Supplementary information for

Incorporation of ammonium fluoride into clathrate hydrate lattice and its significance for inhibiting hydrate formation

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S1. Experimental Method

<u>Materials</u>

CH₄ of 99.95 mol % purity was purchased from the Special Gas Company (Daejeon, Korea). High purity distilled water was obtained from a Millipore purification unit. Ammonium fluoride (\geq 99.99% trace metals basis) was purchased from Aldrich. Methanol (anhydrous, 99.8%), which showed the best performance among thermodynamic hydrate inhibitor, was purchased from Sigma-Aldrich, Inc.

Apparatus and procedure

Two types of experiments were performed, i.e., non-isothermal and isothermal. To determine the equilibrium condition of clathrate hydrate, the non-isothermal method was implemented using an impeller-type stirring cell. The thermal cycle includes the following two steps: a cooling step, in which the system temperature is decreased from 288.0 K to a temperature below the hydrate formation, ranging from 253.0 K to 268.0 K (1.0 K/h), and a heating step, in which the system temperature is brought back to the initial temperature (0.1 K/h). A four-wire-type PT-100 Ω (±0.05% accuracy of full scale) and a PMP4070 device from Druck Inc. were used as temperature and pressure sensing devices, respectively.

The isothermal method is used to measure the kinetics of CH_4 hydrate formation with and without NH_4F .¹ Aqueous solutions of 30 ml containing the NH_4F were charged in a highpressure cell with a volume of 100 ml. The temperature of the cooling bath was adjusted to 2.0 K above the hydrate equilibrium temperature. The cell was then loaded with CH_4 gas to a pressure of about 9.11 MPa while stirring at 300 rpm, although the experimental setting pressure was 9.0 MPa. This is because the cooling bath temperature was a little bit higher than equilibrium temperature prior to the beginning of the experiment. When the temperature and pressure were kept constant, the stirring was stopped and the cell was cooled to the experimental temperature (subcooling $\Delta T = 10.0$ K). When the temperature and pressure in the cell had stabilized, the stirring was restarted. The pressure and temperature of the high-pressure cell were measured throughout the whole experiment, and a sudden pressure drop was detected when gas hydrate formation occurred.

Microscopic analysis

The hydrate samples were synthesized from aqueous NH_4F solutions of various concentrations slowly frozen at 200 K. The frozen solutions were ground into fine powders with a 200 µm sieve in liquid nitrogen. Then, a powdered sample was placed in a high-pressure cell and pressurized with CH_4 gas up to 10.0 MPa at 243 K. The high-pressure cell was stored at 243 K for 5 days. After synthesis of the hydrate samples, the high-pressure cell was cooled down to liquid nitrogen temperature, and the pressure was slowly released. The powder samples then were collected and stored in liquid nitrogen.

The high-resolution powder diffraction (HRPD) patterns of the samples were recorded at 80 K using the Pohang Synchrotron of the Pohang accelerator laboratory ($\lambda = 1.46470$ Å) in the $\theta / 2\theta$ scan mode. The experiments were carried out in step mode with a fixed time of 4 s and at a step size of 0.005° for $2\theta = 5.0^{\circ}$ to 145.5°. The obtained patterns were indexed using the Checkcell program.² A Varian (Agilent VNMRS600) 600-MHz solid-state NMR spectrometer was used. The powdered (~200µm) samples were placed in a 4.0 mm o.d. zirconia rotor loaded into a variable temperature probe. All ¹³C NMR spectra were recorded at a Larmor frequency of 150.9 MHz with MAS at about 5 kHz, and the measurement temperature was fixed at 203 K. A pulse length of 5 µs and a pulse repetition delay of 10 s under proton decoupling were used with a radio-frequency field strength of 50 kHz, corresponding to a 5 µs 90° pulse. The downfield carbon resonance peak of hexamethyl benzene (HMB), assigned a chemical shift of 17.3 ppm at 298 K was used as an external

chemical shift reference. To obtain CH_4 signals of a higher intensity, a gaseous mixture of ${}^{13}CH_4$ and ${}^{12}CH_4$ was used. For Raman measurements, a Horiba Jobin-Yvon LabRAM HR UV/Vis/NIR high-resolution dispersive Raman microscope equipped with an electrically cooled (203 K) CCD detector was used. It was cooled by liquid nitrogen. The samples were kept at 93.0 K during the measurements. The excitation source was an Ar-ion laser emitting a 514.53 nm line. The laser intensity was typically 30 mW.

Reference

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NH ₄ F concentration.	

Conc. of NH ₄ F	$A_{L,CH4}\!/A_{S,CH4}$	$\theta_{L,CH4}\!/\theta_{S,CH4}$
0 mol%	3.32	1.11
5 mol%	3.72	1.24
10 mol%	3.91	1.30
15 mol%	4.26	1.42