

Electronic Supplementary Information

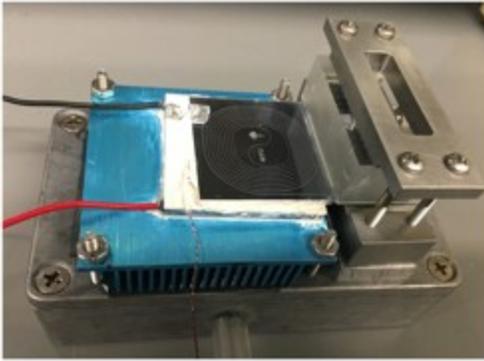
Title: Flash crystallization
kinetics of methane (sI) hydrate
in a thermoelectrically-cooled
microreactor

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(a)



(b)

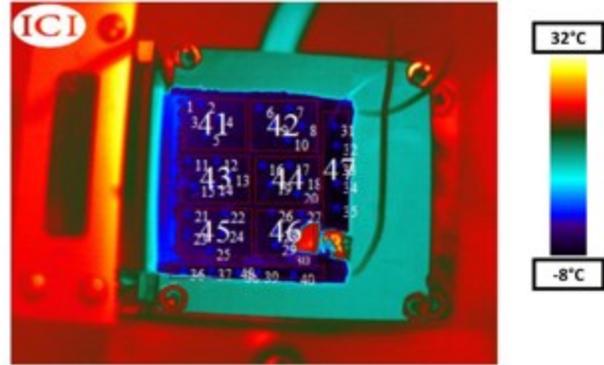
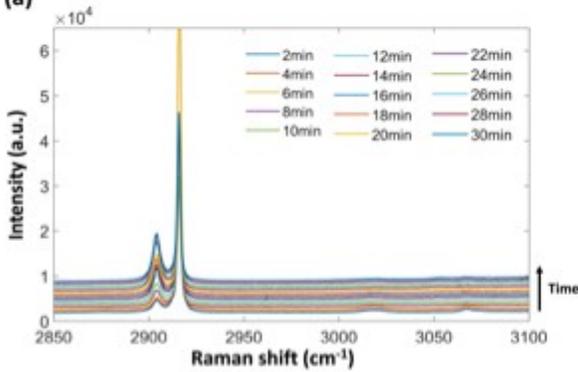


Figure S.2 (a) Image of microsystem assembly (b) IR image of temperature distribution across the microsystem. The temperature distribution across the experiment observation zone is 0.1033 K.

(a)



(b)

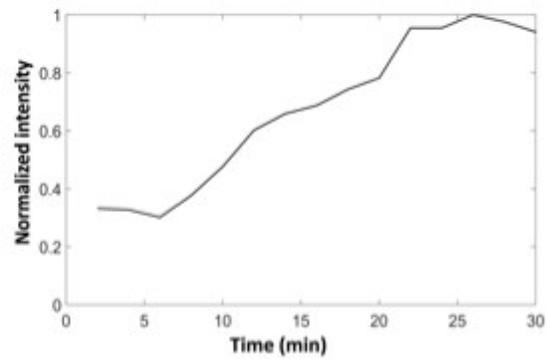


Figure S.1 (a) Raman spectra on same spot of channel taken for 30 min with 2-min interval. The intensity of signature peak at 2904 cm^{-1} over time is proportional to the methane hydrate growth in the perpendicular direction to the $\text{CH}_4/\text{H}_2\text{O}$ interface. (b) Normalized intensity of 2904 cm^{-1} peak over time. During first 6 minutes, the unchanged intensity indicates the initial thin film thickness could be assumed to be constant during the propagation stage. **The increase of intensity from 6 minutes to 26 minutes shows the process of thin film thickening.**

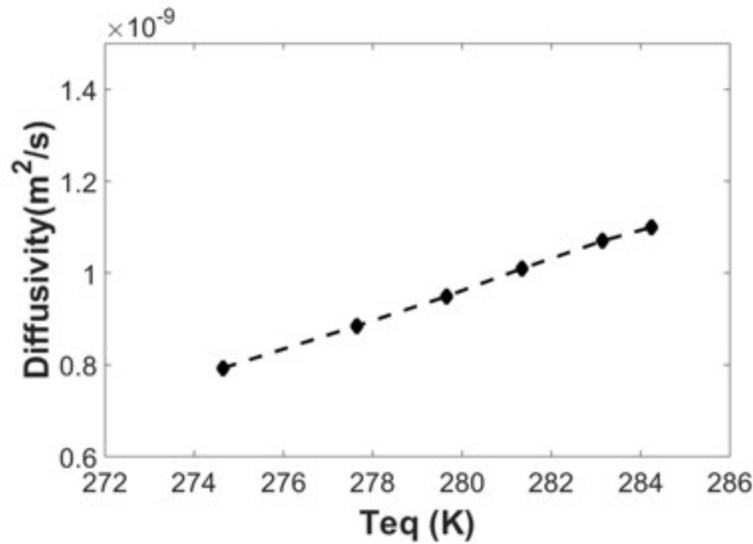


Figure S. 3 The correlation of diffusivity to temperature based on Stokes-Einstein equation. The viscosity data is retreated from NIST Chemistry WebBook.⁴

Influence of pressure drop on methane hydrate formation

Figure S.4 shows an example of pressure drop measurement of the microfluidic system during the methane hydrate formation. Compared with the pressure of system P , the pressure drop ΔP is negligible while measuring the propagation rate. Allowing hydrate formation to continue for extended periods (an order of magnitude longer than the time scale of the propagation rate measurement) can lead to constriction.

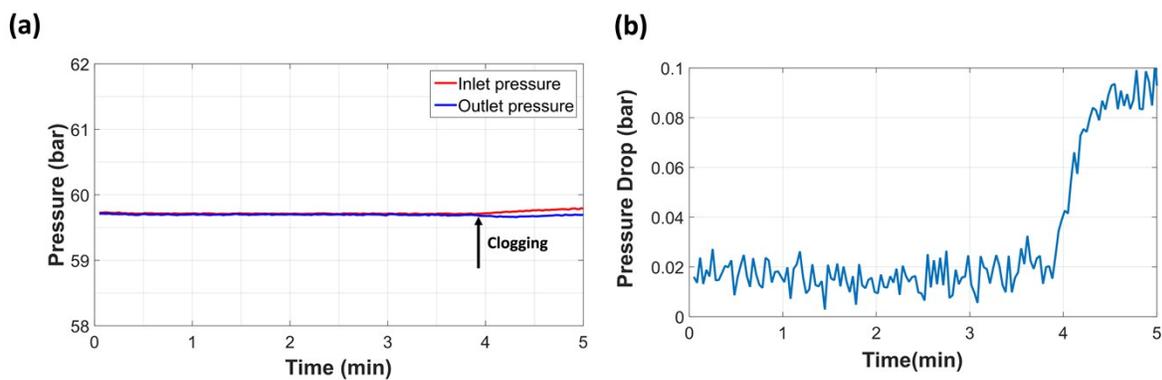


Figure S. 4 The pressure profile of the microfluidic system during methane hydrate formation at 59.8 bar, sub-cooling temperature of 1.0 K, and methane flow rate of 20 $\mu\text{L}/\text{min}$. (a) Inlet and outlet pressure of the microfluidic system in the first 5 min of methane hydrate formation. (b) The pressure drop across the microfluidic system. The increase of pressure drop at around 4 min indicates the onset of constriction. Even after 4 min, , which confirms that the pressure drop is negligible.

Derivation of propagation rate and heat transfer

Performing an energy balance on the adsorption layer yields the rate of heat transfer across the adsorption layer,

$$\left(\frac{dq}{dt}\right)_i = h_i A (T_{eq} - T_i) \quad (S1)$$

where A is the cross-sectional area of the film and h_i is the heat transfer coefficient of the adsorption layer, defined by,

$$h_i = \frac{\kappa_i}{\delta_i} \quad (S2)$$

Here κ_i is the thermal conductivity and δ_i is the thickness of the adsorption layer. Similarly, the rate of heat transfer across the stagnant film can be expressed as,

$$\left(\frac{dq}{dt}\right)_s = h_s A (T_i - T_b) \quad (S3)$$

$$h_s = \frac{\kappa_s}{\delta_s} \quad (S4)$$

Here h_s is the heat transfer coefficient of the stagnant film, κ_s is the thermal conductivity, and δ_s is the thickness of the stagnant film. At steady-state, the heat transfer rate in either the adsorption layer or the stagnant film are equal. Since the temperature at the interface T_i and the thicknesses δ_i and δ_s are difficult to directly measure, equations (S1) and (S3) may be expressed by,¹

$$\left\{ \begin{array}{l} r_h = h' A (T_{eq} - T_b)^n \\ = h_i A (T_{eq} - T_i) \\ = h_s A (T_i - T_b) \end{array} \right\} \quad (S5)$$

where h' is the effective heat transfer coefficient and the exponent n is the order of the overall heat transfer process. Values of n have previously been reported in the range of 1.5 to 2.5 for heat-transfer-dominated hydrate crystallizations.¹ The heat generated can be further expressed in terms of the propagation rate (dx/dt) and the enthalpy of hydrate crystallization (ΔH),

$$\left(\frac{dq}{dt}\right)_g = \frac{dm}{dt} \Delta H = \frac{dx}{dt} A \rho_H \Delta H \quad (S6)$$

where ρ_H is the hydrate density ($\sim 920 \text{ kg/m}^3$), and ΔH is 436.5 kJ/kg .² Equation (S6) implies the relationship between the heat required and propagation rate of methane hydrate. Based on our conditions, an order of magnitude smaller propagation rate (minimum $3.1 \text{ }\mu\text{m/s}$) was observed than propagation rate in previous work (minimum $21 \text{ }\mu\text{m/s}$).³ The rate of heat added or removed by conduction from the microreactor indeed is proportional to the temperature gradient (i.e., the driving force). It is important to note that we examined sub-cooling temperatures on the order of 1 K whereas previous works have focused primarily on sub-cooling on the order of 10 K. Thus, the present work examines conditions where methane hydrates form even when the rate of heat removed from the system is an order of magnitude less than conventional experiments designed to study hydrates. The thermal conductivity of our silicon reactor is also 1 to 2 orders of magnitude larger than the thermal conductivities of reactor materials (e.g., glass and stainless steel) used previously to study hydrates. Upon substitution of equation (S5) into (S6), one can obtain the propagation rate when heat transfer controls crystal growth,

$$\frac{dx}{dt} = \frac{h'(T_{eq} - T_b)^n}{\rho_H \Delta H} \quad (S7)$$

Derivation of propagation rate and mixed mass-transfer-crystallization

The mixed mass-transfer-crystallization limited rate for first order kinetics is expressed by the rate of methane consumption,

$$r_c = k_{eff} a C_m \quad (S8)$$

where C_m is the concentration of methane at the interface, k_{eff} is the effective specific crystallization rate, and a is the interface area per unit volume. The rate of methane hydrate formation, $(dm/dt)_g$, can be expressed in terms of propagation rate (dx/dt) ,

$$\left(\frac{dm}{dt}\right)_g = \frac{dx}{dt} a \rho_H \quad (S9)$$

Performing a mass balance on methane yields the relationship between the methane consumption rate and the methane hydrate formation rate,

$$\frac{r_c M_{CH_4}}{\omega_{CH_4}} = \left(\frac{dm}{dt}\right)_g \quad (S10)$$

where ω_{CH_4} is the weight fraction of methane in the hydrate (~ 0.13), and M_{CH_4} is the molecular weight of methane (0.016 kg/mol). Combining equations (S8), (S9), and (S10) gives the propagation rate when mixed mass-transfer-crystallization kinetics control the crystal growth:

$$\frac{dx}{dt} = k_{eff} \left(\frac{M_{CH_4}}{\omega_{CH_4} \rho_H} \right) C_m = \left(\frac{k' k_c}{k' + k_c} \right) \left(\frac{M_{CH_4}}{\omega_{CH_4} \rho_H} \right) C_m \quad (S11)$$

Derivation of dimensionless quantities

$$M_H = \sqrt{\frac{\text{maximum reaction rate}}{\text{maximum mass diffusion rate}}} = \sqrt{\frac{k' C_m}{\frac{D}{\delta_s} C_m}} = \sqrt{\frac{k'}{k_c}} \quad (S8)$$

$$\beta_B = \frac{\text{heat generated rate}}{\text{heat remove rate}} = \frac{r_i \Delta H}{r_h} = \frac{k' A C_m M_{CH_4} \Delta H}{h' A (T_{eq} - T_b)^n} = \frac{k' C_m M_{CH_4} \Delta H}{\omega_{CH_4} h' (T_{eq} - T_b)^n} \quad (S9)$$

$$Le = \frac{\text{thermal diffusivity}}{\text{mass diffusivity}} = \frac{\kappa}{\rho D c_p} \quad (S10)$$

where κ is the thermal conductivity of water (0.58 W/m·K), ρ is the water density (1.00×10^3 kg/m³) and c_p is the specific heat of water (4.18×10^3 J/kg·K).⁴ And the values of κ , ρ and c_p are assumed to be constant in the range of experimental conditions.

Reference:

- 1 J. Mullin, *Crystallization, 4th Ed.*, 2001.
- 2 E. D. Sloan and A. C. Koh, *Clathrate Hydrates of Natural Gases, 3rd Ed.*, 2007.
- 3 E. M. Freer, M. Sami Selim and E. Dendy Sloan Jr, *Fluid Phase Equilib.*, 2001, **185**, 65–75.
- 4 *NIST Stand. Ref. Databse #69*.