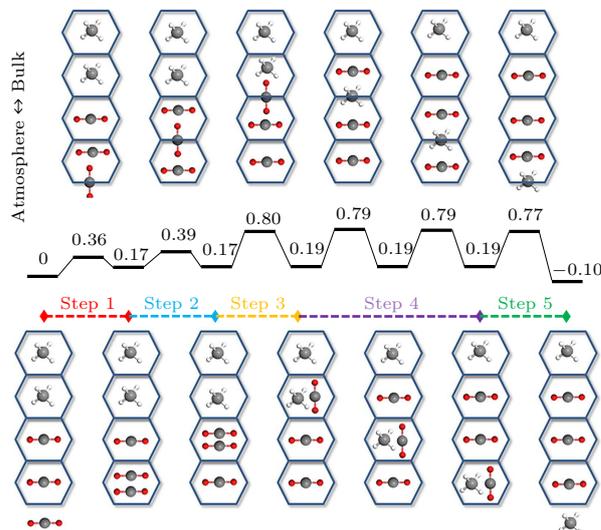


Fig. 4. Schematic representation of the molecular mechanism for iterative exchange of CH₄ in the bulk sI clathrate hydrate with CO₂, and the corresponding potential energy profile for the exchange process (black line).

Additional diffusion barriers for guest molecules were calculated for the DOC. As depicted in Fig. 4, assuming that the 5¹²6² cages in the outermost shell of the clathrate hydrate are already occupied by CO₂, the generalized exchange procedure, starting from the outer shell to the deep interior, can be divided into 5 steps: Step 1, a gaseous CO₂ molecule penetrates a CO₂ singly occupied cage (SOC) in the outermost layer of the clathrate to form a CO₂-CO₂ DOC. Step 2, the CO₂ molecule from the DOC moves into the clathrate and creates a CO₂ DOC adjacent to a CH₄ SOC. Step 3, one CO₂ molecule in the DOC diffuses to a neighboring CH₄ SOC to form a CH₄-CO₂ DOC. Step 4, the CH₄ molecule moves outward from the doubly occupied cage. Step 5, CH₄ is displaced to a DOC with CO₂ in a 5¹²6² cage of the outermost clathrate layer, then finally diffuses into the gas phase. Energy barriers for these steps were computed, as shown in Fig. 4. Compared to the extremely unfavorable process (1.29 eV) for diffusion of CH₄ with single occupation, the largest diffusion barrier for CH₄ in the doubly occupied cages is around 0.6 eV, indicating that the diffusion of CH₄ can be significantly enhanced by CO₂. The diffusion barrier for CO₂ in the CO₂ DOC (0.22 eV) is also much lower than that of CO₂ in the SOC (0.52 eV). Therefore, the diffusions of both CH₄ and CO₂ in the clathrate are more favorable with DOCs. Gas phase CO₂ diffusing into a CO₂ SOC also

experiences a low energy barrier of 0.36 eV. Furthermore, the process can be accelerated by increasing the partial pressure of CO₂. Therefore, our calculations clearly demonstrate the exchange mechanism is feasible for CH₄/CO₂ replacement without damaging the clathrate hydrate lattice.

Using *in situ* high-pressure and low-temperature neutron diffraction, we have confirmed that CH₄ in bulk sI MCH can be replaced by gaseous CO₂ with a substitution ratio of ~44% without melting the clathrate lattice. An exchange mechanism for CH₄/CO₂ replacement is proposed, based on first-principles calculations, in which the diffusion barriers of CH₄ and CO₂ through the lattice of clathrate hydrate are reduced by 51% (from 1.29 to 0.63 eV) and 31% (from 0.52 to 0.36 eV), respectively, via doubly occupied 5¹²6² cages. High CH₄/CO₂ substitution ratios in MCH under moderate conditions (35 bar, 270 K) clearly demonstrate that using CO₂ to gradually substitute for CH₄ in clathrate hydrates presents a safe efficient method to harness these rich combustible ice resources.

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