Supporting Information

Kinetics of Methane Hydrate Replacement with Carbon Dioxide and Nitrogen Gas Mixture using *in-situ* NMR Spectroscopy

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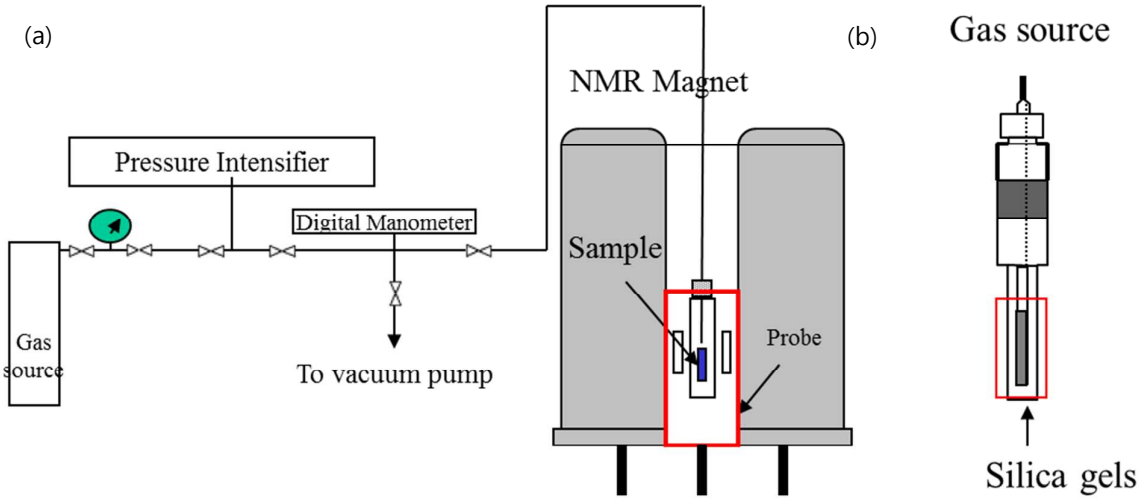

Figure S1. (a) NMR spectrometer coupled with gas handling system and (b) high pressure cell for spectroscopic experiments.

Experiments with NMR spectrometer

(NMR Spectrometer) All experiments were performed on a Bruker DSX-400 instrument (magnetic field 9.4 T, proton resonance frequency 400.1 MHz and 100.6 MHz for ^{1}H and ^{13}C, respectively). All measurements used a single pulse acquisition program with a spectral width of 150 KHz and $\pi/2$ pulse of 6 μs.

(High pressure cell) Figure S1 shows the schematic diagram of the gas handling system connected to the NMR spectrometer. The detection cell of the probe was custom-built around 7 mm O.D. ZrO_2 cell, which is suitable for in-situ measurement with vertical orientation of the magnet. The cell is connected to a gas handling system, which is shown in Figure S1 (a) and (b), and is capable of withstanding pressures up to 20 MPa. It equipped with a built-in valve and can be separated from the gas lines without depressurization and therefore is convenient for use in a conventional vertical-bore NMR magnet. During the experiments, the temperature was controlled using a Bruker BVT3000 temperature control unit.

(Experimental procedures) Methane hydrate was formed in silica gel pores at 276 K and 140 bar for one day. After confirming the formation of methane hydrate, methane gas was removed under vacuum and a CO_2/N_2 gas mixture was charged into the cell to a pressure of 100 bar with the gas handling system. ^{1}H NMR spectra were recorded to follow the

replacement reaction and to observe the possible occurrence of a free water phase. In addition, ^{13}C NMR spectra were obtained to observe the changes of the methane resonance intensity, indicating the number of methane molecules in cages of the hydrate structure as a function of time. Both ^{1}H NMR and ^{13}C NMR spectra for the replacement reaction are collected at 273 K.

Each experiment followed a six-step procedure:

1. The cell was loaded with 0.5 cm^3 of silica gel particles saturated with UHP water.
2. The vapor space was purged three times with methane, after which the cell was pressurized to the target of 140 bar at 276K.
3. Methane hydrate formation process was monitored with ^{1}H NMR spectra for one day, which showed intensity decrease due to conversion of water to hydrate.
4. Methane gas in vapor phase was removed under vacuum and then N2/CO2 gas mixture was introduced until the pressure reached 100 bar using the gas handling system. The pressure gauge was used to measure the pressure of the cell and the gas handling system.
5. ^{1}H NMR spectra was recorded for 4000 min to follow the replacement process of methane in hydrate cages. The intensity of methane in hydrate cages decreased as the replaced methane evacuated to vapor phase.
6. Same experiment was carried out again to monitor 1H NMR spectra. Then two more experiments were repeated to record 13C NMR spectra during the replacement process.

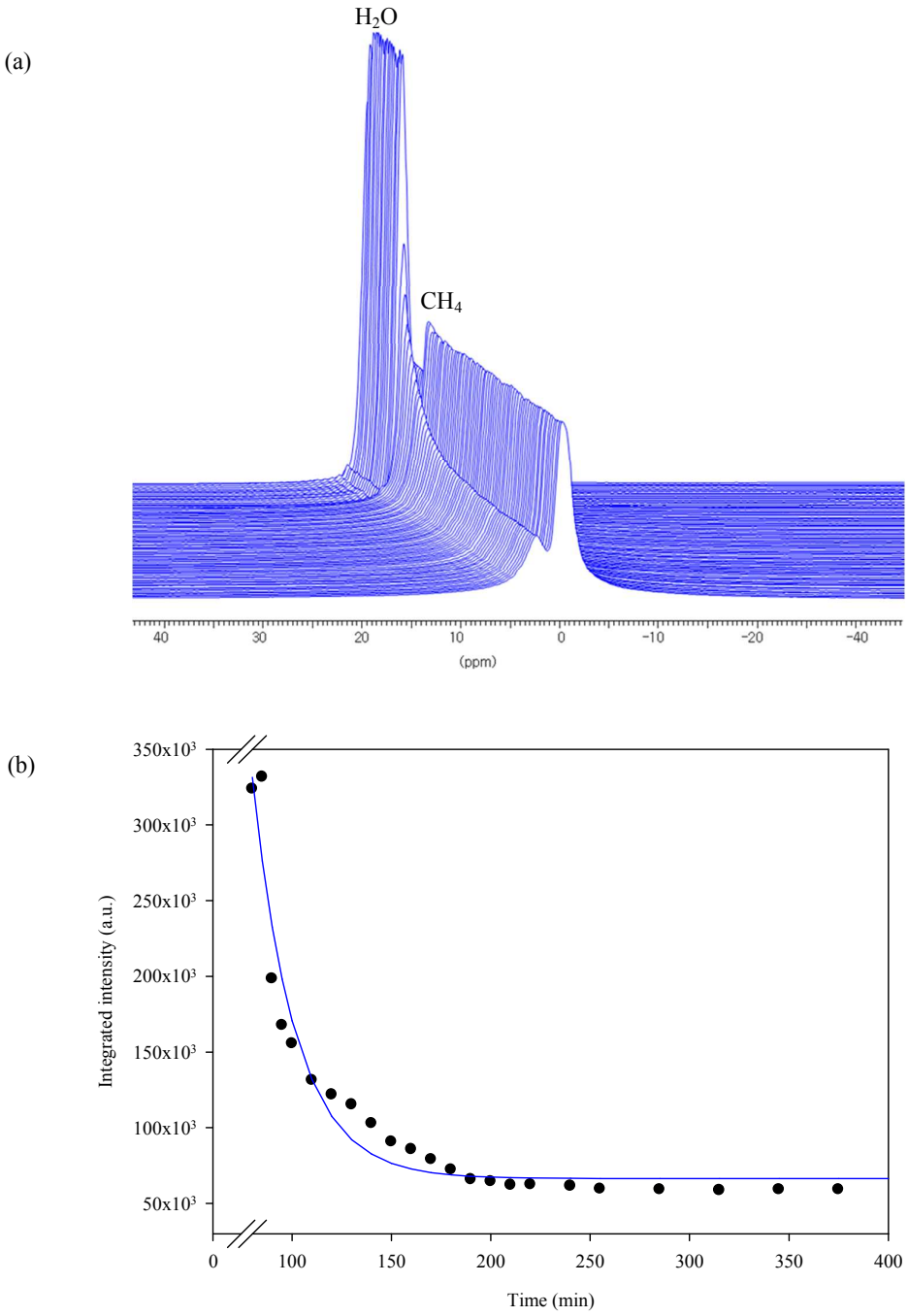

Figure S2. (a) ^{1}H NMR spectra in 15 nm silica gel at 276K and 140 bar and (b) the integrated intensity of the resonance of free water as a function of time.

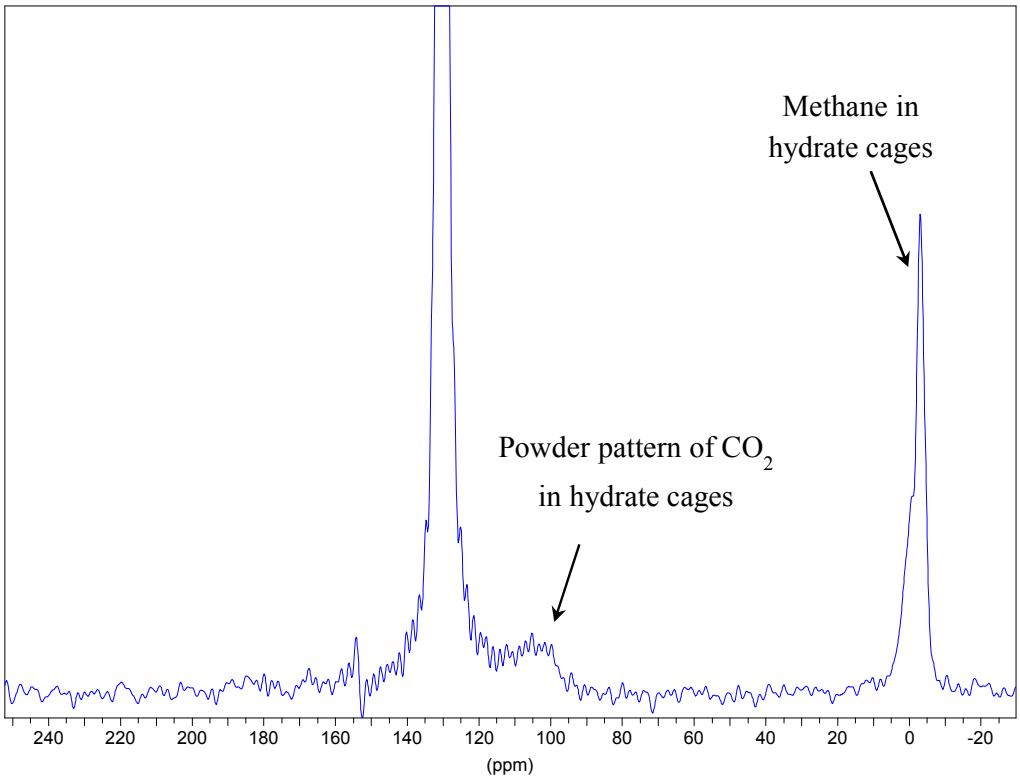

Figure S3. Full range spectra of ^{13}C NMR spectra after the replacement reaction is finished with 20 mol% of CO_2 and balance N_2 gas mixture at 273 K and 100 bar. (Final time = 980 min)

Table S1. Composition of vapor and hydrate phases when CH_4 hydrate in silica gel is exposed to 20mol% of CO_2 and balanced N_2 gas mixture at 273 K and 100 bar.

Pore size of silica gel. (nm)	Vapor phase concentration (mol%)			Hydrate phase concentration (mol%)		
	N_2	CO_2	CH_4	N_2	CO_2	CH_4
30	63	10	27	26	37	37
15	69	10	21	23	24	53
6	68	9	23	24	21	55

Table S2. Composition of vapor and hydrate phases when CH_4 hydrate in silica gel is exposed to 40mol% of CO_2 and balanced N_2 gas mixture at 273 K and 100 bar.

Pore size of silica gel. (nm)	Vapor phase concentration (mol%)			Hydrate phase concentration (mol%)		
	N_2	CO_2	CH_4	N_2	CO_2	CH_4
30	52	20	28	15	45	40
15	53	20	27	14	36	50
6	56	19	25	10	35	55