CH_4 from Methane Hydrate

Recovering Methane from Solid Methane Hydrate with Carbon Dioxide**

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The discovery of vast hydrocarbon resources in hydrate form on the continental margins and in permafrost regions has sparked an interest in the possible recovery of relatively clean-burning methane gas,[1] especially in resource-poor national economies. At the same time, it has been proposed that CO_2, obtained as a by-product of combustion processes, possibly could be stored either in the deep ocean as liquid, or as a solid hydrate,[2] in order to reduce the release of greenhouse gas into the atmosphere. As such, the conversion of methane hydrate to CO_2 hydrate with the net recovery of methane seems quite attractive.[3] The limiting equilibrium composition of the mixed hydrate and the kinetics of conversion then become of primary interest in assessing this potential technology. In this communication we address these various issues, which have been considered so far only from a macroscopic point of view, by following not only kinetics, but also the distribution of guests over different cages using solid-state NMR methods. This combined approach allows the derivation of thermodynamic and kinetic information and also gives a molecular-level rationale for the observations; thus it is a powerful way of studying solid-state reactions.

Both CO_2 and CH_4 form a structure I (sI) hydrate,[4] as do mixtures of these gases,[5] with an icelike framework that consists of hydrogen-bonded water molecules. It has eight cagelike guest sites in the unit cell, including two pentagonal dodecahedra (5^{12}) and six tetrakaidecahedra ($5^{12}6^2$) consisting of 12 pentagonal and two hexagonal faces. The ideal unit cell can be written as $2\,M_S{\cdot}6\,M_L{\cdot}46\,H_2O$ with an ideal hydration number $M{\cdot}5^3\!/_4H_2O$ if a single type of guest is present. However, sI hydrates are non-stoichiometric, and the actual hydration numbers usually lie somewhere between 6 and 8.[4] The latter can be measured by the careful application of direct methods,[6] and also from cage occupancies obtained from structures derived by single crystal X-ray diffraction,[7] or from spectroscopy[8] where the cage occupancy ratio can be linked to the hydration number by using the van der Waals–Platteeuw,[9] or related, models.

To observe favorable exchange between CO_2 and methane hydrate, there must be preferential partitioning of CO_2 and CH_4 between the gas and the hydrate solid phases. The only way this can arise is if CO_2 has a preference for the large cage ($5^{12}6^2$) in the hydrate, as the larger cages outnumber the smaller by a factor of three. This premise was investigated by examining the distribution of methane over the two cage sites by MAS ^{13}C NMR for hydrate samples prepared from gas mixtures (Figure 1). One can see that for pure methane hydrate $\theta_{L,CH_4}/\theta_{S,CH_4}$ is ≈ 1.26, so that the small cage is occupied to a smaller degree than the larger cage, as reported before for synthetic and natural methane hydrates.[8,10] With increasing CO_2 in the gas mixture, the ratio declines steadily to a value that shows that now fewer than half as many large as small cages are filled with methane. This behavior can be explained in terms of the molecular sizes of CO_2 and CH_4. The size of CO_2 is almost the same as the cavity diameter of the small 5^{12} cage in the sI hydrate, the molecular diameter to cavity diameter ratio being 1.00 for CO_2 and 0.855 for CH_4. For CO_2 hydrate, NMR and diffraction techniques have

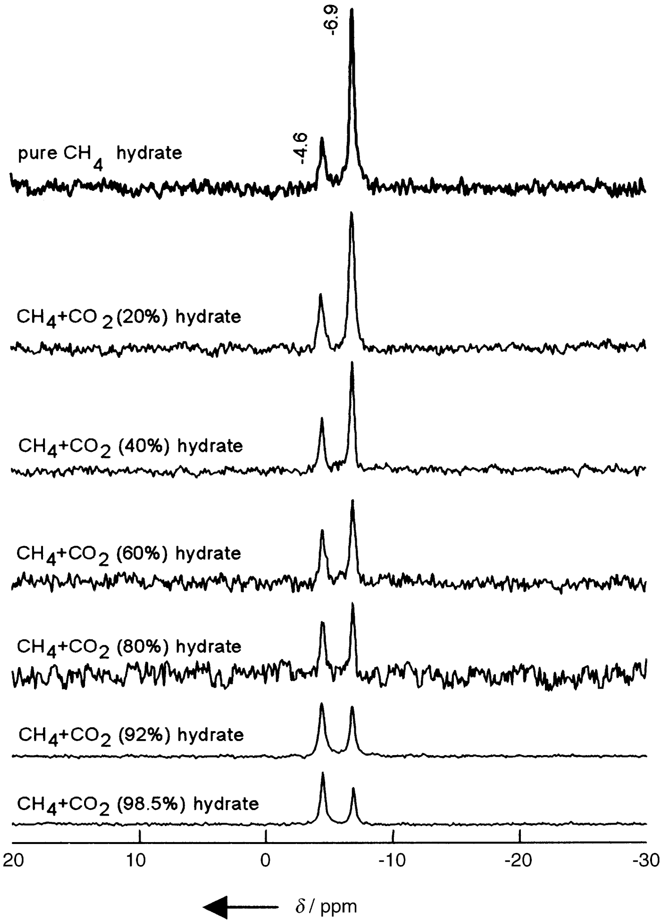

Figure 1. ^{13}C HPDEC MAS NMR spectra of an sI hydrate prepared using CH_4/CO_2 mixtures with compositions as indicated.

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indicated that the 5^{12} cages have smaller fractional occupancies than the large cages. Hydration numbers of ≈6.0 for methane and 6.2 for CO_2 hydrate are consistent with fractional occupancies of the small cages θ_S of ≈0.8 and ≈0.7, respectively. Thus, when CO_2 competes with CH_4 in occupying the small cage of the sI hydrate, CO_2 is a relatively poorer guest, so that the occupancy ratio for CH_4 ($\theta_{L,CH_4}/\theta_{S,CH_4}$) becomes lower at higher CO_2 compositions because CO_2 preferentially occupies the large $5^{12}6^2$ cage in the mixed CH_4/CO_2 hydrate. Another aspect to be noted is that the equilibrium occupancy ratios ranged from 1.26 (100% CH_4) to 0.23 (very dilute CH_4). Thus when the CH_4 concentration becomes infinitely dilute, the value of 0.23 for $\theta_{L,CH_4}/\theta_{S,CH_4}$ shows that there is a limit to the degree of substitution that one can expect under equilibrium conditions, even when the gas composition approaches 100% CO_2. A second plot (Figure 2) shows the composition of the hydrate as a function of the corresponding gas composition at equilibrium. Considerable enrichment in CO_2 of the hydrate with respect to the gas occurs for concentrations between ≈10 and 70% CO_2. When considering the data in Figure 1 and Figure 2, along with some assumptions,[11] a limiting composition of the mixed hydrate can be estimated showing that at least 64% of methane should be recoverable from a hydrate of composition $CH_4 \cdot 6.05\,H_2O$, which after reaction with CO_2 gives a product hydrate with a CO_2/CH_4 ratio of 1.8 or greater.

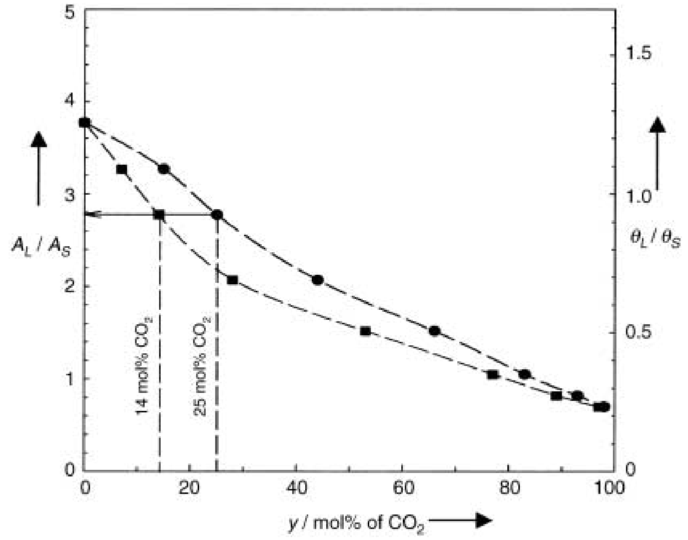

Figure 2. Equilibrium composition of the sI hydrate as a function of the composition of the source gas in mol% CO_2. The circles show the hydrate phase composition at the corresponding vapor phase composition of the source gas, as represented by squares. A_L/A_S is the intensity ratio of the ^{13}C MAS NMR resonance lines of methane molecules in large and small cages. θ_L/θ_S is the occupancy ratio of methane molecules in large and small cages, as calculated from the intensity ratio.

The kinetics of transformation are also a key element in considering the feasibility of the gas-replacement reaction. First of all we follow the reaction of CO_2 with powdered ice by measuring the intensity of the ^{13}C CO_2 powder pattern as a function of time. This reaction is remarkably slow at 268 K, with the reaction incomplete after 30 h (rate $k_1 \approx 0.0026$ min^{-1} at 268 K, $k_1 \approx 0.0025$ min^{-1} at 270 K, $P = 58$ bar).[12] Similarly, the reaction of methane with powdered ice is very slow (rate $k_1 \approx 0.0009$ min^{-1} at 270 K, $P = 215$ bar). On the other hand, when methane hydrate is exposed to CO_2 gas, the guest replacement reaction appears to be complete in less than 5 h (rate $k_1 \approx 0.01$ min^{-1} at 270 K). The amount of methane obtained from the reaction is about half of the total methane present in the initial hydrate (Figure 3), which indicates that the product is a hydrate with a CO_2/methane ratio of ≈1. This suggests that the conversion is limited by considerations other than thermodynamics, as this predicted a product with a CO_2/methane ratio of ≈1.8.[11] It is likely that sample morphology plays an important part, where the conversion reaction proceeds so as to isolate volumes of pure methane hydrate surrounded by the converted hydrate. Sample grinding clearly would allow the reaction to proceed to equilibrium rather than to the pseudo-equilibrium state observed in this study.

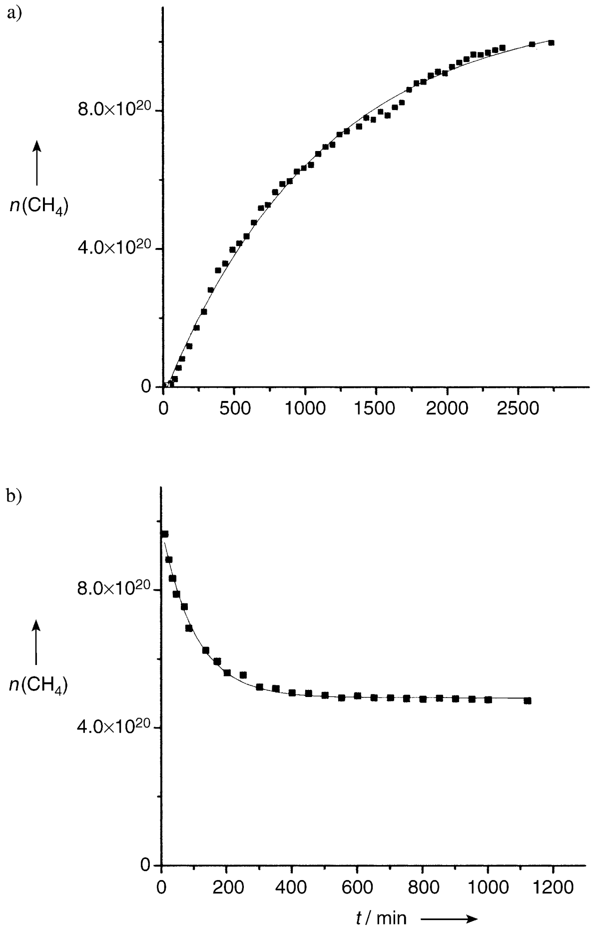

Figure 3. Formation and conversion of sI methane hydrate: a) Integrated intensity of the ^1H NMR signal during formation of sI methane hydrate from CH_4 and powdered ice (268 K, 215 bar). The solid line represents an exponential fit with a rate constant of 9×10^{-4} min^{-1}; b) conversion of the sI methane hydrate with CO_2, as obtained from the integrated ^{13}C powder-pattern intensity due to CO_2 in the large cage of sI hydrate (60 bar $^{13}CO_2$ at 270 K). The solid line is an exponential fit with a rate constant of 0.97×10^{-2} min^{-1}.

We note that the reaction of CO_2 hydrate with methane, on the other hand, is again very slow (Figure 4), with a steady state established after ≈ 60 h. We note that this experiment reports only the replacement of CO_2 in the large cages, so that just over 10 % of the large cages in the product contain methane. The reaction of CO_2 with methane hydrate and the reverse reaction of methane with CO_2 hydrate are obviously completely different. One may argue that since CO_2 is a much better large-cage guest than methane, two factors that control the kinetics may be identified. From an equilibrium point of view, it appears that CO_2 should replace methane rather easily, but this requires the lattice to be disrupted completely, as it involves changing the guests in a majority of the $5^{12}6^2$ cages, which are the major constituents of the hydrate lattice. So, the process is likely to lead relatively easily to the pseudo-equilibrium composition, with the replacement of methane by CO_2 accomplished as the hydrate particles recrystallize from the outside in. On the other hand, CO_2 at the hydrate particle surface apparently is not easily replaced by methane, as it is the favored guest only in the small cages; only ≈ 10 % of the CO_2 in the large cages is replaced. The hydrate crystal likely remains largely intact, so that methane can only find its way to the interior sites by diffusing through a near-intact hydrate lattice; such a process must be very inefficient.

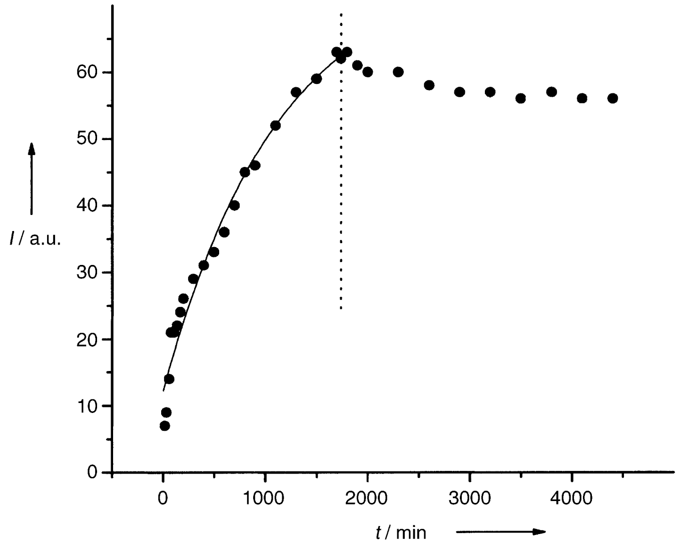

Figure 4. Intensity of the ^{13}C NMR signal due to CO_2 in the large cages of the sI hydrate shown as a function of time during the formation of sI CO_2 hydrate (on the left side of the dotted vertical line; $T = 268$ K, $P = 58$ bar) and after exposure of the material to CH_4 (152 bar; points on the right side of the dotted line).

The results presented here show that, at least in a laboratory setting, the replacement of CH_4 by CO_2 is favored both from the points of view of equilibrium thermodynamics and kinetics. Reaction rates and the total yield of the replacement reaction in actual natural gas hydrate deposits will depend on a variety of factors, such as the degree of hydrate dispersion in sediment, hydrate particle size[12], and gas transport.

Experimental Section

For composition studies, pure and mixed-phase hydrates were prepared in porous silica gel (Aldrich, pore size = 15 nm) to facilitate the rapid equilibration of hydrates. ^{13}C NMR spectra were recorded at 200 K by placing the hydrate samples in a 4-mm diameter Zr-rotor that was loaded into the variable-temperature (VT) probe on a Bruker 400 MHz solid-state NMR spectrometer. All spectra were recorded at a Larmor frequency of 100.6 MHz with magic-angle spinning (MAS) at about 2–4 kHz under high-power proton decoupling (HPDEC). A pulse length of 2 μs and pulse repetition delay of 20 s with radio-frequency field strengths of 50 kHz corresponding to 90° pulses of 5 μs duration were used. The downfield carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference. For the mixed hydrate samples of CO_2 compositions over 80 mol %, $^{13}CH_4$ gas was used to obtain higher intensity CH_4 peaks.

Kinetic studies of the reaction of powdered solids (deuterated ice or hydrate, particle size 5–50 μm) with gases were carried out in a high-pressure NMR cell connected to a gas handling system. For CO_2, the reactions were followed by measuring the integrated ^{13}C powder pattern, characteristic of the guest in the large cage of the sI hydrate, as a function of time. The variation of methane content in the hydrate with time was obtained from the integrated ^{1}H NMR signal. The absolute amount of product was obtained by comparing the signal with that of known samples.

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[11] For sI hydrates of a single guest component, the large cage occupancies are essentially indistinguishable from 1, thus $\theta_L = 1$, giving $\theta_S = 0.8$, and a hydration number of 6.05, well within the range of measured values. Therefore, in a mixed hydrate, θ_S for

methane will never be greater than 0.8, the value for the pure hydrate, thus giving a maximum of 1.6 small cages per unit cell of methane. Since θ_L/θ_S is 0.23, then there will be at most 1.12 large cages per unit cell filled with methane, which leaves 4.88 large cages filled with CO_2. So the limiting composition for the mixed hydrate is $4.9\,CO_2 \cdot 2.7\,CH_4 \cdot 46\,H_2O$. If we assume that this represents the minimum amount of CO_2 in the mixed hydrate at equilibrium, the minimum expected recovery level for methane is 64%.

[12] The kinetics of conversion can be described roughly as exponential, and does not have significant pressure dependence in the range of pressures used. On the other hand, the ice-particle size has a profound effect on the conversion rate. When the experiments on ice to CO_2 hydrate conversion were performed at the same pressure and temperature but with ≈ 0.1 mm rather than 50 μm particles, the conversion rate dropped by nearly a factor of three. Our preliminary measurements indicate that the substitution rate of methane with carbon dioxide has only a small dependence on the pressure of CO_2, as long as it is kept above the pressure of CO_2 hydrate formation at a given temperature.