Understanding the Kinetics of CO_2 Hydrate Formation in Dry Water for Carbon Capture and Storage: X-Ray Diffraction and In Situ Raman Studies

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Videos

Video S1- CO_2 hydrates morphology in pure water

Video S2- CO_2 hydrates morphology in dry water

Video S3- CO_2 hydrates morphology in dry water + 500 ppm L-trp

Video S4- CO_2 hydrates morphology in dry water + 1000 ppm L-trp
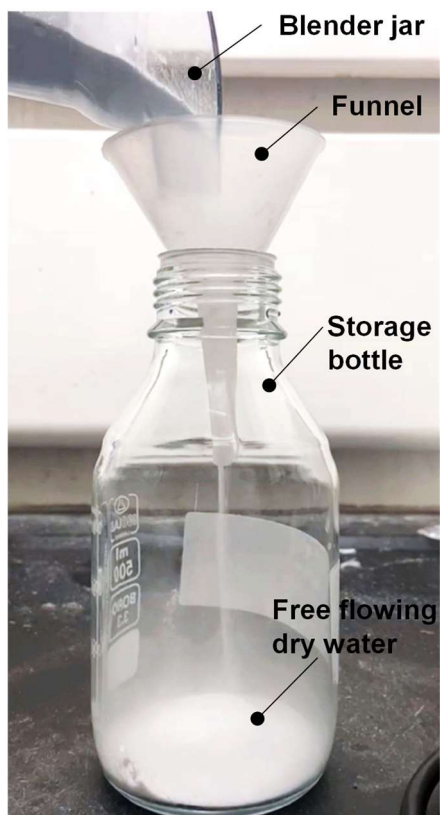
Supporting Information 1

Figure S1. Photograph showing the transfer of dry water (DW) from a blender jar to a storage bottle. DW was prepared by blending 95 g of deionized water with 5 g of nanosilica particles at ~24,000 rpm for 90 seconds (in three 30-second bursts). The resulting free-flowing white powder transferred easily without leaving residue.
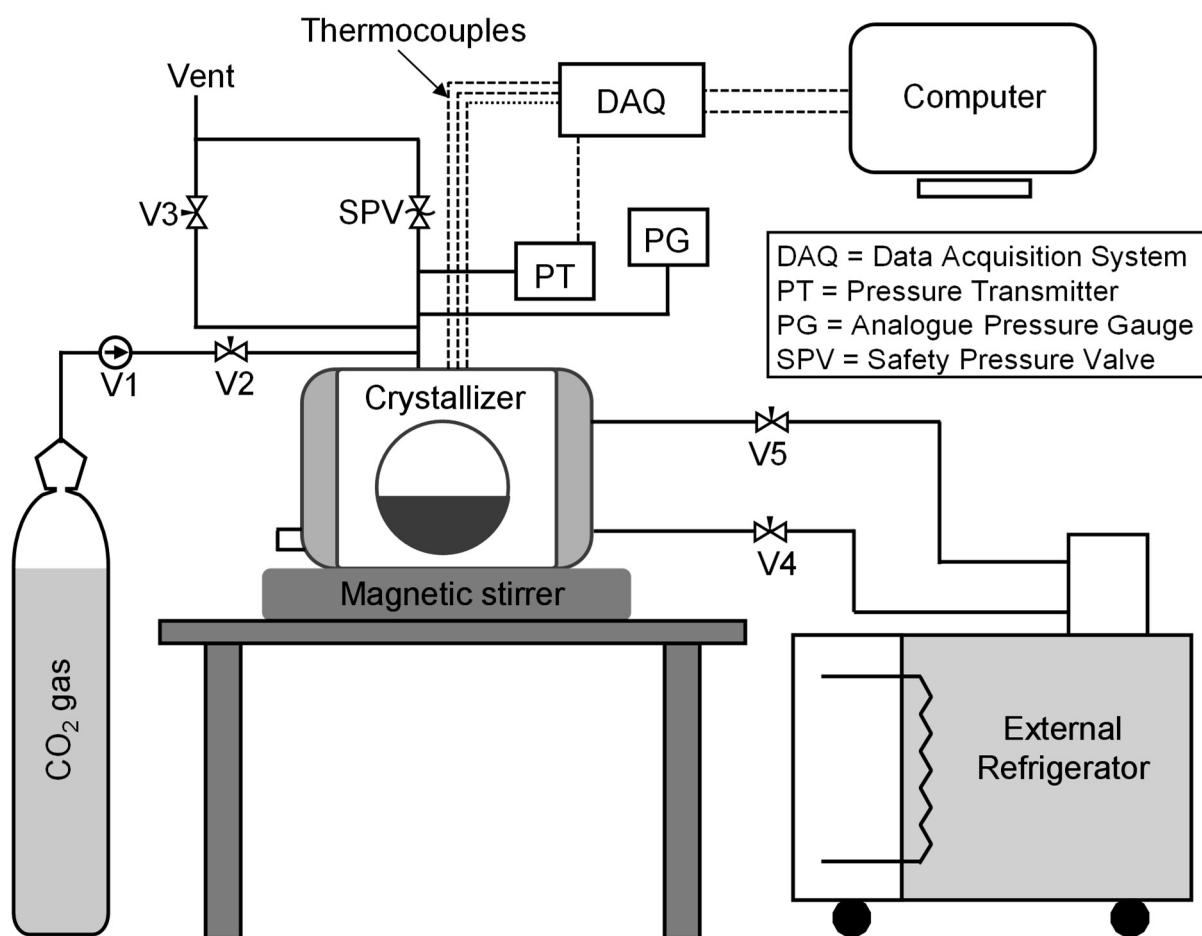
Supporting Information 2

Figure S2. Experimental setup for studying CO_2 hydrate formation kinetics and morphology, as well as for sample preparation for PXRD analysis. The setup includes a high-pressure crystallizer chamber, external refrigerator, gas inlet, and data acquisition system.
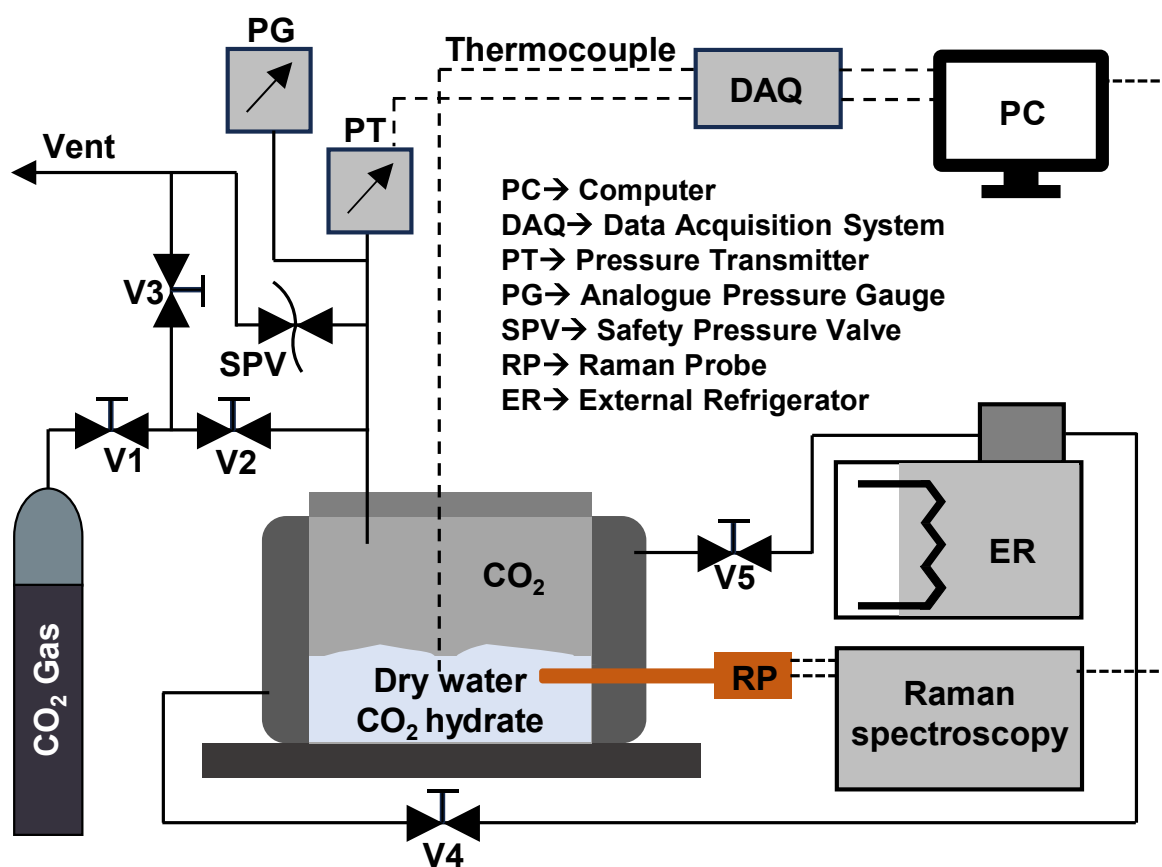
Supporting Information 3

Figure S3. Schematic of the in situ Raman setup coupled with high-pressure reactor. The setup consists of a high-pressure crystallizer chamber, Raman spectrometer, external refrigerator, gas inlet, and data acquisition systems.

Calculation of the Lattice Parameter of the CO_2 (sI) Hydrate Using the Observed PXRD Data

Two equations were employed to determine the lattice parameter (a) of DW-CO_2 (sI) hydrate. The procedure is outlined as follows:

Initially, eqn. (S1) utilizes Bragg's law to calculate "d," which denotes the interplanar spacing of the crystal:

$$n\lambda = 2d \sin\theta \qquad\qquad (S1)$$

Here, "λ" denotes the wavelength of the incident X-ray (1.542 Å in this case), and "θ" is the incident angle (the angle between the incident ray and the scattering plane) obtained from the PXRD peak position. "n" is set to 1 for the first order of diffraction.

Subsequently, the p-XRD pattern is indexed against the standard sI hydrate PXRD pattern.[1, 2] At least three peaks with known Miller Indices ("hkl") are selected. For cubic crystals, the interplanar spacing "d" between adjacent (hkl) lattice planes is described by eqn. (S2):

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \qquad\qquad (S2)$$

Given the other known parameters, solving eqn. (S2) yields the lattice parameter "a" for the cubic unit cell of the sI hydrate.
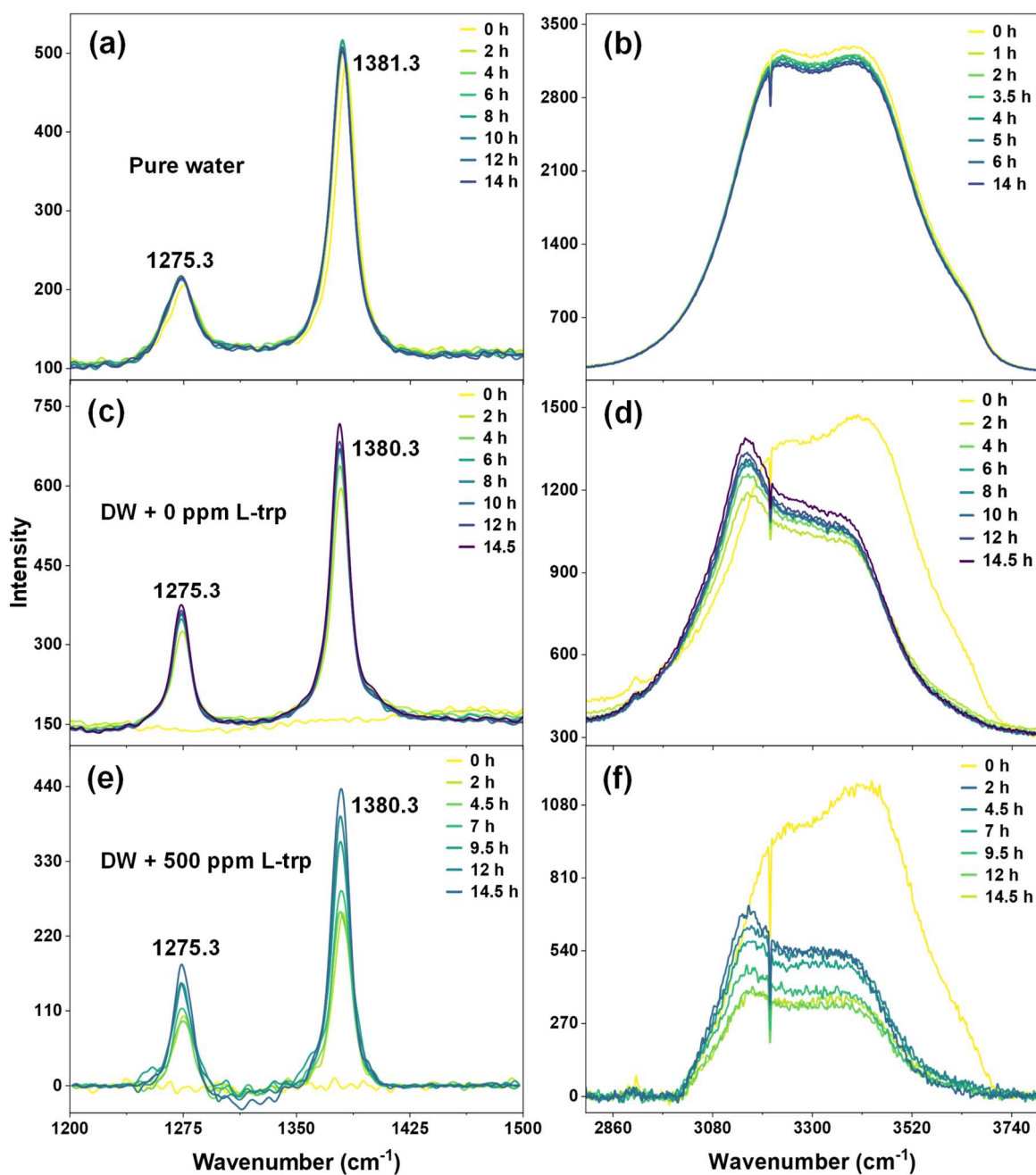
Supporting Information 4

Figure S4. Time-dependent in situ Raman spectra for CO_2 hydrate formation in (a, b) pure water, (c, d) DW, and (e, f) DW + 500 ppm L-trp. Here, the first and second columns present Raman spectra for the CO_2 Fermi dyad, and O-H stretching bands, respectively. In all cases, CO_2 hydrate formation was achieved at 3.5 MPa and 274.65 K. While the presence of two Fermi dyad peaks at ~1380.3 and 1275.3 cm^{-1} confirms the formation of CO_2 hydrates, the O-H stretching suggests that the water molecules are forming the hydrate cages.
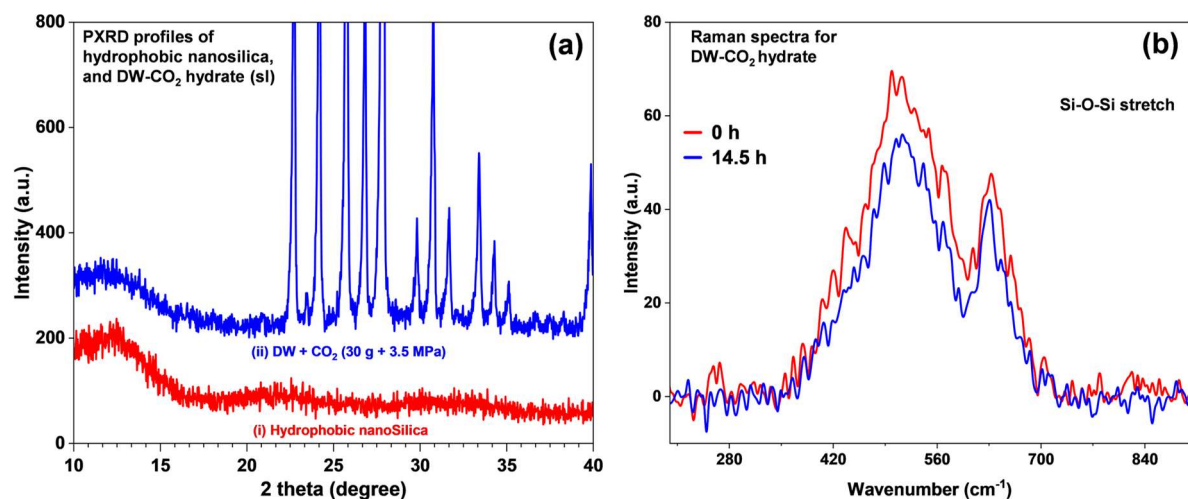
Supporting Information 5

Figure S5. (a) PXRD pattern of the (i) hydrophobic nanosilica, and (ii) DW-CO_2 hydrate formed at 3.5 MPa and 274.65 K (initial conditions). A broad PXRD pattern in the 2θ range of 10-15° corresponding to silica particles can be seen in both systems. (b) In situ Raman spectra before and after DW-CO_2 hydrate formation in the Si-O-Si stretching region of silica. The reduced peak intensity after hydrate formation suggests that a small fraction of CO_2 hydrates formed above the silica shell.
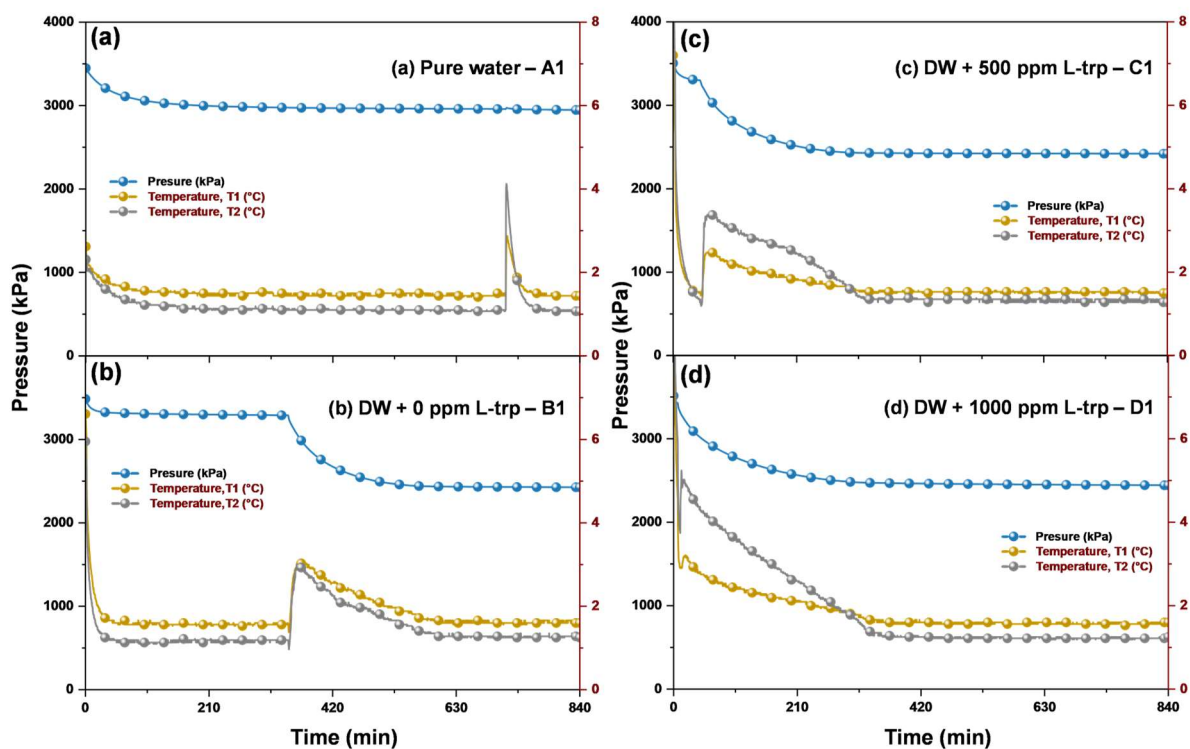
Supporting Information 6

Figure S6. Changes in the *P-T* with respect to time during CO_2 hydrate formation in (a) pure water, (b) DW without L-trp, (c) DW with 500 ppm L-trp, and (d) DW with 100 ppm L-trp at 3.5 MPa. The onset of hydrate formation is realized by observing a sudden drop in pressure and an increase in temperature.

References

(1) Kumar, A.; Daraboina, N.; Linga, P.; Kumar, R.; Ripmeester, J. A. Experimental study on hydrate structure transition using an in situ high-pressure powder X-ray diffractometer: application in CO_2 capture. *ACS Sustainable Chemistry & Engineering* **2022**, *10* (35), 11473-11482.

(2) Jin, Y.; Kida, M.; Nagao, J. Clathrate Hydrates Coexisting Thiazole: Two Roles of Structure II Hydrate Former and Structure I Thermodynamic Inhibitor. *Energy & Fuels* **2023**, *37* (3), 2467-2474.