Supporting Information

for

Quantitative measurement and mechanisms for CH₄ production from hydrates with the injection of liquid CO₂

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1. Hydrate conversion (Nearly full conversion)

(1) Volume of gas phase in the cell:

CH₄ hydrates are prepared from approximately 33 grams of powdered hexagonal ice grains sieved to obtain well size-controlled particles (e.g., diameter of 75-90 or 125-150 μ m).

Initial call values	Ice particle	Cas nhasa yaluma	
Initial cell volume	Mass	Volume	Gas phase volume
150 ml	33 g	35.99 ml	114 ml

(2) Equation of state:

The amount of hydrate formed is determined from the difference between the initial and final pressures in the cell.

Initial		Final	
V	114 ml	V	114 ml
Р	1500 psig	Р	1038 psig
Ζ	0.7545	Ζ	0.8438
R	82.06 atm*ml/mol*K	R	82.06 atm*ml/mol*K
Т	263.15 K	Т	275.15 K
n	0.7199 mol	п	0.4275 mol

* Z, a compressibility factor, calculated with Multiflash^{\mathbb{R}}.

(3) Calculation of hydrate conversion:

The conversion to hydrates is estimated by an equation of state assuming a hydration number of 6. To obtain high conversion, a temperature ramping method between 263 K and 272 K is used, resulting in a final conversion generally corresponding to over 95%.

n _{CH4} occupied in hydrate	Hydration number	Initial n _{Water} prepared	n _{CH4} expected (100% conversion)	% Hydrate
0.2924 mol	5.99	1.8333 mol	0.3058 mol	95.6%

* Hydration number obtained from CSMGem.

(4) Summary of all experimental runs (Hydrate conversion)

	Run1	Run2	Run3	Run4	Run5	Run6	Run7	Run8
Mass of ice particles	29 g	28 g	29 g	30 g	30 g	33 g	33 g	33 g
% Hydrate	93.7%	88.3%	91.8%	94.2%	91.6%	95.6%	93.9%	95.5%

2. Mole fraction of CH₄

(1) Sweep: After CH₄ hydrate formation in the pressure cell, liquid CO₂ is injected (123 ml/hour) into the pressure cell to sweep the residual CH₄ gas, ensuring no free CH₄ is left in the gas phase. The final mole fraction of CH₄ in the sweep stage generally reaches below 0.2%.



(2) Soak: After soaking hydrates in liquid CO_2 for several hours, any CH_4 produced from the hydrates and dissolved in liquid CO_2 is moved into a sample cylinder by further injection of liquid CO_2 . (Figure for Run6)



(3) Dissociation: To dissociate the hydrates completely, first the cell temperature is increased to room temperature at a constant pressure (~9.00 MPa), then liquid CO_2 is injected to sweep all CH₄ from the cell, and finally the cell pressure is decreased to atmospheric pressure. (Figure for Run6)



(4) Mass balance check:

Error was calculated in terms of the amount of CH_4 in each section; this provides a quantitative measure to confirm the closure of the total CH_4 mass balance in the experiment.

(a) n _{CH4} in gas phase	(b) n _{CH4} in hydrates	(c) n _{CH4} in sweep	(d) n _{CH4} produced in soaks	(e) n _{CH4} in dissociation
0.5464 mol	0.2924 mol	0.5526 mol	0.0653 mol	0.2214 mol

*(b) n_{CH4} in hydrates = (d) n_{CH4} produced in soaks + (e) n_{CH4} in dissociation, 1.93% error

*(a) n_{CH4} in gas phase + (b) n_{CH4} in hydrates = (c) n_{CH4} in sweep + (d) n_{CH4} produced in soaks + (e) n_{CH4} in dissociation, 0.06% error

3. Demonstration of CH₄-CO₂ exchange (Explanation with Run3 data)

To determine the mechanism for CH_4 production, we utilize the pressure increase data along with the proposed mechanism for "exchange" and "no exchange"



(1) n_{CH4} produced from hydrates during soaks

Run3	1 st Soak (12 hours)	2 nd Soak (12 hours)	3 rd Soak (12 hours)
n _{CH4} produced	0.0275 mol	0.0218 mol	0.0192 mol

(2) Total moles (Initial n_{CO2}) before soak

V	Initial P	Ζ	R	Initial n _{Total}
130 ml	1280 psig	0.1862	82.06 atm*ml/mol*K	2.7184 mol

* Over the course of each experiment and soak time, the cell pressure always increased. Therefore, to measure the n_{Total} before soak, we use the initial pressure.

(3) "No exchange" system:

For the "no exchange" case, CH_4 is released from the hydrates but no CO_2 hydrates are formed (CO_2 only causes the CH_4 hydrate to dissociate).

	1 st Soak	2 nd Soak	3 rd Soak			
(a) Initial n _{Total}	2.7184 mol	2.7205 mol	2.7226 mol			
(b) n _{CH4} produced	0.0275 mol	0.0218 mol	0.0192 mol			
(c) n _{Water} dissolved	0.0052 mol	0.0052 mol	0.0052 mol			
(d) Final n _{Total}	2.7510 mol	2.7475 mol	2.7470 mol			
V	130.35 ml	130.41 ml	130.48 ml			
Ζ	0.2105	0.2045	0.2016			
R		82.06 atm*ml/mol*K				
Т		275.15 K				
(d) Final n _{Total}	2.7510 mol	2.7475 mol	2.7470 mol			
(e) P traced	1474.3 psi	1429.4 psi	1408.4 psi			

* n_{Water} dissolved was calculated to consider the volume change after hydrate dissociation. (Introduced in detail at the "Calculation of volume change" part.)

(4) "Exchange" system:

	1 st Soak	2 nd Soak	3 rd Soak	
(a) Initial n _{Total}	2.7184 mol	2.7205 mol	2.7226 mol	
(b) n _{CH4} produced	0.0275 mol	0.0218 mol	0.0192 mol	
(c) n _{CO2} trapped	0.0267 mol	0.0213 mol	0.0195 mol	
(d) n _{Water} dissolved	0.0052 mol	0.0052 mol	0.0052 mol	
(e) Final n _{Total}	2.7244 mol	2.7262 mol	2.7275 mol	
V	130.10 ml	130.20 ml	130.30 ml	
Ζ	0.1979	0.1944	0.1923	
R		82.06 atm*ml/mol*K		
Т	275.15 K			
(e) Final n _{Total}	2.7244 mol	2.7262 mol	2.7275 mol	
(f) P traced	1375.3 psi	1350.6 psi	1335.7 psi	

In the "exchange" case, CH_4 hydrates are dissociated and a mixed CO_2/CH_4 hydrate is immediate re-formed.

* Final $n_{Total} = (a)$ Initial $n_{Total} + (b) n_{CH4}$ produced $- (c) n_{CO2}$ trapped $+ (d) n_{Water}$ dissolved * n_{CO2} trapped was calculated by using cage occupancy generated by CSMGem.

(5) Calculation of volume change:

Once CH_4 hydrates partially dissociate, CH_4 gas and water is liberated, and volume of initial hydrates can be changed due to the difference of density.

• n_{Water} dissolved (*J. Chem. Eng. Data* 2011, 56, 2626-2629)

X _{CO2}	X _{Water}	Initial n _{CO2}	n _{Water} dissolved
0.9981	0.0019	2.7184 mol	0.0052 mol

Water volume

n _{Water} dissolved in CO ₂	0.0052 mol
Mass of water dissolved	0.0931 g (calculated by 18 g/mol)
Volume of water dissolved	0.0931 ml (calculated by 1 g/ml)
n _{Water} dissociated from hydrates	0.1637 mol (calculated by hydration number of CH ₄ hydrate)
Mass of water dissociated	2.9471 g
Volume of water dissociated	2.9471 ml
Hydrate volume dissociated	3.2139 ml (calculated by density of hydrate)

• Volume change

(a) Initial hyd	(b) Hyd volume	(c) Initial water volume	(d) Water volume	(e) Final hyd
volume	dissociated		solved in CO ₂	volume
36 ml	3.2139 ml	2.9471 ml	0.0931 ml	35.6401 ml

* Final hyd volume = (a) Initial hyd volume – (b) Hyd volume dissociated + (c) Initial water volume – (d) Water volume solved in CO_2

(6) Demonstration of CH_4 - CO_2 exchange: CO_2 and CH_4 were exchanged completely initially, however, as a factor of soak time, the exchange ratio was gradually decreased.

