Supporting Information

Aluminum-Based Promotion of Nucleation of Carbon Dioxide Hydrates

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S.1 Images of experimental setup





Figure S.1. Images of the experimental setup.

S.2 Details of the experimental procedure

All the metallic surfaces (Al, Cu and SS) had a polished mirror-like texture to minimize the influence of surface roughness on nucleation promotion. The rms value of the surface roughness for Al, Cu and SS plates were 40, 49 and 61 nm respectively (surface roughness profiles provided in S.3). The rectangular surfaces had a dimension of 4.5×3 cm. New surfaces were used for every experiment with the protective covering on the surface peeled off just before the experiment to ensure minimal oxidation/contamination. The metal surfaces were rinsed with isopropanol (IPA) and DI water, and then dried with N₂ gas. Droplets were dispensed with a micropipette at a sufficient distance from each other (a minimum distance of 10 mm) to ensure that a nucleating droplet did not influence its neighbors.

The surfaces were placed inside the pressure vessel and purged with CO₂ gas for about 60 seconds. The pressure vessel was then cooled to a temperature of 20 °C followed by CO₂ pressurization to 3 MPa. Droplets were allowed to stay in the CO₂ environment for 90 minutes. After this, the chamber was isochorically cooled down to 0.5 °C to bring the p-T conditions into the hydrate stability region. Visualization was turned on, and hydrate nucleation and growth was recorded. All experiments were stopped after all droplets had nucleated or after a duration of 24 hours.

S.3 Surface roughness profiles for metallic plates used in the present study

Mirror-like polished surfaces were used for all the nucleation experiments. The surface roughness profiles for the metallic plates are provided below. The rms values of surface roughness for Al, Cu and T316SS surfaces are 40, 49 and 61 nm respectively.







Figure S.2. Surface roughness profiles for aluminum (top), copper (middle) and stainless steel (bottom) plates.

It is highlighted that no nucleation was observed on Cu and SS plates which had higher rms roughness than Al plates. The nucleation promotion associated with the Al surface can therefore be ascribed to Al-water reactions with surface roughness-related effects playing a secondary role.

S.4 Confirmation of the stochastic nature of nucleation in our experiments

The below figure shows the nucleation order of the droplets on three plates for two experiments (with 40 μ L and 20 μ L droplets). It is seen that the droplets nucleate randomly, and that a nucleating droplet does not influence its surrounding droplets.





Lower plate

Middle plate

Top plate

20 µL droplets



Lower plate

Middle plate

Top plate

Figure S.3. Nucleation order of the droplets for experiments employing 40 (top) and 20 (bottom) μ L droplets

The table below shows the induction time of 40 μ L droplets in the order in which they nucleated. The droplets show stochastic nucleation (as expected).

Droplet #	Induction time (mins.)
1	8.05
2	11.92
3	56.73
4	66.32
5	77.02
6	77.87
7	81.75
8	97
9	184.15
10	199.99
11	205.22
12	300.62
13	302.52
14	316.15
15	352.49
16	376.37
17	506.01

The table below shows the induction time of $20 \,\mu\text{L}$ droplets in the order in which they nucleated. The droplets show stochastic nucleation (as expected).

Droplet #	Induction time (mins.)
1	21
2	79
3	83.32
4	99.37
5	205
6	332
7	464.3
8	498.87
9	523

10	524.7
11	565
12	627
13	943.4
14	1062
15	1073

S.5 Comparison of droplet morphologies for different dissolution times of CO₂



t=0

t=8 mins

t=40 mins



Figure S.4. Droplet morphologies for a CO_2 dissolution time of 90 minutes (top) and 24 hours (bottom) for a droplet volume of 20 μ L.

Droplets (20 μ L) in the top and bottom rows are exposed to high-pressure CO₂ for 90 minutes and 24 hours respectively. Higher concentrations of dissolved CO₂ in the droplet in the bottom row lead to more vigorous growth characterized by whisker formation.

S.6 Calculation of nucleation rate

The nucleation probability (P) at a given subcooling ($\Delta T=T_{equilibrium}-T$) and pressure as per classical nucleation theory is estimated as:

$$P(t) = 1 - \exp(-Jt)$$

where, J is the nucleation rate, which can be obtained by fitting the above equation to the induction time data as obtained from experiments. The probability that a droplet will nucleate in time (t) will be the ratio of the total number of droplets nucleating before time t divided by the total number of droplets in the sample set. By dividing the entire duration into an equal number of time bins one can obtain the cumulative nucleation probability for successive times as depicted in the figure below for 3 different droplet volumes (10, 20 and 40 μ L).



Figure S.5. Cumulative probability distribution for 3 different droplet volumes (10, 20 and 40 μ L).

The solid lines represent the fitted equation with nucleation rates of 0.0018, 0.0032 and 0.0048 (min^{-1}) for droplet volumes of 10, 20 and 40 μ L, respectively.

S.7 Histograms showing fraction of droplets nucleating in different time intervals



Figure S.6. Fraction of 20 μL droplets nucleating in different time intervals (droplets contain 3.5





Figure S.7. Fraction of 20 μL droplets nucleating in different time intervals (24 hour CO₂ dissolution time).