Electronic Supplementary Material (ESI) for Energy & Environmental Science.

# Supporting information

# Synthesis of methane hydrate at ambient temperature with ultra-rapid formation and high gas storage capacity

Ye Zhang[a,1], Jie Zhao[a,b,c,1], Gaurav Bhattacharjee[a,*], Huanzhi Xu[a], Mingjun Yang[c,*], Rajnish Kumar[d,*], and Praveen Linga[a,*]

[a] Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 117585

[b] College of Metrology and Measurement Engineering, China Jiliang University, Hangzhou 310018, China

[c] Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, Dalian 116024, China

[d] Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai, India

[1]Equal contribution from both authors.

***Corresponding Author(s):** chegaur@nus.edu.sg (G. Bhattacharjee); yangmj@dlut.edu.cn (M. Yang); rajnish@iitm.ac.im (R. Kumar); chepl@nus.edu.sg (P. Linga);

# 1. MATERIALS AND METHODS

## 1.1. Materials

1,3-Dioxane (>98.0% purity (GC assay)) was purchased from Tokyo Chemical Industry Co., Ltd. Reagent grade L-tryptophan (≥ 98% purity (HPLC assay)) was purchased from Sigma Aldrich Pte. Ltd. Methane gas (99.995 mol% purity) was purchased from Air Liquide Singapore Pvt. Ltd. All experiments utilized deionized water obtained using an Elga Micromeg (Merck Millipore Direct-Q® 3 UV) deionization apparatus.

## 1.2. Methods

### 1.2.1. Experimental setup used for the measurement of three-phase equilibrium points

The experimental setup employed in the present study for three-phase equilibrium data measurement is similar to the one described in our recently published work [1], the sole exception being that the current reactor was equipped with a cooling jacket to control the experimental temperature, as opposed to being submerged in a water bath. To expound on the setup briefly, the main component was a customized high-pressure stainless-steel reactor with an internal volume of ~150 mL. Two acrylic viewing windows (30 mm in diameter) were fitted at the front and back of the reactor for the visual observation of reactor contents during the experiments. To control the temperature of the reactor at a desired experimental value, the reactor was equipped with an external cooling jacket to allow the circulation of coolant from an external chiller bath. An Omega T-type thermocouple having an uncertainty of ±0.1 K was positioned about 1 cm below the gas-liquid interface to monitor the system temperature accurately, while a pressure transducer (PT) – WIKA S-20 type with a measurement range of 0-250 bar and an uncertainty of 0.02 MPa over the span was employed to detect the reactor pressure at all times during the experiment. Agitation to the reactor contents was provided using a 4 cm stirrer bar placed inside the reactor and controlled via a magnetic stirring plate located underneath the reactor. The PT and the thermocouple were connected to a data acquisition (DAQ) system to record the instantaneous pressure and temperature data at 20 second intervals.

### 1.2.2. Experimental procedure followed for the measurement of three-phase equilibrium points

In our recently published work we have proposed the dissociation along the phase boundary (PB) method for accurate and efficient measurement of the phase equilibrium conditions of bulk gas hydrate systems [1]. The same PB method was employed in the present work to measure the three-phase (gas, liquid, and hydrate) equilibrium conditions of mixed $CH_4$/Dioxane hydrates. First, 25.33 g of water and 7.29 g of 1,3-Dioxane (Dioxane) were weighed using a Mettler Toledo (MS1200TS) weighing balance that had an uncertainty of ±0.01 g and added to the reactor, thereby creating a 5.56 mol% Dioxane aqueous solution with a total volume of 32.4 ml. The temperature of the reactor was controlled at 283.2 K using an external chiller and prior to starting the experiments, the reactor waspurged three times with methane gas at about 0.3 MPa to remove the air present inside the reactor. The reactor was then pressurized to 7.2 MPa to induce hydrate formation. Hydrate nucleation may be determined through any one of several simultaneous indicators, namely a sudden change in the appearance of the reactor contents (apparent clouding of the hydrate forming solution or a thin hydrate film formed at the gas-liquid interface), a sudden exothermic spike in the system temperature, or a sudden drop in the reactor pressure. Hydrate formation is assumed to be finished when the pressure decrease inside the system was less than 0.02 MPa over one hour. Once hydrate formation was over, the system pressure and temperature were either increased or decreased, stepwise, towards such values that were pre-determined to be starting points for hydrate dissociation. When the reactor temperature and pressure had stabilized at these pre-determined values, controlled venting of the reactor pressure was effected – at a rate of about 1-4 kPa/sec – to instigate hydrate dissociation. Actual hydrate dissociation began when the pressure inside the reactor coincided with the equilibrium pressure for mixed $CH_4$/Dioxane hydrates at a particular temperature; as a result, beyond this point, the true phase boundary of the mixed $CH_4$/Dioxane hydrate system was traced automatically. Three-phase (gas, liquid, and hydrate) equilibrium data for the mixed $CH_4$/Dioxane (5.56 mol%) hydrate system were then extracted from the obtained phase boundary trace at suitable pressure or temperature intervals.

### 1.2.3. Experimental setup and procedure for studying the formation kinetics of mixed $CH_4$/Dioxane hydrate

The apparatus employed for optimization of the hydrate formation kinetics was similar to the one described earlier for the measurement of three-phase equilibrium points. The only point of difference was that the customized high-pressure stainless-steel reactor used for the kinetic experiments was equipped with an additional top viewing window (25 mm diameter) to allow for more comprehensive visual examination of the reactor contents. To avoid redundancy, in this section, we primarily provide a detailed description of the procedure followed for the experiments conducted to optimize the kinetics of mixed $CH_4$/Dioxane hydrate formation. A stoichiometric concentration (5.56 mol%) Dioxane aqueous solution (total volume of 32.4 ml) was created by mixing 25.33 g of water and 7.29 g of 1,3-Dioxane, weighed using a Mettler Toledo make (MS1200TS) weighing balance having an uncertainty of ±0.01 g, and loaded into the reactor. Whenever L-tryptophan was used in the current experiments (concentrations of 300, 500, or 1000 ppm), it was weighed relative to the total mass of the original solution (Dioxane+water) introduced into the reactor. Once the hydrate forming solution had been introduced into the reactor and its lid tightly fastened, the reactor temperature was regulated to the desired value (283.2 K, 288.2 K, 293.2 K or 298.2 K) using an external chiller. Any excess air present inside the reactor was then purged through rapid pressurization (~0.3MPa) and depressurization cycles using methane gas, preceding continuous methane injection until the pressure inside the reactor reached a pre-determined experimental value (from 7.2 MPa to 16.7 MPa). For the experiments conducted at 283.2 K, no agitation was provided to the reactor contents, i.e. mixed

$CH_4$/Dioxane hydrate formation occurred under unstirred tank reactor (UTR) configuration at 283.2 K. There is some uncertainty about the nucleation time for the experiments conducted at 283.2 K under unstirred tank reactor (UTR). However, we found that the hydrate nucleation was unpredictable at elevated temperatures (288.2 K, 293.2 K or 298.2 K), and occasionally did not occur even after more than 24 hours if no agitation is provided. Therefore, for the experiments conducted at temperature above 283.2 K, a hybrid combinatorial reactor (HCR) approach was used to reduce the intrinsic stochasticity of hydrate nucleation, i.e. stirred tank reactor (STR) configuration is employed to induce hydrate nucleation and the subsequent hydrate growth is conducted under unstirred tank reactor (UTR) configuration. Hydrate nucleation was observed visually through the front and top viewing windows of the reactor or identified via simultaneous markers in the reactor temperature and pressure profiles - a sudden exothermic spike in the reactor temperature or a sudden drop in the reactor pressure. For the experiments conducted at 283.2 K, the time elapsed between the completion of gas pressurization and the first observable instance of hydrate nucleation is referred to as the ‘nucleation or induction time’. For the experiments conducted at temperature above 283.2 K, the period between initiating stirring and the nucleation point is referred as the ‘nucleation or induction time’. A long-enough run-time is allowed for the completion (the pressure drop of the reactor is less than 10 kPa/hour) of hydrate growth for all the kinetic experiments performed in the course of the present work. Given that the current experiments were conducted entirely under batch mode, the pressure inside the reactor decreased continually with hydrate growth, a consequence of methane molecules migrating from the gas phase into the solid hydrate phase. In the present work, overpressure is used as the driving force and we maintained the same initial driving force of 7.6 MPa for the experiments conducted at elevated temperature (288.2 K, 293.2 K, and 298.2 K). However, the pressure goes into the formation zoon of sI methane hydrate if we use 7.6 MPa initial driving force for the experiments conducted at 283.2 K. Therefore, the initial driving force is changed to 6.2 MPa for the experiments conducted at 283.2 K, which is almost the highest possible drive force that can be used at 283.2 K to avoid the formation of sI methane hydrate from the thermodynamic point of view.

### 1.2.4. Experimental setup used and procedure followed for both in-situ and ex-situ Raman spectroscopic analysis

The equipment employed for the in-situ Raman spectroscopic analysis conducted presently is the same as the one detailed in our previously published works [2, 3]. Here, we provided a brief account of the same. The setup consisted of a dispersive laser Raman Spectrometer (Model: SRaman-532) and a customized high-pressure stainless-steel reactor. The reactor vessel had a total internal volume of ~~230 ml. The pressure and temperature of the reactor were detected using a pressure transducer (PT) and a thermocouple, respectively, the latter located at the gas-liquid interface. A Raman probe capable of sustaining high pressures (up to ~12 MPa) was located at a point close to the bottom of the reactor to allow appropriate detection of the reactor contents. The Raman probe was equipped with two optical fibers which were used to transmit the laser to the reactor and to transmit the ensuing signals back to the spectrometer. The laser used had a wavelength of 532 nm, produced by a Nd:Yag laser source carrying a maximum power of 42 mW. The spectral coverage range was 150-4490 $cm^{-1}$ with a resolution of 2.8 $cm^{-1}$/pixel at 2200 $cm^{-1}$. The experimental procedure followed for hydrate formation using the in-situ Raman spectroscopy setup was largely identical to that discussed in the section immediately preceeding the current one. However, the expreiments conducted using the in-situ Raman spectroscopy setup involved the additional aspect of real-time Raman signal acquisition, which was initiated as soon as the reactor pressurization with methane gas up to the desired experimental value had been achieved. Raman spectra were recorded at regular (30 seconds) intervals throughout the hydrate formation process, with the integration time for the Raman Spectra fixed at 1 second. For these experiments conducted at 16.7 MPa beyond the operating limit (~12 MPa) of the Raman prob, the ex situ Raman analysis was conducted on the mixed $CH_4$/Dixoane hydrate synthesized. The mixed $CH_4$/Dixoane hydrate was formed using the common kinetic setup as discussed in the section above. After the completion of hydrate growth process, the hydrate samples were recovered using liquid nitrogen. The Raman spectra of the samples were measured at atmospheric pressure under the temperature of liquid nitrogen.

### 1.2.5. Procedure followed for powder X-ray diffraction (p-XRD) characterization

Powder X-ray diffraction (p-XRD) characterization is a universally accepted tool to determine the structure of a synthesized hydrate sample. Therefore, in the present study, crystal structure elucidation for the sysntheized mixed $CH_4$/Dioxane hydrates was realized through p-XRD measurements. To beign, a typical mixed $CH_4$/Dioxane hydrate formation experiment was conducted at 283.2 K and 7.2 MPa without the presence of L-tryptophan. Once hydrate formation was completed, the residual pressure inside the reactor was rapidly vented, the reactor opened up and the synthesized hydrates instantaneously quenched using liquid nitrogen. Quenching allowed uncomplicated collection of the hydrates, which could then be crushed into a roughly uniform powder using a mortar and pestle and under a liquid nitrogen environment. The liquid nitrogen helped ensure that the synthesized hydrates remained stable while being operated upon under atmospheric pressure conditions. Finally, the hydrate powder created was transferred into the p-XRD unit to be characterized. A BRUKER D8 advance diffractometer (40 kV, 30 mA) was employed for the p-XRD measurements. CuKα radiation ($\lambda = 1.542$ Å) was used as the X-ray. The p-XRD patterns were collected in the $2\theta$ range from 10° to 40°, with a step size of 0.02°. Details regarding the calculation of the lattice parameter of the hydrate crystals sysnthesized may be found in the literature [3].

### 1.2.6. Experimental setup used and procedure followed for stability testing of mixed $CH_4$/Dioxane hydrate.

A customized SNG technology prototype consisting of separate hydrate formation and pelletization zones was used to synthesize the mixed $CH_4$/Dioxane hydrate pellet that was subjected to stability testing. A detailed description of this apparatus may be found in the literature [4]. The experiment began with loading 100 mL of 5.56 mol% Dioxane aqueous solution into the hydrate formation zone of the SNG prototype. This solution also contained 1000 ppm of L-tryptophan as an additional kinetic promoter. Mixed $CH_4$/Dioxane hydrate formation was conducted under unstirred tank reactor configuration, at a constant temperature of 283.2 K and an initial pressure of 7.2 MPa. During hydrate formation, the hydrate formation and pelletization zones were kept isolated from one another through a ball valve maintained at the closed position. Once hydrate formation had completed, indicated by a pressure drop of less than 0.02 MPa over one hour, the residual pressure inside the hydrate formation zone was vented out, and the ball valve separating the two zones was opened up to create a continuous reactor interior. The mixed $CH_4$/Dioxane hydrates formed were then extruded towards the hydrate pelletization using a piston until such a time that compaction of the hydrate mass into a pellet could be affected by pressing the extruded hydrate particles at a sufficient pressure (~10.0 MPa), against the sealed end of the hydrate pelletization zone. Prior to opening the ball valve, it was ensured that the hydrate pelletization zone was cooled to a temperature of 263.2 K so as to prevent dissociation of the formed hydrates during the pelletization process. Next, the reactor lid at the end of the hydrate pelletization zone was removed and the piston was used to push out the compacted hydrate pellet, now under atmospheric pressure condition, into a storage vessel which had been pre-cooled using liquid nitrogen. After quickly measuring the pellet dimensions and weight, the storage vessel containing the hydrate pellet was tightly closed and the entire affair was transferred into a conventional laboratory refrigerator (maintained at the desired storage temperature) for mixed $CH_4$/Dioxane hydrate stability testing. Measurements of hydrate pellet dimensions and weight and sealing of the storage vessel containing the hydrate pellet both occurred under atmospheric pressure condition. The storage vessel was equipped with a pressure transducer (WIKA make – A-10 model) and an Omega T-type thermocouple to measure pressure and temperature changes within the storage vessel, respectively, at all times during the stability test. A data acquisition (DAQ) system connected to the pressure transducer and the thermocouple recorded the requisite data at regular intervals through the length of hydrate pellet storage.

## 1.3 Data treatment

The methane gas uptake due to hydrate formation was calculated using a modified ideal gas equation (eqn (3)), where Z is the compressibility factor that can be obtained using the Pitzer correlation [4]); $V_R$ is the volume gas available for the gas phase inside the reactor; R is the universal gas constant; P and T are the pressure and temperature of the reactor, respectively; *"0"* in the subscript represents the start of the experiment and ''*t*'' in the subscript represents any time "*t*" during the experiment.

$$\Delta n_{methane\ uptake} = V_R\left[\left(\frac{P}{ZRT}\right)_0 - \left(\frac{P}{ZRT}\right)_t\right] \qquad (3)$$

The normalized molar gas uptake (mmol/mol: mmol of gas consumed/mol of water) was calculated as shown in eqn (4) below, where $\Delta n_{methane\ uptake}$ is the methane gas uptake at any time "*t*" during the experiment (calculated using eqn (3)), and $n_{water}$ is the moles of water added to the reactor for hydrate formation.

$$\left(Normalized\ molar\ gas\ uptake\left(\frac{mmol\ of\ gas\ consumed}{mol\ of\ water}\right)\right)_t = \frac{\left(\Delta n_{methane\ uptake}\right)_t \times 1000}{n_{water}} \qquad (4)$$

The volumetric gas storage capacity (v/v: volume of gas at STP/volume of hydrate) was calculated as shown below in eqn (5):

$$\left(Volumetric\ methane\ storage\ capacity\left(\frac{Volume\ of\ gas\ (STP)}{Volume\ of\ hydrate}\right)\right)_t = K\left(Normalized\ molar\ gas\ uptake\left(\frac{mmol\ of\ gas\ consumed}{mol\ of\ water}\right)\right)_t \qquad (5)$$

$K$, a coefficient of proportionality, can be described as:

$$K = \frac{v}{M_{r.hydrate}/\left(\rho_{hydrate} \times n_{w,h}\right)} \qquad (6)$$

where $v$ is the standard molar volume of gas at STP (22.4 $cm^3$ $mmol^{-1}$ of gas); $n_{w,h}$

represents the moles of water per mole of hydrate (136 for the sII hydrate formed presently); $M_{r.hydrate}$ is the molecular mass of sII hydrate (g $mol^{-1}$), a function of the thermodynamic promoter used and $\rho_{hydrate}$ is the density of hydrate (g $cm^{-3}$), calculated based on the lattice parameter obtained for a unit cell of cubic sII mixed methane hydrate synthesized currently. Mathematically, $\rho_{hydrate}$ can be expressed as eqn (7) shown below:

$$\rho_{hydrate} = \frac{M_{r.hydrate}}{(A \times \lambda^3)} \quad (7)$$

where $A$ is the Avogadro constant $(6.023 \times 10^{23}\ mol^{-1})$[5]; $\lambda$ is the lattice parameter (17.281 Å), calculated for a unit cell of cubic sII mixed $CH_4$/Dioxane hydrate synthesized under the current experimental conditions ; with 1,3-Dioxane (Dioxane) used as the thermodynamic promoter, assuming that the hydrate cages were fully occupied,

$$M_{r.hydrate} = (136 \times 18) + (8 \times 88.106) + (16 \times 2)$$

$$\therefore \rho_{hydrate} = 1.098\ (g\ cm^{-3})$$

The hydrate formation rate for the first 15 mins of hydrate growth was calculated by simply fitting the relevant portion of the volumetric methane storage capacity curve (eqn 5) using the least squares method.

## 2. RESULTS AND DISCUSSIONS

**Table S1** Three-phase (liquid, gas, and hydrate) equilibrium conditions for the mixed $CH_4$/Dioxane (5.56 mol%) hydrate system obtained using the dissociation along the phase boundary (PB) method.[α]

| T/K | P/MPa | T/K | P/MPa |
|---|---|---|---|
| 298.2 | 9.10 | 291.4 | 3.40 |
| 298.0 | 8.90 | 291.2 | 3.30 |
| 297.8 | 8.50 | 291.1 | 3.20 |
| 297.6 | 8.20 | 290.8 | 3.10 |
| 297.4 | 8.00 | 290.6 | 3.00 |
| 297.2 | 7.70 | 290.4 | 2.90 |

| | | | |
|---|---|---|---|
| 296.9 | 7.40 | 290.2 | 2.80 |
| 296.5 | 7.00 | 289.7 | 2.70 |
| 296.3 | 6.80 | 289.5 | 2.60 |
| 296.1 | 6.60 | 289.2 | 2.50 |
| 295.9 | 6.40 | 288.9 | 2.40 |
| 295.7 | 6.20 | 288.7 | 2.30 |
| 295.5 | 6.00 | 288.4 | 2.20 |
| 295.3 | 5.80 | 288.1 | 2.10 |
| 294.9 | 5.60 | 287.9 | 2.00 |
| 294.7 | 5.40 | 287.5 | 1.90 |
| 294.4 | 5.20 | 287.2 | 1.80 |
| 294.2 | 5.00 | 286.3 | 1.60 |
| 293.9 | 4.80 | 286.0 | 1.50 |
| 293.6 | 4.60 | 285.5 | 1.40 |
| 293.2 | 4.40 | 285.0 | 1.30 |
| 292.9 | 4.20 | 284.5 | 1.20 |
| 292.6 | 4.00 | 283.9 | 1.10 |
| 292.3 | 3.80 | 283.4 | 1.00 |
| 291.9 | 3.60 | 282.8 | 0.90 |
| 291.7 | 3.50 | 282.3 | 0.80 |

[α] Uncertainties u are u(T)= ± 0.1 K, and u(P)= ± 0.02 MPa.

**Table S2** Summary of the hydrate formation experiments conducted at 283.2 K temperature and 7.2 MPa initial pressure under unstirred tank reactor (UTR) configuration using a traditional high-pressure reactor with viewing windows. Relevant parameters listed are induction time in minutes (min), methane uptake (mmol of gas consumed/mol of water (mmol/mol)) and volumetric methane storage capacity (volume of gas (STP)/volume of hydrate (v/v)) achieved at the end of two hours of hydrate growth, the time required (min) for 90% completion of the methane uptake ($t_{90}$), and the hydrate formation rate (($R_{15}$ (v/v min$^{-1}$)) for the first 15 min of the growth phase.

| **System** | **Expt No.** | **Induction Time (min)** | **$t_{90}$ (min)** | **Methane uptake (mmol/mol)** | **Volumetric $CH_4$ Storage Capacity (v/v)** | **$R_{15}$ (v/v min$^{-1}$)** |
|---|---|---|---|---|---|---|
| Water + 5.56 mol% Dioxane | NA1* | 2.78 | 72.33 | 89.66 | 87.92 | 0.40 ($R^2$=0.93) |
| | NA1 | 3.15 | 50.33 | 88.41 | 86.69 | 0.70 ($R^2$=0.95) |
| | NA1 | 21.87 | 59.67 | 91.68 | 89.90 | 0.47 ($R^2$=0.96) |
| | Average (± SD) | 9.27 (± 0.91) | 60.78 (± 11.04) | 89.92 (± 1.65) | 88.17 (± 1.62) | 0.52 (± 0.16) |
| Water + 5.56 mol% Dioxane + 300 ppm L-tryptophan | PA1# | 35.95 | 17.67 | 71.07 | 69.69 | 3.98 ($R^2$=0.97) |
| | PA2 | 1.28 | 21.00 | 71.19 | 69.81 | 4.21 ($R^2$=0.94) |

| | | | | | | |
|---|---|---|---|---|---|---|
| | PA3 | 2.67 | 17.00 | 68.14 | 66.82 | 4.23 ($R^2$=0.99) |
| | Average (± SD) | 13.30 (± 9.63) | 18.56 (± 2.14) | 70.13 (± 1.73) | 68.77 (± 1.69) | 4.14 (± 0.14) |
| Water + 5.56 mol% Dioxane + 1000 ppm L-tryptophan | PA4 | 3.67 | 14.67 | 77.95 | 76.44 | 4.94 ($R^2$=0.99) |
| | PA5 | 0.93 | 15.67 | 73.14 | 71.72 | 4.48 ($R^2$=0.99) |
| | PA6 | 0.67 | 14.00 | 75.59 | 74.12 | 5.14 ($R^2$=0.99) |
| | Average (± SD) | 1.76 (± 1.66) | 14.78 (± 0.84) | 75.56 (± 2.41) | 74.09 (± 2.36) | 4.85 (± 0.34) |
| Water + 5.56 mol% Dioxane + 3000 ppm L-tryptophan | PA7 | 22.42 | 15.67 | 78.58 | 77.05 | 4.69 ($R^2$=0.99) |
| | PA8 | 5.00 | 13.33 | 76.40 | 74.91 | 4.84 ($R^2$=0.99) |
| | PA9 | 15.45 | 14.67 | 73.21 | 71.79 | 4.53 ($R^2$=0.99) |
| | Average (± SD) | 14.29 (± 8.77) | 14.56 (± 1.17) | 76.06 (± 2.70) | 74.59 (± 2.65) | 4.69 (± 0.16) |

[*]Nomenclature: NA-Experiments conducted without promoter at 283.2 K temperature using a traditional high-pressure reactor with viewing windows

[#]Nomenclature: PA-Experiments conducted with promoter (amino acid L-tryptophan) at 283.2 K temperature using a traditional high-pressure reactor with viewing windows

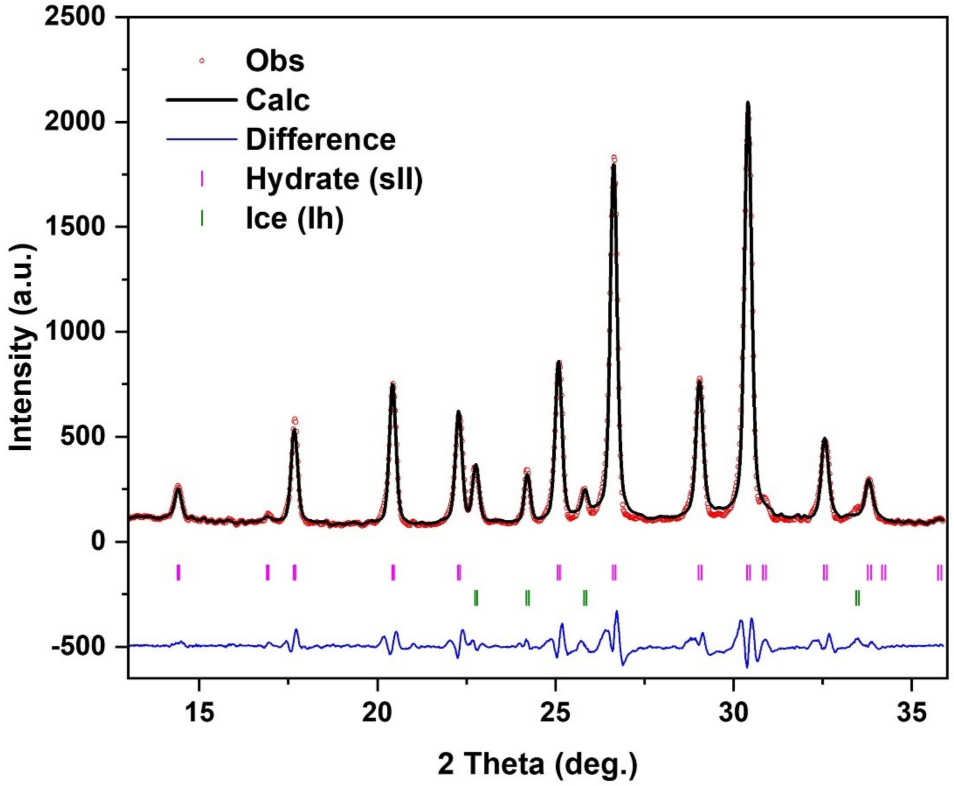

**Figure S1** Le-Bail fitting of the p-XRD pattern obtained for mixed $CH_4$/Dioxane (5.56 mol%) hydrate synthesized at 283.2 K temperature and 7.2 MPa initial pressure. Red circles- observed XRD pattern; black solid line-calculated XRD pattern from several phases; Color ticks below the diffraction curve represent the reflections of the phases described in the legend. $R_{wp}$=17.5%, $\chi^2$= 2.27.[6, 7]

**Figure S2**: Typical visual observation of the hydrate growth from the top viewing window of the reactor for the "$CH_4$/Dioxane (5.56 mol%)" system; experimental conditions of 283.2 K temperature and 7.2 MPa initial pressure.

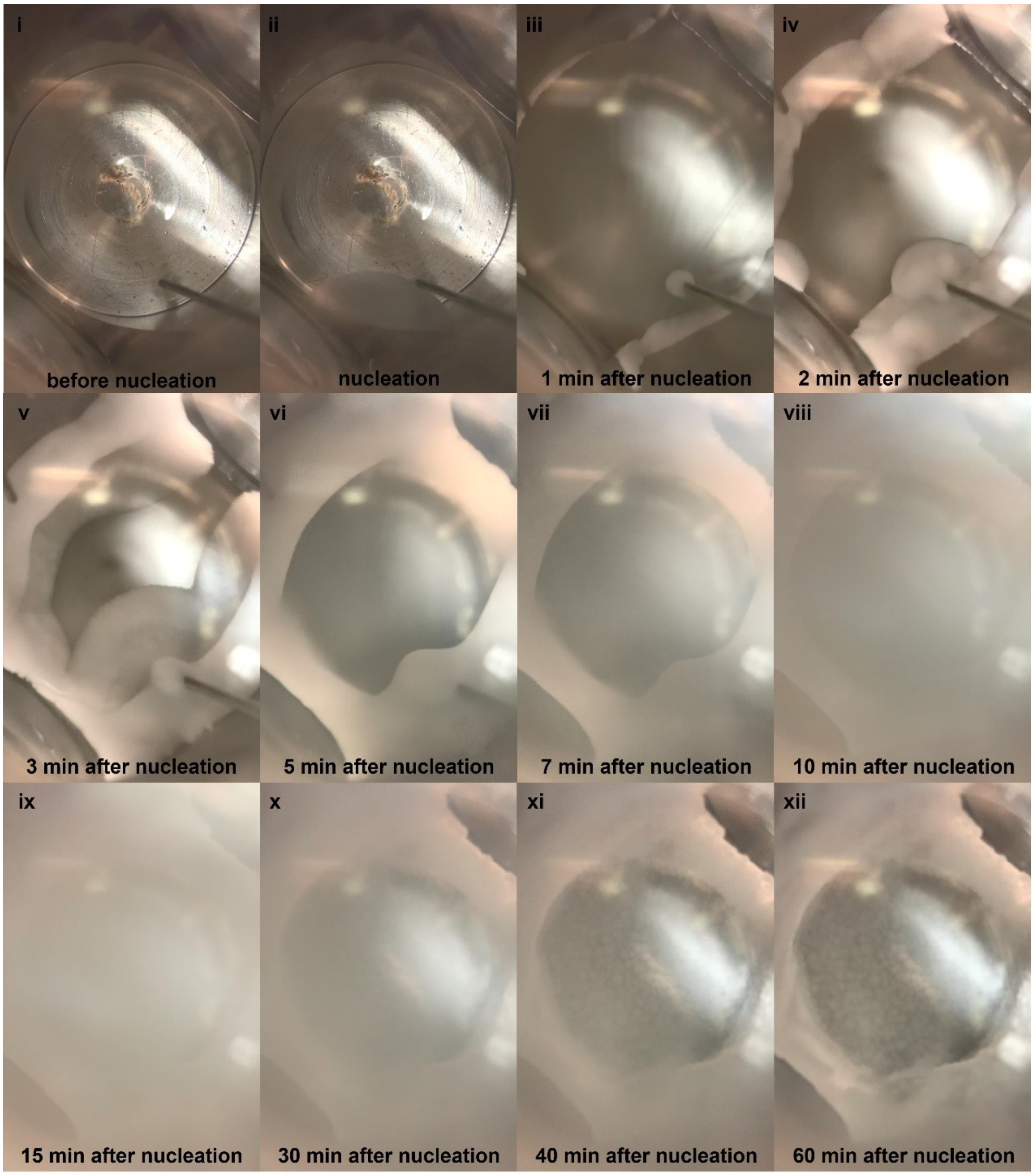

**Figure S3** Typical visual observation of the hydrate growth from the top viewing window of the reactor for the "$CH_4$/Dioxane (5.56 mol%)/L-tryptophan (1000 ppm)" system; experimental conditions of 283.2 K temperature and 7.2 MPa initial pressure.

**Table S3** Summary of the hydrate formation experiments conducted at 283.2 K temperature and 7.2 MPa initial pressure under unstirred tank reactor (UTR) configuration using the in-situ Raman spectroscopy setup. The run time for these particular experiments was three hours of hydrate growth, i.e., three hours following hydrate nucleation. The relevant parameters listed in the table are the induction time in minutes (min), methane uptake (mmol of gas consumed/mol of water (mmol/mol)) and volumetric methane storage capacity (volume of gas (STP)/volume of hydrate (v/v)) achieved at the end of three hours of hydrate growth, the time required (min) for 90% completion of the methane uptake ($t_{90}$), and the hydrate formation rate (($R_{15}$ (v/v $min^{-1}$)) for the first 15 min of the growth phase.

| **System** | **Expt No.** | **Induction Time (min)** | **$t_{90}$ (min)** | **Methane uptake (mmol/mol)** | **Volumetric $CH_4$ Storage Capacity (v/v)** | **$R_{15}$ (v/v $min^{-1}$)** |
|---|---|---|---|---|---|---|
| Water + 5.56 mol% Dioxane | RNA1[*] | 3.12 | 137.00 | 68.07 | 66.75 | 0.07<br>($R^2$=0.76) |
| | RNA2 | 1.18 | 124.00 | 68.85 | 67.52 | 0.09<br>($R^2$=0.82) |
| | RNA3 | 3.78 | 147.00 | 66.99 | 65.69 | 0.06<br>($R^2$=0.75) |
| | Average (± SD) | 2.69 (± 1.35) | 136.00 (± 11.53) | 67.97 (± 0.93) | 66.65 (± 0.92) | 0.07 (± 0.02) |
| Water + 5.56 mol% Dioxane + 1000 ppm L-tryptophan | RPA1[#] | 1.98 | 15.30 | 54.19 | 53.13 | 3.74<br>($R^2$=0.98) |
| | RPA2 | 1.38 | 15.30 | 54.11 | 53.06 | 3.40<br>($R^2$=0.99) |
| | RPA3 | 3.70 | 19.30 | 49.91 | 48.94 | 2.76<br>($R^2$=0.92) |
| | Average (± SD) | 2.36 (± 1.20) | 16.63 (± 2.31) | 52.74 (± 2.45) | 51.71 (± 2.40) | 3.30 (± 0.50) |

[*] Nomenclature: RNA-Experiments conducted without promoter at 283.2 K temperature using the in-situ Raman setup

[#] Nomenclature: RPA-Experiments conducted with promoter (amino acid L-tryptophan) at 283.2 K temperature using the in-situ Raman setup

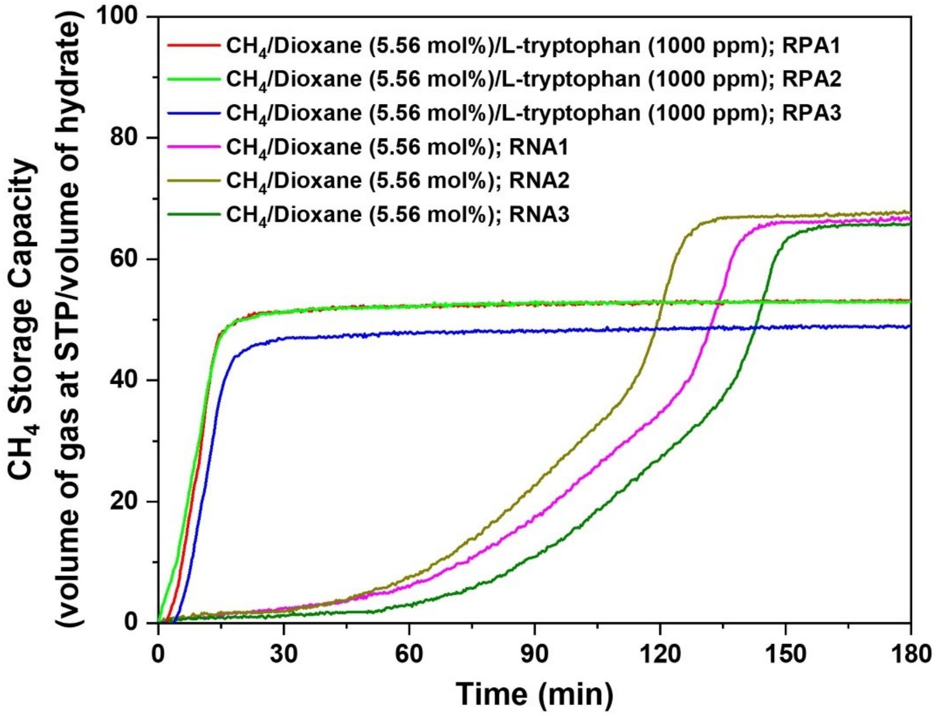

**Figure S4** Individual gas uptake profiles obtained for mixed CH$_4$/Dioxane (5.56 mol%) hydrate formation conducted under unstirred tank reactor configuration using the in-situ Raman spectroscopy setup, with and without the presence of 1000 ppm of L-tryptophan; experimental conditions employed were 283.2 K temperature and 7.2 MPa initial pressure.

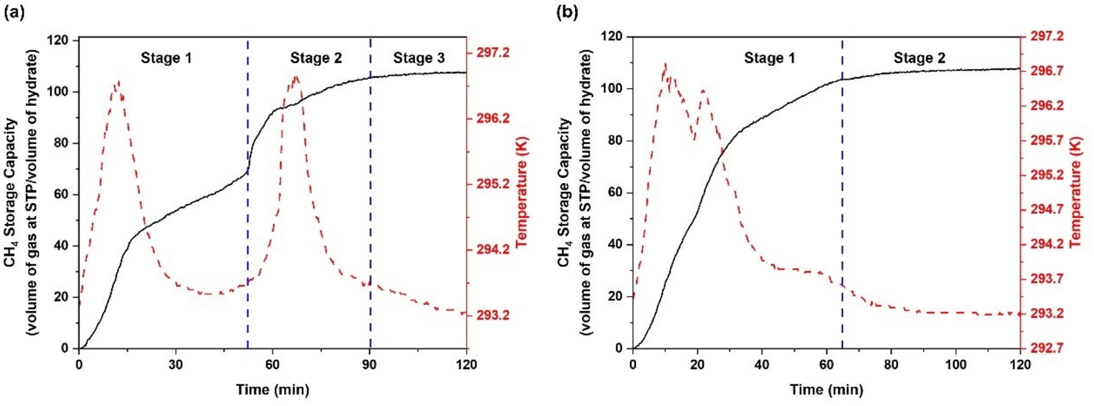

**Figure S5** (a) The typical gas uptake and temperature profile obtained for mixed CH$_4$/Dioxane (5.56mol%) hydrate formation at the temperature of 293.2 K and the initial pressure of 12 MPa without the presence of 1000 ppm L-tryptophan (Case 3); (b) The typical gas uptake and temperature profile obtained for mixed CH$_4$/Dioxane (5.56mol%) hydrate formation at the temperature of 293.2 K and the initial pressure of

12 MPa with the presence of 1000 ppm L-tryptophan (Case 4).

The hydrate formation associated with the formation of new hydrogen bonding is an exothermic process which can be captured by the thermocouples placed inside the reactor. In fact, the rapid slope change in the gas uptake profile is always accompanied by an increase in the temperature profile because of intensive hydrate formation. **Figure S5(a)** shows the gas uptake profile along with temperature profile conducted at temperature of 293.2 K and initial pressure of 12 MPa. The increase of temperature is huge at the earlier period of Stage 1 as a result of the extensive hydrate growth leading to a rapid hydrate growth rate. Subsequently, the hydrate growth rate is reduced as the temperature reduces. However, another stronger temperature peak is observed again leading to a significantly enhanced gas uptake rate at the earlier period of Stage 2. Then, the temperature starts to drop all the way back to experimental temperature of 293.2 K through Stage 3 indicating the completion of hydrate formation. In fact, the two temperature spikes observed in the Stage 1 and Stage 2, respectively surprisingly echo the similar shape of gas uptake profile in the two stages. The visual observation of the experiment mentioned above is shown in **Figure S6(a)**. Since hydrate formation is a three phase (gas, liquid, and solid) reaction and as such there are always certain mass transfer resistance accompanying the hydrate growth process which can play an important role behind the three-stage growth behavior. However, by adding 1000 ppm L-tryptophan to the system and keeping other experimental conditions the same, the hydrate system displayed a two-stage hydrate growth as shown in **Figure S5(b)**. Two very strong temperature spikes observed in Stage 1 imply intensive hydrate formation leading to the fast growth rate. In Stage 2, the reactor temperature is gradually brought back to the experimental temperature by the external chiller. Compared with the hydrate system in the absence of L-tryptophan, using L-tryptophan can enhance hydrate formation kinetics significantly by altering the hydrate growth behavior (see **Figure S6(b)**) and resulting in a different mass transfer resistance accompanying the hydrate growth process, which is consistent with the result discussed throughout the main manuscript. Similar explanations can be applied to other experimental conditions employed in the current work such as the experiments conducted at 283.2 K temperature and 7.2 MPa initial pressure using the in-situ Raman spectroscopy setup (see **Figure S4**), as well as the experiments conducted at temperature of 288.2 K and 9.7 MPa using a traditional high-pressure reactor with viewing windows (see **Figure 5c**). In short, the deflection points observed in plot (a) has to do with multiple nucleation and growth event which were separated from each other on time scale. This type of gas uptake curve is typical of mass transfer-controlled regime. However, in presence of L-tryptophan (plot (b)), formed hydrates were porous which resulted in better gas-water contact and in turn a more homogenous growth, however, here as well multiple nucleation and growth event were seem however, not as pronounced as plot (a).

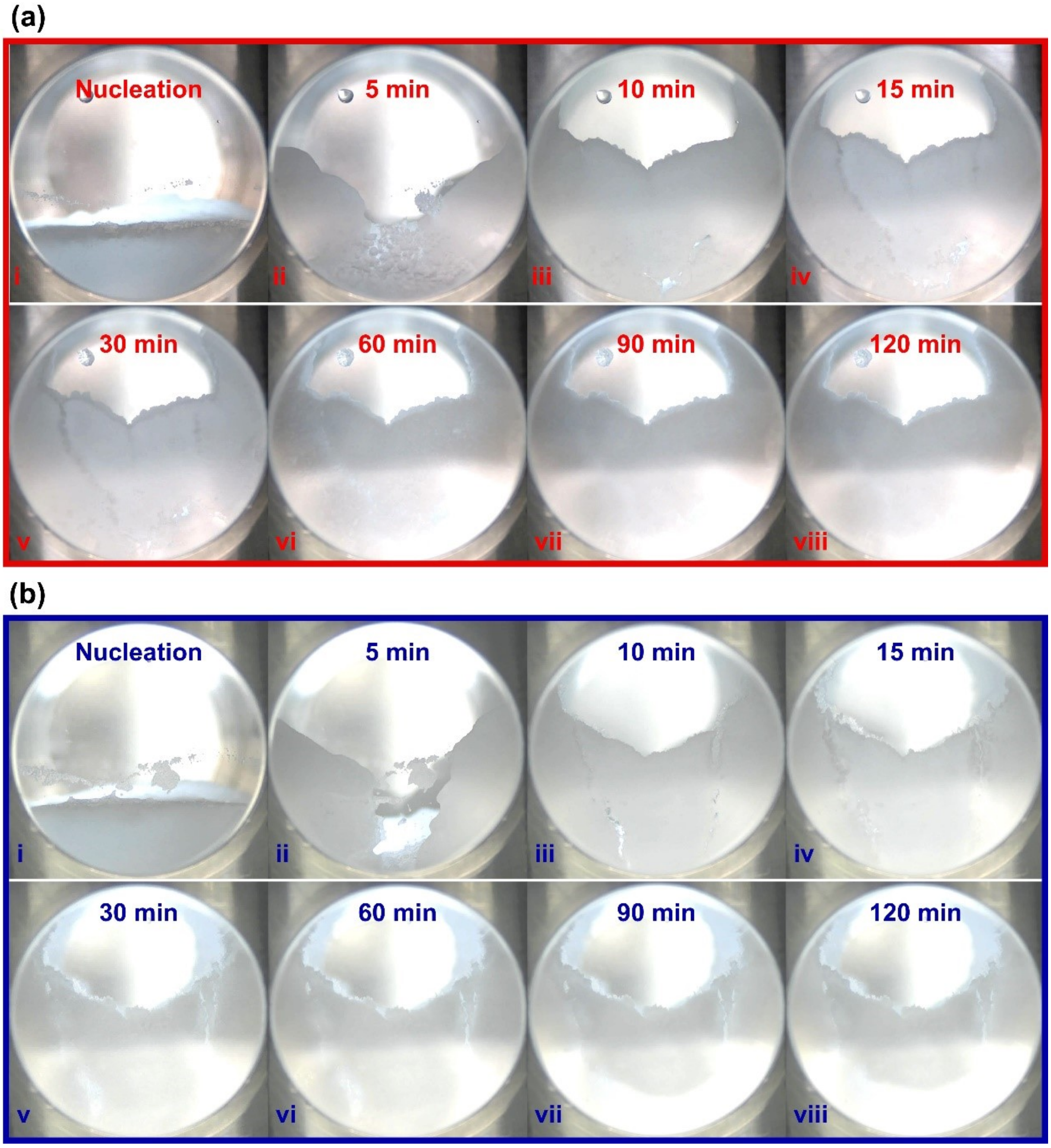

**Figure S6** (a) Typical visual observation made through the front viewing window of the reactor mapping the hydrate growth for the "$CH_4$/Dioxane (5.56 mol%)" system at 293.2 K and 12 MPa (Case 3). (b) Typical visual observation made through the front viewing window of the reactor mapping the hydrate growth for the "$CH_4$/Dioxane (5.56 mol%)/L-tryptophan (1000 ppm)" system at 293.2 K and 12 MPa (Case 4).

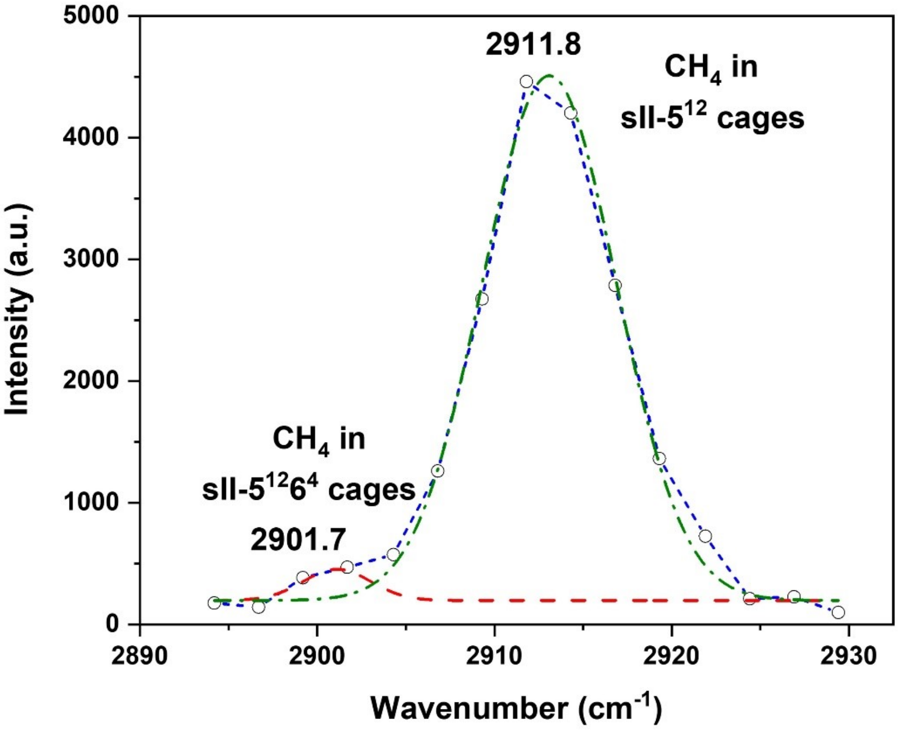

**Figure S7** Peak fitting to Raman spectra obtained for mixed $CH_4$/Dioxane (5.56 mol%) hydrate samples synthesized at 293.2 K and 16.7 MPa. The unfilled circles represent the measured Raman data; The red dash line and olive dash dot line represent the fitted peaks.

**Table S4** Summary of the hydrate formation experiments conducted at temperature of 288.2 K and 293.2 K with the initial pressure driving force of 7.6 MPa under hybrid combinatorial reactor (HCR) approach. The run time for these particular experiments was two hours of hydrate growth, i.e., two hours following hydrate nucleation. The relevant parameters listed in the table are experimental temperature, experimental pressure, the induction time in minutes (min), methane uptake (mmol of gas consumed/mol of water (mmol/mol)) and volumetric methane storage capacity (volume of gas (STP)/volume of hydrate (v/v)) achieved at the end of two hours of hydrate growth, the time required (min) for 90% completion of the methane uptake ($t_{90}$), and the hydrate formation rate (($R_{15}$ (v/v min$^{-1}$)) for the first 15 min of the growth phase.

| System | Expt No. | T (K) | Initial Pressure (Driving Force) (MPa) | Nucleation Time (min) | $t_{90}$ (min) | Methane uptake at 2h (mmol/mol) | Volumetric Methane Storage Capacity at 2h (v/v) | $R_{15}$ (v/v min$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| Water + 5.56 mol% Dioxane (Case 1) | NB1$^*$ | 288.2 | 9.7 (7.6) | 0.47 | 56.67 | 98.82 | 96.90 | 4.29 ($R^2$=0.97) |
| | NB2 | | | 0.38 | 42.67 | 101.54 | 99.57 | 3.56 ($R^2$=0.94) |
| | NB3 | | | 0.25 | 41.33 | 101.84 | 99.86 | 3.54 ($R^2$=0.90) |
| | Average (± SD) | | | 0.37 (± 0.11) | 46.89 (± 8.49) | 100.74 (± 1.67) | 98.78 (± 1.63) | 3.80 (± 0.43) |
| Water + 5.56 mol% Dioxane (Case | NC1$^*$ | 293.2 | 12 (7.6) | 0.80 | 69.33 | 109.87 | 107.73 | 2.83 ($R^2$=0.97) |
| | NC2 | | | 0.83 | 87.00 | 108.42 | 106.31 | 2.69 ($R^2$=0.96) |

|  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  | NC3 |  |  | 0.85 | 76.33 | 109.02 | 106.90 | 2.74 ($R^2$=0.97) |
|  | Average<br>(± SD) |  |  | 0.83<br>(± 0.03) | 77.56<br>(±8.90) | 109.10<br>(± 0.73) | 106.98<br>(± 0.71) | 2.75<br>(± 0.07) |
| Water + 5.56 mol% Dioxane + 1000 ppm L-tryptophan (Case 2) | PB1[#] | 288.2 | 9.7 (7.6) | 0.57 | 19.33 | 94.63 | 92.79 | 5.48 ($R^2$=1.00) |
|  | PB2 |  |  | 0.43 | 20.00 | 94.68 | 92.84 | 5.61 ($R^2$=1.00) |
|  | PB3 |  |  | 0.13 | 19.33 | 91.69 | 89.91 | 5.71 ($R^2$=0.99) |
|  | Average<br>(± SD) |  |  | 0.38<br>(± 0.22) | 19.56<br>(± 0.38) | 93.66<br>(± 1.71) | 91.84<br>(± 1.68) | 5.60<br>(± 0.12) |
| Water + 5.56 mol% Dioxane + 1000 ppm L-tryptophan (Case 4) | PC1[#] | 293.2 | 12 (7.6) | 0.73 | 52.00 | 109.52 | 107.39 | 2.98 ($R^2$=0.98) |
|  | PC2 |  |  | 1.87 | 56.00 | 108.71 | 106.60 | 2.86 ($R^2$=0.99) |
|  | PC3 |  |  | 1.33 | 53.33 | 108.51 | 106.41 | 2.92 ($R^2$=0.99) |
|  | Average<br>(± SD) |  |  | 1.31<br>(± 0.57) | 53.78<br>(± 2.04) | 108.91<br>(± 0.53) | 106.80<br>(± 0.52) | 2.92<br>(± 0.06) |

[*] Nomenclature: NB and NC - Experiments conducted without promoter at 288.2 K and 293.2 K temperature, respectively using a traditional high-pressure reactor with viewing windows

[#] Nomenclature: PB and PC -Experiments conducted with promoter (amino acid L-tryptophan) at 288.2 K and 293.2 K temperature, respectively using a traditional high-pressure reactor with viewing windows

**Table S5** Summary of the hydrate formation experiments conducted at initial experimental pressure of 16.7 MPa under hybrid combinatorial reactor (HCR) approach. The run time for these particular experiments was ten hours of hydrate growth, i.e., ten hours following hydrate nucleation.

The relevant parameters listed in the table are experimental temperature, experimental pressure, the induction time in minutes (min), methane uptake (mmol of gas consumed/mol of water (mmol/mol)) and volumetric methane storage capacity (volume of gas (STP)/volume of hydrate (v/v)) achieved at the end of ten hours of hydrate growth, the time required (min) for 90% completion of the methane uptake ($t_{90}$), and the hydrate formation rate (($R_{15}$ (v/v min$^{-1}$)) for the first 15 min of the growth phase.

| **System** | **Expt No.** | **T (K)** | **Initial Pressure (Driving Force) (MPa)** | **Nucleation Time (min)** | **$t_{90}$ (min)** | **Methane uptake at 10h (mmol/mol)** | **Volumetric Methane Storage Capacity at 10h (v/v)** | **$R_{15}$ (v/v min$^{-1}$)** |
|---|---|---|---|---|---|---|---|---|
| Water + 5.56 mol% Dioxane | ND1* | 298.2 | 16.7 (7.6) | 2.13 | 126.00 | 68.35 | 67.03 | 1.41 ($R^2$=0.97) |
| | ND2 | | | 2.00 | 122.67 | 69.20 | 67.86 | 1.41 ($R^2$=0.99) |
| | ND3 | | | 4.35 | 114.67 | 68.59 | 67.26 | 1.64 ($R^2$=0.98) |
| | Average (± SD) | | | 2.83 (± 1.32) | 121.11 (± 5.82) | 68.72 (± 0.44) | 67.38 (± 0.43) | 1.49 (± 0.13) |
| Water + 5.56 mol% Dioxane + 1000 ppm L-tryptophan | PD1# | 298.2 | 16.7 (7.6) | 4.52 | 240.67 | 137.16 | 134.49 | 1.26 ($R^2$=0.99) |
| | PD2 | | | 5.18 | 198.67 | 139.08 | 136.38 | 1.47 ($R^2$=0.99) |
| | PD3 | | | 4.40 | 200.00 | 137.18 | 134.51 | 1.42 ($R^2$=0.99) |
| | Average (± SD) | | | 4.70 (± 0.42) | 213.11 (± 23.87) | 137.81 (± 1.10) | 135.13 (± 1.08) | 1.38 (± 0.11) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | PC4 | 293.2 | 16.7(12.3) | 0.08 | 94.33 | 132.64 | 130.06 | 4.69 ($R^2$=0.99) |
| | PC5 | | | 0.87 | 84.33 | 134.67 | 132.06 | 3.44 ($R^2$=0.93) |
| | PC6 | | | 0.52 | 83.67 | 134.14 | 131.53 | 5.73 ($R^2$=0.97) |
| | Average (± SD) | | | 0.49 (± 0.39) | 87.44 (± 5.97) | 133.82 (± 1.05) | 131.22 (± 1.03) | 4.62 (± 1.15) |

[*] Nomenclature: ND - Experiments conducted without promoter at 298.2 K temperature using a traditional high-pressure reactor with viewing windows

[#] Nomenclature: PD - Experiments conducted with promoter (amino acid L-tryptophan) at 298.2 K temperature using a traditional high-pressure reactor with viewing windows

**Video SV1:** A video of the typical morphology evolution for hydrate formation conducted using the "$CH_4$/Dioxane (5.56 mol%)" system at 283.2 K temperature and 7.2 MPa initial pressure; this video was captured through the front viewing window of the reactor.

**Video SV2:** A video of the typical morphology evolution for hydrate formation conducted using the "$CH_4$/Dioxane (5.56 mol%)/L-tryptophan (1000 ppm)" system at 283.2 K temperature and 7.2 MPa initial pressure; this video was captured through the front viewing window of the reactor.

**Video SV3:** A video of the typical morphology evolution for hydrate formation conducted using the "$CH_4$/Dioxane (5.56 mol%)/L-tryptophan (1000 ppm)" system at 283.2 K temperature and 7.2 MPa initial pressure; this video was captured through the top viewing window of the reactor.

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