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Effect of Gas Exchange Interval on CH_4 Recovery Efficiency and Study of Mechanism of CH_4 Hydrate Replacement by CO_2 Mixture

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As an environment-friendly natural gas hydrate exploitation method, CO_2 replacement method can not only achieve the purpose of mining natural gas hydrate, but also store the current greenhouse gas CO_2 in the form of hydrate on the seabed, and maintain the stratum stability of hydrate deposit area. In order to improve the rate and efficiency of CH_4-CO_2 replacement reaction, researchers proposed to use CO_2 contained gas mixture instead of pure CO_2 to replace CH_4 in natural gas hydrate. Based our previous work about CH_4 hydrate recovery with 40% CO_2 + 60% H_2, in this study, the effect of gas concentration in gas phase on final CH_4 recovery are investigated by implying different time interval of gas exchange operation. Experimental results show that The CH_4 recovery efficiency is 10.41 when the gas exchange is continues through the whole replacement process, and CH_4 recovery efficiency changes to 12.25, 32.24 and 28.86 when gas exchange operation is carried out every 12, 24, 36 h. Indicating that replaced CH_4 needs to be discharged in time to avoid CH_4 molecules being replaced to form hydrates again, and it is necessary to accurately control the time interval of gas exchange operation to avoid insufficient contact time between CO_2 and H_2 molecules and CH_4 hydrate, which affects the final replacement efficiency. In addition, the mechanism of CO_2 gas mixture containing small gas molecule such as H_2, N_2 are studied. The results indicate that when CO_2 containing small molecules such as H_2 and N_2 displace CH_4 hydrate, the existence of small molecules (H_2, N_2) can give rise to decompose the hydrate lattice and release CH_4 gas. If the gas molecules (CO_2, N_2, H_2, CH_4) in the gas phase have enough driving force to enter the hydrate lattice and remain stability, CH_4 hydrate will not decompose completely; If not, CH_4 hydrate will be completely decomposed.

Keywords: CH_4 hydrate, CO_2 replacement, gas exchange interval, mechanism, small molecules

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INTRODUCTION

Natural gas hydrate (NGH), which is widely distributed in continental margin and permafrost, is naturally formed when excess gas and water molecules exist in high and low temperature zones (Sloan and Koh, 2007; Chong et al., 2016). The estimated worldwide NGH reserves are about 105–108 trillion cubic feet, twice the total reserves of natural gas, coal and oil resources (Kvenvolden et al., 1993; Boswell and Collett, 2011; Chong et al., 2016). The traditional scheme of recovering CH_4

gas from reservoirs is to use the driving potential based on temperature, pressure and chemical potential difference to change the equilibrium condition of NGH reservoir and decompose NGH (Li et al., 2016), including thermal stimulation (Wang et al., 2017; Li et al., 2008; Fitzgerald and Castaldi, 2013), depressurization (Yang et al., 2012; Zhao et al., 2013) and chemical inhibitor injection (Yuan et al., 2011; Javanmardi et al., 2013). Besides these methods, CH_4 recovery with CO_2 injection into the NHG reserves was firstly proposed by Ohgaki et al. (1996), and it has become a promising way to exploit CH_4 from NGH reserves while sequestrating CO_2 at the same time (Koh et al., 2012; Lee et al., 2013; Bo et al., 2014; Cha et al., 2015; Zhang et al., 2017). In this method, the heat required for the decomposition of CH_4 hydrate (54.49 kJ mol^{-1}) is provided by the heat released during the formation of CO_2 hydrate (-57.98 kJ mol^{-1}) (Lee et al., 2003; Ersland, 2007; Falenty et al., 2016; Mu and Solms, 2017). Subsequently, the researchers proposed the exploitation of CH_4 hydrate with CO_2 containing mixture (Koh et al., 2012; Sun et al., 2019; Tupsakhare and Castaldi, 2019; Wang et al., 2017) and the combined use of the above methods (Li et al., 2011; Kou et al., 2019; Kou et al., 2020; Wan et al., 2020) But there are still many problems, such as low efficiency due to large energy loss to surrounding stratum for thermal stimulation, obstacles of front propagation resulted from hydrate regeneration for depressurization, environmental issues and low productivity for inhibitor injection, and inability of monitoring CO_2 utilization for CO_2-CH_4 replacement. In addition, the influence of instability of NGH reserves has not been well understood, which may lead to sea sediment instability and more serious environmental problems because methane is an about 20 times more efficient greenhouse gas than CO_2 (Dlugokencky et al., 2003).

The feasibility of replacing methane hydrate with CO_2 has been proven previously (Ohgaki et al., 1996; Nakano et al., 1999), Uchida et al. (2010) investigated the CO_2-CH_4 replacement process with Raman spectroscopy, and found that methane can occupy large and small cages of sI hydrate, and CO_2 often occupies large cages in the process of hydrate reformation. Ota et al. (2005a); Ota et al. (2005b) found that, CH_4 hydrate was decomposed during the replacement process, and the decomposition rate of large cage in CH_4 hydrate was faster than that of small cage. Lim et al. (2017) investigated the cage occupancy of CH_4/N_2/CO_2 with different gas concentration and found that N_2 and CO_2 preferentially occupied small cages and large cages respectively. Sun et al. (2017) demonstrated that CO_2 molecules in gas mixture control the entrance into hydrate cages. Wang et al. (2017) and Sun et al. (2018) studied the CH_4 recovery by CO_2/H_2 gas mixture, and demonstrated that addition of H_2 can improve the CH_4 recovery.

During the replacement of CH_4 in hydrate with CO_2 or CO_2 containing gas mixture, the concentration of each gas component in the gas phase changes as the replacement reaction proceeds. These concentration variations, especially for the CH_4, affect the driving force of the gas molecule participating in the replacement and final replacement efficiency. Replaced CH_4 molecules can form CH_4 hydrate again or form CH_4-CO_2 mixed hydrate together with CO_2 molecules, as a result, the new hydrate formed on the surface of the original CH_4 hydrate becomes an obstacle to the further contact between CO_2 or gas mixture containing CO_2 with CH_4 hydrate, this will eventually affect the replacement efficiency. Therefore, based on the experimental results of replacement of CH_4 hydrate with 40% CO_2 + 60% H_2 mixture at 275.15 K, 4.5 and 6.0 MPa in our previous work (Ding et al., 2017; Ding et al., 2020), the effects of gas exchange every 12, 24, 36 h and continuous gas exchange (i.e., time interval of gas exchange) on the final replacement efficiency were studied.

Besides, the replacement mechanism of CH_4 replacement from CH_4 hydrate with CO_2 + H_2 gas mixture is also proposed: when H_2 molecules contact with CH_4 hydrate, the lattice of hydrate is disturbed and decomposed, and CH_4 molecules escape out. If CO_2 has enough driving force to replace CH_4 and simultaneously occupy the hydrate cages, the hydrate lattice becomes stable again; If the driving force of CO_2 molecule is not enough to occupy the hydrate cages, the lattice will be unstable and decompose to produce water and gas molecules. But when methane hydrate replaced by other gas mixtures containing small gas molecules, is the displacement mechanism the same as that of CO_2 + H_2 gas mixture? Therefore, 40% CO_2 + 60% N_2 and 20% CO_2 + 80% N_2 are used to study the replacement mechanism of CH_4 hydrate with CO_2 containing gas mixture.

EXPERIMENTAL DEVICE AND METHOD

Experimental Apparatus and Materials

The experimental device is composed of gas supply system, reactor for hydrate formation and decomposition, cooling water circulation system and detection system, as shown in **Figure 1**. The pure CH_4 gas and 40% CO_2 + 60% H_2, 40% CO_2 + 60% N_2, 20% CO_2 + 80% N_2 mixtures used in experiments are supplied by Foshan Huate Gas Co., Ltd. The deionized water used in experiments is supplied by Nanjing ultrapure water technology Co, Ltd. The Raman spectrometer (LabRam, Jobin Yvon) uses 50 times long focusing lens, a 600 grooves/mm monochromator and a multi-channel air-cooled electrically coupled device (CCD) detector. It can release 532 nm wavelength laser Ar ion laser source as the laser emission source. The single crystal silicon standard sample with Raman band at 520.7 cm^{-1} is used to calibrate the Raman spectrometer.

The gas samples collected during the experiment were analyzed on Agilent 7890A, which is equipped with FID and TCD detector. The test method for gas samples is: the detector is heated from 298.15 to 523.15 K at a constant speed, the flow rate of combustion gas H_2 is 30 ml min^{-1}, the flow rate of combustion gas air is 400 ml min^{-1}, and the flow rate of carrier gas helium is 250 ml min^{-1}.

Experimental Steps

In order to compare the effects of different gas mixture on CH_4 recovery efficiency, all experiments were carried out at 275.15 K and 6.0 MPa. The volume of reactor is 100 ml, and the amount of water used to form hydrate is 60 ml. The CH_4 hydrate is

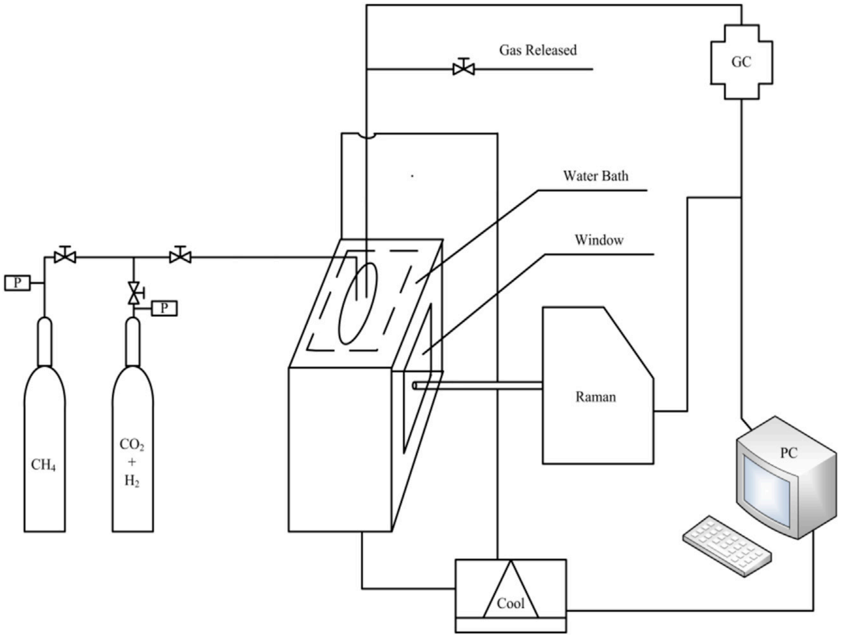

FIGURE 1 | The diagram of experimental device.

generated by bubbling at the bottom of the reactor under magnetic stirring, and the gas mixture is injected through the bottom of the reactor. About 120 h later, the water in reactor has completely transformed to hydrate which is confirmed by Raman spectroscopy where there is no characteristic peak of water, as the same as the method used before (Ding et al., 2017; Ding et al., 2020). What should be noted is that the experimental data is the average value of two groups of experiments, because each experiment was carried out in two parallel reactors.

Experiment 1, 2 and 3 were conducted using 40% CO_2 + 60% H_2 to replace CH_4 hydrate. In Experiment 1, the mixture of 40% CO_2 + 60% H_2 was injected after the complete transformation of H_2O to hydrate which was confirmed by Raman spectroscopy, and the top vent valve of the reactor was opened at the same time to exhaust slowly (0.45 ml min^{-1} of exhaust speed) to shift the CH_4 in gas phase to 40% CO_2 + 60% H_2. The top vent valve and the bottom inlet valve were kept open during the whole replacement process. What should be noted is that the pressure in reactor was remained at 6.0 MPa.

In Experiment 2, when the concentration of CH_4 in the gas phase was lower than 2% during gas exchange operation, the top vent valve of the reactor was shut off, and the time marked as the beginning of the replacement reaction. After the replacement reaction proceeded 12 h, one gas sample was collected, and then the gas exchange operation was carried out. Till that CH_4 concentration was lower than 2% again, another gas sample was collected as beginning of next 12 h of replacement reaction, and the top vent valve was shut off. Afterwards, the gas exchange operation was carried out every 12 h (the inlet and vent valves were opened simultaneously to inject 40% CO_2 + 60% H_2 gas mixture) to renew the gas in the gas phase till CH_4 concentration was lower than 2% again. The gas samples were collected at the beginning and end of the exchange process and detected by gas chromatography to determine the amount of CH_4 that were replaced out from hydrate phase within 12 h. Notedly, the inlet valve at the bottom of reactor was open during the whole replacement reaction. The only one difference between Experiment 3 and Experiment 2 is that the gas exchange operation was carried out every 36 h.

In order to study the reaction mechanism of CH4 hydrate replacement by CO_2 mixture containing small molecules, the replacement of CH_4 hydrate by CO_2/N_2 mixture with different concentrations was studied at different pressure. CH_4 hydrate was replaced by 40% CO_2 + 60% N_2 mixture at 275.15 K and 6.0 MPa in Experiment 4, 20% CO_2 + 80% N_2 mixture at 275.15 K and 6.0 MPa in Experiment 5, and 20% CO_2 + 80% N_2 mixture at 275.15 K and 8.0 MPa in Experiment 6. The comparison of experimental conditions of three experiments is also listed in **Table 1**. Gas samples were collected every 24 h during the replacement reaction, and the concentration changes of each gas component in the gas phase in the reactor were determined by gas chromatography. After the replacement reaction, the reactor was treated with liquid nitrogen, and then the hydrate was decomposed at room temperature. The decomposed gas was collected and each component concentration in the hydrate phase was determined by gas chromatography.

RESULTS AND DISCUSSION

In our previous work (Ding et al., 2017; Ding et al., 2020), it has been repeatedly proved that the pure CH_4 hydrate formed at 275.15 K and 4.5–6.0 MPa is structure I hydrate, and the

TABLE 1 | The conditions of three different gas exchange intervals in Experiment 1, 2, 3, 4, 5 and 6.

Experiment number	Temperature (K), pressure (MPa)	Injected gas	Time interval
1	275.15 K, 6.0 MPa	40% CO_2 + 60% H_2	Continuous
2	275.15 K, 6.0 MPa	40% CO_2 + 60% H_2	12 h
3	275.15 K, 6.0 MPa	40% CO_2 + 60% H_2	36 h
4	275.15 K, 6.0 MPa	40% CO_2 + 60% N_2	24 h
5	275.15 K, 6.0 MPa	20% CO_2 + 80% N_2	24 h
6	275.15 K, 8.0 MPa	20% CO_2 + 80% N_2	24 h

TABLE 2 | The CH_4 increment and CO_2 decrement in gas samples collected every 12 h in Experiment 2.

Time item	12 h	24 h	36 h	48 h	60 h	72 h	84 h	96 h	108 h	120 h
CH_4 Increment	6.51	5.37	3.71	2.30	1.27	1.33	1.15	0.82	0.49	0.51
CO_2 Decrement	7.66	6.83	4.46	3.91	1.57	1.72	1.67	1.22	0.71	0.60

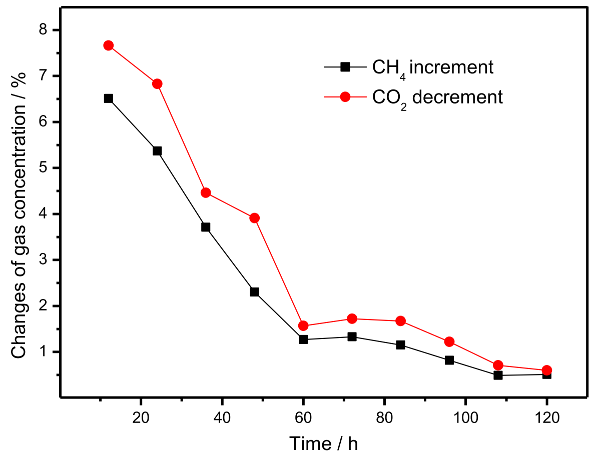

FIGURE 2 | The curve of CH_4 increment and CO_2 decrement in gas samples collected every 12 h in Experiment 2.

TABLE 3 | The CH_4 increment and CO_2 decrement in gas samples collected every 36 h in Experiment 3.

Time Item	36 h	72 h	108 h	144 h	180 h	196 h
CH_4 increment (%)	13.74	10.81	7.38	4.26	1.87	0.77
CO_2 decrement (%)	15.32	11.45	7.78	5.11	2.06	0.99

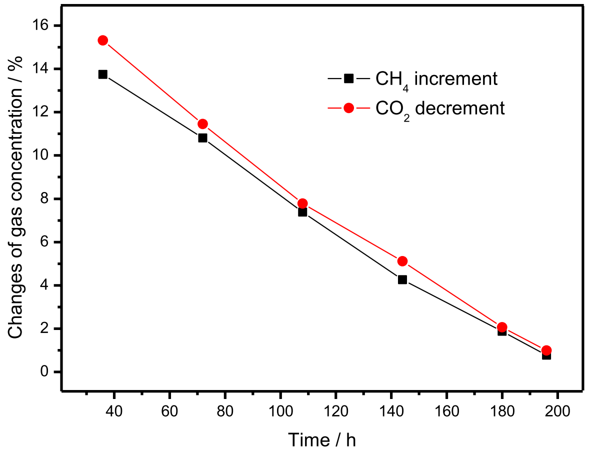

FIGURE 3 | The curve of CH_4 increment and CO_2 decrement in gas samples collected every 36 h in Experiment 3.

proportion of CH_4 molecules in large and small cages is about 3:1, so the structure of pure CH_4 hydrate formed at 275.15 K and 6.0 MPa and the proportion of CH_4 molecules in large and small cages are not determined in this study.

Effect of Ventilation Interval on Displacement Efficiency

In Experiment 1, the gas was continuously discharged at the rate of 0.45 ml min^{-1} during the whole replacement reaction (the inlet valve of 40% CO_2 + 60% H_2 was also open and the pressure in reactor was maintained at 6.0 MPa). After the replacement reaction, the gas phase was discharged quickly and the reactor was treated with liquid nitrogen. Immediately, the hydrate phase in reactor was decomposed at room temperature, and the content of each gas component originating from hydrate decomposition was determined by gas chromatography. In Experiment 1, the composition of the final hydrate decomposition gas is 89.59% CH_4 and 10.41% CO_2, that is, the recovery rate of CH_4 is 10.41%.

In Experiment 2, gas samples were collected at the beginning and end of the gas exchange operation, and the gas content in each gas sample were compared to have a deeper understanding of the replacement process. The increment of CH_4 and the decrement of CO_2 in the gas samples collected during the experiment are listed in **Table 2**, and is plotted in **Figure 2**.

TABLE 4 | The contrast of replacement results in Experiment 1, 2, 3 and EP1.

Item experiment	Temperature(K), pressure (MPa)	Injected gas	Ventilation interval (h)	CH_4 yields (%)
Experiment 1	275.15 K, 6.0 MPa	40% CO_2 + 60% H_2	Continuous	10.41
Experiment 2	275.15 K, 6.0 MPa	40% CO_2 + 60% H_2	12 h	12.25
EP1	275.15 K, 6.0 MPa	40% CO_2 + 60% H_2	24 h	32.24
Experiment 3	275.15 K, 6.0 MPa	40% CO_2 + 60% H_2	36 h	28.86

TABLE 5 | The changes of CH_4 and CO_2 concentration in Experiment 4.

Time item	24 h	48 h	72 h	96 h	120 h	144 h	168 h	192 h
CH_4 Increment (%)	8.45	4.41	1.74	1.86	0.81	0.62	0.61	0.40
CO_2 Decrement (%)	10.02	4.84	2.12	2.0	1.15	0.98	0.88	0.57

It can be seen that the increment of CH_4 and the decrement of CO_2 in the gas samples collected every 12 h are gradually decreasing, and the decrement of CO_2 every 12 h is slightly higher than the increment of CH_4, indicating that more CO_2 is consumed due to the decomposition of hydrate in the replacement process. This result is consistent with the experimental results of CH_4 hydrate replacement with 40% CO_2 + 60% H_2 mixture, which are present in our previous work (Ding et al., 2017; Ding et al., 2020). The composition of final hydrate decomposition gas is 87.75 CH_4 and 12.25% CO_2, that is, the CH_4 recovery rate is 12.25%.

In Experiment 3, gas samples were collected at the beginning and end of the gas exchange operation every 36 h, the increment of CH_4 and the decrement of CO_2 in the gas samples collected during the experiment are listed in **Table 3**, and is plotted in **Figure 3**. It can be seen from the figure that the increment of CH_4 and the decrement of CO_2 decrease almost linearly, and the decrement of CO_2 is also slightly higher than the increment of CH_4 which is agreement with Experiment 2. The composition of the final hydrate decomposition gas is 72.64% CH_4 and 28.36% CO_2, that is, the CH_4 recovery rate is 28.36%.

The results of Experiment 1, 2 and 3 and experimental results in our previous work (Ding et al., 2020) signed as EP1, are compared in **Table 4**. It can be seen that different time intervals of gas exchange operation eventually led to different CH_4 recovery efficiency in replacement reaction. The lowest CH_4 recovery efficiency (10.41%) is obtained with continuous gas exchange meaning that the condition of continuous gas exchange, i.e., the mixture of 40% CO_2 + 60% H_2 passes through the hydrate area at a relatively faster speed, result in a shorter contact time between CO_2 or H_2 molecules and CH_4 hydrate. Thus, the replacement reaction was cannot effectively carried out, resulting in the final lower CH_4 recovery efficiency. The CH_4 recovery efficiency increased (12.25%) with the time interval changed to 12 h, and was significantly improved (32.24%) as the gas exchange interval increase to 24 h. However, when time interval increased to 36 h, the recovery efficiency decreased slightly (28.86%). The reason may be that as the time interval increases, CH4 gas that replaced from hydrate phase during the replacement reaction reformed CH_4 hydrate again or formed CH_4-CO_2 mixed hydrate together with CO_2.

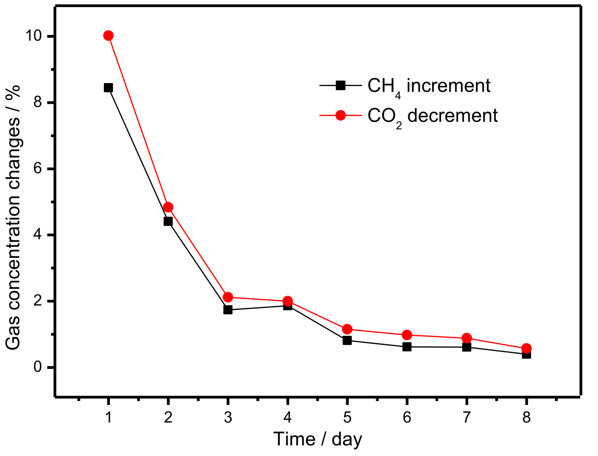

FIGURE 4 | The curve of change of CH_4 and CO_2 concentration in Experiment 4.

With the above experimental results, it can be proposed that in the real process of using gas replacement method to exploit NGH, the replaced CH_4 needs to be discharged from the sediment in time to avoid the replaced CH_4 gas forming CH_4 hydrate again or forming CH_4-CO_2 mixed hydrate together with CO_2 and so affecting the exploitation efficiency. At the same time, it is necessary to control the frequency of gas extraction from hydrate sediment, so as to avoid the incomplete contact between CO_2 molecules or other small gas molecules and CH_4 hydrate, which makes the lower CH_4 recovery efficiency.

The Replacement Mechanism of CH_4 Hydrate by CO_2 Mixture Containing N_2, H_2

In Experiments 4, 5 and 6, CH_4 hydrate was replaced by 40% CO_2 + 60% N_2 at 6.0 MPa, and by 20% CO_2 + 80% N_2 at 6.0 and 8.0 MPa. Combined with the experimental results of replacing

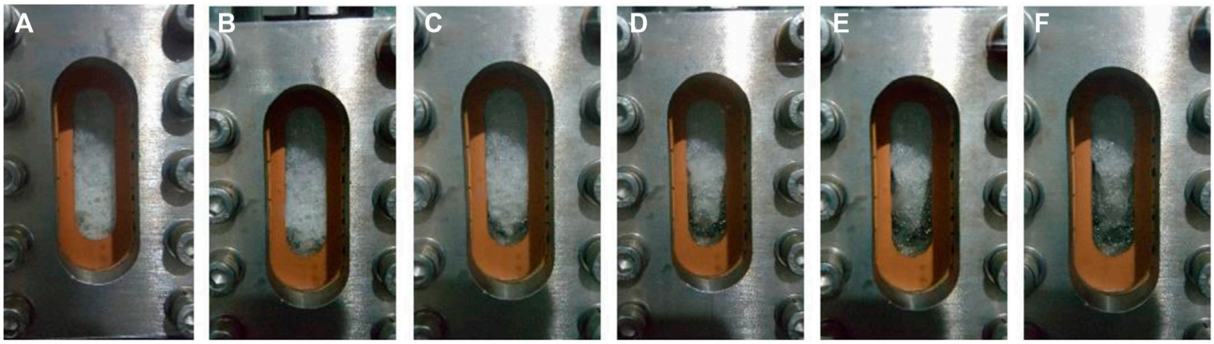

FIGURE 5 | The captured pictures during Experiment 5.

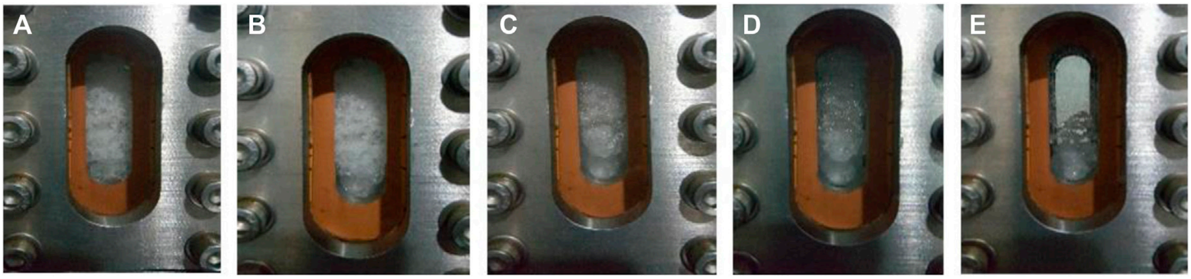

FIGURE 6 | The pictures during replacement process with pure N_2 (A~0 h, B~4 h, C~8 h, D~12 h, E~20 h).

CH_4 hydrate with 40% CO_2 + 60% H_2, the replacement mechanism of CH_4 hydrate by CO_2 mixture containing H_2 or N_2 was discussed.

In Experiment 4, after the water in the reactor was completely converted into hydrate, the gas mixture of 40% CO_2 + 60% N_2 was injected into the reactor until the CH_4 concentration in the gas phase was less than 2%, the replacement reaction began. The gas exchange operation was carried out every 24 h. **Table 5** shows the CH_4 and CO_2 content changes in the gas samples collected during the replacement process of Experiment 4, and these data are plotted in **Figure 4**. It can be seen that more CH_4 is replaced in the first 48 h of the replacement process (the increments of CH_4 concentration in the gas sample every 24 h were 8 and 4% respectively), while less CH_4 is replaced out in the subsequent replacement process. This result is quite different from that of CH_4 hydrate replacement with CO_2/H_2 mixture (more CH_4 is replaced in the first 5 days). Similar to that of CH_4 hydrate replacement with CO_2/H_2 mixture, the reduction of CO_2 in gas samples is slightly higher than the increment of CH_4 every 24 h. It is suggested that the decomposition of CH_4 hydrate may also occur in the process of CH_4 hydrate replacement with 40% CO_2 + 60% N_2, resulting in the decrement of CO_2 being higher than the increment of CH_4, as observed in CH_4 hydrate replacement with 40% CO_2 + 60% H_2.

Finally, the concentration of each gas component in the hydrate decomposition gas was detected by gas chromatography, and showed as 26.31% CO_2, 2.54% N_2 and 71.15% CH_4. In other words, at 275.15 K and 6.0 MPa, the CH_4 recovery efficiency is 28.85% by using 40% CO_2 + 60% N_2, which is lower than that using 40% CO_2 + 60% H_2 at the same temperature and pressure (32.24%). However, in the experiment of replacing CH_4 hydrate with 40% CO_2 + 60% H_2, there are only CO_2 and CH_4 in the final hydrate dissociation gas, and H_2 does not exist in the hydrate phase; In contrast, there is 2.5% N_2 in the final hydrate phase in the experiment of replacing CH_4 hydrate with 40% CO_2 + 60% N_2, indicating that N_2 molecules entered the hydrate lattice and occupied the hydrate cages.

The obtained low CH_4 recovery efficiency may be resulted from that the partial pressure of CO_2 reaches 2.4 MPa (above the pressure of CO_2 hydrate formation at 275.15 K) during the replacement process, which bring about CO_2 hydrate formed quickly on the surface of CH_4 hydrate and hindered the further contact between the injected gas mixture and CH_4 hydrate, resulting in the low final replacement efficiency. So, in the following Experiment 5, CH_4 hydrate was replaced by 20% CO_2 + 80% N_2 at 275.15 K and 6.0 MPa, and the partial pressure of CO_2 was only 1.2 MPa (below the pressure of CO_2 hydrate formation at 275.15 K).

After the water in the reactor is completely converted into hydrate, 20% CO_2 + 80% N_2 is injected and the CH_4 gas in the gas phase area of the reactor is discharged at the same time. The photos of the reactor taken during the experiment are shown in **Figure 5**. Figure a is the picture of the reactor before injecting

20% CO_2 + 80% N_2 mixture, and figure b, c, d, e and f are the picture of the reactor at 4, 6, 8, 10 and 12 h after injecting gas respectively. It can be seen that most of the hydrate decomposes within 12 h, and the hydrate completely decomposes within 24 h. It shows that the mixture of 20% CO_2 + 80% N_2 cannot react with the decomposed water to form stable hydrate at this temperature and pressure (275.15 K, 6.0 MPa).

On the basis of Experiment 5, the reaction of CH4 hydrate with 20% CO_2 + 80% N_2 mixture at 275.15 K and 8.0 MPa, where the partial pressure of CO_2 increased to 1.6 MPa, was carried out in Experiment 6. The experimental results are the same as those of Experiment 5. CH_4 hydrate is decomposed in 24 h and no new hydrate is formed in the reactor.

In addition to the above experiments, the interaction between CH_4 hydrate and pure N_2 was also carried out. The pictures taken during the experiment are shown in **Figure 6**, the pictures a, b, c, d and e in the figure are the pictures of the reactor taken before the start of reaction and after 4, 8, 12 and 20 h of reaction respectively. It can be seen that CH_4 hydrate gradually decomposes after the replacement process begins, and almost decomposes within 24 h. It shows that the contact of N_2 with CH_4 hydrate will lead to the destruction of hydrate lattice and release CH_4 gas.

Through the above experiments, it can be seen that CH_4 hydrate will be completely decomposed when the partial pressure of CO_2 in the mixture is too small to form hydrate; When the mixture can form hydrate stably, CH_4 hydrate will not decompose completely.

CONCLUSION

According to Experiments 1, 2, 3 and previous work, in the process of replacing CH_4 hydrate with CO_2/H_2 mixture, the replaced CH_4 needs to be discharged in time to avoid the replacement of CH_4 molecules to form hydrate again. At the same time, the time interval of CH_4 gas exchange process needs to be controlled accurately to avoid that the contact time of CO_2, N_2, H_2 molecules with CH_4 hydrate is not enough which affect the final replacement efficiency.

Probably, when CO_2 mixture containing small molecules such as H_2 and N_2 replace CH_4 hydrate, small molecules such as H_2 and N_2 attack the hydrate lattice, which can give rise to decompose the hydrate lattice and release CH_4 gas. If the gas molecules (CO_2, N_2, H_2, CH_4) in the gas phase have enough driving force to enter the hydrate lattice and remain stability, CH_4 hydrate will not decompose completely; If CO_2 in the mixture does not have enough driving force to form hydrate or mixed hydrate, CH_4 hydrate will be completely decomposed. Nevertheless, the further research is needed to elaborate the mechanism more thoroughly.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

Y-LD did the initial experiment and wrote the first draft. H-QW assisted in the experiment and revised the paper. TL proofread the figures and tables.

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