

Article

Raman Spectroscopic Observations on the Structural Characteristics and Dissociation Behavior of Methane Hydrate Synthesized in Silica Sands with Various Sizes

Changling Liu, Hailong Lu, Yuguang Ye, John A. Ripmeester, and Xunhua Zhang

Energy Fuels, **2008**, 22 (6), 3986-3988 • Publication Date (Web): 10 September 2008

Downloaded from <http://pubs.acs.org> on November 24, 2008

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
High quality. High impact.

Energy & Fuels is published by the American Chemical Society, 1155 Sixteenth Street N.W., Washington, DC 20036

Raman Spectroscopic Observations on the Structural Characteristics and Dissociation Behavior of Methane Hydrate Synthesized in Silica Sands with Various Sizes

Changling Liu,^{*,†} Hailong Lu,[‡] Yuguang Ye,[†] John A. Ripmeester,[‡] and Xunhua Zhang[†]

Qingdao Institute of Marine Geology, Qingdao 266071, China, and The Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario K1A 0R6, Canada

Received June 8, 2008. Revised Manuscript Received August 10, 2008

Raman spectroscopic observations of the characteristics and dissociation of methane hydrate were carried out on hydrates synthesized in silica sands with particle sizes of 53–75, 90–106, 106–150, and 150–180 μm . The results obtained indicate that methane hydrates formed in silica sands had similar characteristics regarding cage occupancy and hydration number (5.99) to bulk hydrate, indicative of no influence of the particle size on hydrate composition. During hydrate dissociation, the change in the average intensity ratio of large to small cages were generally consistent with that of bulk hydrate but dropped dramatically after a certain time, and this turning point seems to be related to the particle size of silica sands.

Introduction

Natural gas hydrate is often taken to be a potential energy source because of its huge amount available in nature.^{1,2} Considering the features of favorable gas hydrate reservoirs, it has been suggested that gas production from hydrate should be exploited by in situ hydrate dissociation.³ As a result, a full understanding of hydrate decomposition in a typical reservoir setting is particularly important. The dissociation rate, which depends upon T – P and other environmental conditions, is an essential parameter for evaluating the efficiency of gas recovery from hydrate in sediment. A number of studies^{4–6} have reported the dissociation rate during depressurization and thermal stimulation. However, studies of the dissociation rate by conventional methods cannot yield information on the mechanism of hydrate dissociation. To investigate the dissociation mechanism, some researchers have applied X-ray CT^{7,8} and

nuclear magnetic resonance (NMR)^{9–11} to study the dissociation kinetics on a micro scale.

Raman spectroscopy has been widely used to study gas hydrates, with the advantage of giving information about cage occupancy in addition to the identification of the guest molecules.¹² Attempts have been made to observe CH_4 hydrate decomposition using Raman spectroscopy.^{13–15} The results obtained showed that gas hydrates dissociate uniformly.

In addition to the visible gas hydrates, appearing as nodule, vein, and massive forms, natural gas hydrates also exist in sediments and are subject to their influence. Studies of the characteristics and dissociation of gas hydrate of different occurrences are important to understand hydrate formation and dissociation mechanisms in nature. Unfortunately, except for the report on the structural information of natural gas hydrates

* To whom correspondence should be addressed. Telephone: 86-532-85755855. Fax: 86-532-85751905. E-mail: qdliuchangling@163.com.

[†] Qingdao Institute of Marine Geology.

[‡] National Research Council of Canada.

(1) Kvenvolden, K. A. Potential effects of gas hydrate on human welfare. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 3420–3426.

(2) Collett, T. S. Energy resource potential of natural gas hydrate. *AAPG Bull.* **2002**, *86*, 1971–1992.

(3) Ji, C.; Ahmadi, G.; Smith, D. H. Natural gas production from hydrate decomposition by depressurization. *Chem. Eng. Sci.* **2001**, *56*, 5801–5814.

(4) Kono, H. O.; Marasimhan, S.; Song, F.; Smith, D. H. Synthesis of methane gas hydrate in porous sediments and its dissociation by depressurizing. *Powder Technol.* **2002**, *122*, 239–246.

(5) Sun, C. Y.; Chen, G. J. Methane hydrate dissociation above 0 °C and below 0 °C. *Fluid Phase Equilib.* **2006**, *242*, 123–128.

(6) Sung, W.; Lee, H.; Kim, S. Experimental investigation of production behaviors of methane hydrate saturated in porous rock. *Energy Sources* **2003**, *25*, 845–856.

(7) Kneafsey, T.; et al. Methane hydrate formation and dissociation in partially saturated sand—Measurements and observations. In Fifth International Conference on Gas Hydrates, Trondheim, Norway, 2005.

(8) Freifeld, B. M.; Kneafsey, T. M. Investigating methane hydrate in sediment using X-ray computed tomography. In *Advances in the Study of Gas Hydrates*; Taylor, C. E., Kwan, J. T., Eds.; Springer: New York, 2004; pp 227–238.

(9) Moudrakovski, I. L.; Ratcliffe, C. I.; McLaurin, G. E.; Simard, B.; Ripmeester, J. A. Hydrate layers on ice particles and superheated ice: A ^1H NMR microimaging study. *J. Phys. Chem. A* **1999**, *103*, 4969.

(10) Dec, S. F.; Bowler, K. E.; Stadterman, L. L.; Koh, C. A.; Sloan, E. D. NMR study of methane + ethane structure I hydrate decomposition. *J. Phys. Chem. A* **2007**, *111*, 4297–4303.

(11) Gupta, A.; Dec, S. F.; Koh, C. A.; Sloan, E. D. NMR investigation of methane hydrate dissociation. *J. Phys. Chem. C* **2007**, *111*, 2341–2346.

(12) Sum, A. K.; Burruss, R. C.; Sloan, E. D., Jr. Measurement of clathrate hydrates via Raman spectroscopy. *J. Phys. Chem. B* **1997**, *101*, 7371–7377.

(13) Komai, T.; Kang, S. P.; Yoon, J. H.; Yamamoto, Y.; Kawamura, T.; Ohtake, M. In situ Raman spectroscopy investigation of the dissociation of methane hydrate at temperatures just below the ice point. *J. Phys. Chem. B* **2004**, *108*, 8062–8068.

(14) Kawamura, T.; Ohga, K.; Higuchi, K. Dissociation behavior of pellet-shaped methane–ethane mixed gas hydrate samples. *Energy Fuels* **2003**, *17*, 614–618.

(15) Charles, E. T.; Dirk, D. L.; Niall, E. Methane hydrate research at NETL: Research to make methane production from hydrates a reality. *J. Pet. Sci. Eng.* **2007**, *56*, 186–191.

(16) Ripmeester, J. A.; Lu, H.; Moudrakovski, I.; Dutrisac, R.; Wright, F.; Dallimore, S. Structure and composition of gas hydrate in sediment recovered from Mallik 5L-38, Mackenzie Delta, N. W. T., Canada: X-ray diffraction, Raman and solid state NMR spectroscopies. In *Scientific Results from Mallik 2002 Gas Hydrate Production Research Well Program, Mackenzie Delta, Northwest Territories, Canada*; Dallimore, S. R., Collett, T. S., Eds.; Geological Survey of Canada: Ottawa, Canada, 2005; Vol. 585, p 106.

Table 1. Characteristics of Methane Hydrate Formed in Silica Sand

sample	sand size (μm)	observation numbers	cage occupancy		hydration number
			small cage	large cage	
sand-ice	150–180	5	0.961 ± 0.007	0.961 ± 0.003	5.98 ± 0.01
mixture	106–150	6	0.950 ± 0.013	0.964 ± 0.004	5.99 ± 0.01
	90–106	5	0.939 ± 0.031	0.965 ± 0.007	6.00 ± 0.01
	53–75	4	0.957 ± 0.019	0.962 ± 0.005	5.99 ± 0.01
CH ₄ hydrate		6	0.947 ± 0.010	0.965 ± 0.003	5.98 ± 0.01

from Mallik, Mackenzie delta,¹⁶ no systematic Raman study has been carried out on hydrate dissociation in sediment. This research reports the characteristics and dissociation of methane hydrates synthesized in silica sands of various sizes with Raman spectroscopy.

Experimental Section

Sample Preparation. The samples were prepared by reacting methane gas with ice, which was mixed with silica sand at a ratio 1:1 (v/v), in a 500 cm³ pressure cell. The silica sand was from Sigma-Aldrich, with a purity >99%, and methane gas (>99.95%) was the product of Praxair Canada. The ice-silica sand mixture ($\sim 10 \text{ cm}^3$) was loaded into the cell at the temperature of dry ice (-78°C), and then, the cell was sealed and evacuated. After the cell was charged with methane gas to 8 MPa, it was moved into a -20°C freezer and left there for 1 h and later it was set in a 2.5°C water bath. When no significant pressure drop was observed for a certain period (~ 2 days), the cell was placed in liquid nitrogen and opened for sample recovery. The sizes of silica sands tested were 53–75, 90–106, 106–150, and 150–180 μm .

Raman Spectroscopic Observation. The experiments were carried out with a Raman spectrometer (Acton Research Corporation, Model: Spectropro 2500i) equipped with a Witec confocal microscope and Ar⁺ laser (Spectro-Physics Laser: Model 177G, 100 mW) operating at 514.5 nm.

The test sample was loaded into an aluminum sample holder, which was precooled down to the temperature of liquid nitrogen and placed in a custom-made box with a 3 cm diameter window covered with sapphire glass.

To study the characteristics of methane hydrate formed in silica sands, the sample holder was cooled with liquid nitrogen throughout the experiments. Signals were collected at 4–6 positions on each sample, and the result was reported as an average.

For hydrate dissociation experiments, the box was filled with dry ice after the sample loading, using a similar procedure for the characterization study. As the dry ice sublimed, the temperature of

the sample holder increased gradually and methane hydrate started to dissociate. The observations were taken over an interval of 2 min, starting 3 min after sample loading, and the signal of each observation was co-added for 50 accumulations. The experiment ended when C–H signals were no longer observed. Throughout the experiments, the laser was focused on a spot on the sample with a $10\times$ lens, although the focus was adjusted at times for a better signal quality.

To determine the integrated intensities, Gaussian multipeak curve fitting was applied to the Raman spectrum obtained with this research. From the fitted curves, the ratio of the integrated intensities of large to small cages of the Raman spectrum was calculated.

Results and Discussion

Characteristics of Methane Hydrate Formed in Silica Sand. Figure 1 shows the Raman spectra of methane hydrates formed in silica sands along with that of the bulk methane hydrate. Similar to that for the bulk hydrate, the signal from hydrate in silica sand has two peaks at 2903 and 2914 cm⁻¹, representing the methane molecule in large and small cages, respectively.¹²

The cage occupancies of methane molecules in large and small cages have been calculated with the method described in refs 16–18. As shown in Table 1, similar to the bulk pure methane hydrate, those formed in silica sands have occupancies of CH₄ over the large cage of about 0.96, while the small cage occupancy of CH₄ varies in a comparatively larger range (0.94–0.96) but still similar to bulk hydrate (0.95). In comparison to results reported on natural samples,^{17,18} the occupancies of CH₄ over cages of hydrates synthesized in silica sands are similar to natural hydrates, with the large cage being almost fully occupied and the small cage occupancy varying in a relatively wide range, probably because of the difference in formation environments. As shown in Table 1, the occupancies of CH₄ in both large and small cages are independent of the particle size, indicative of no influence of the particle size on the structure of hydrate formed in sands.

Estimates of the hydration number were made as well as referring to the occupancies of CH₄ over hydrate cages (Table 1). The values of the hydration number of the samples studied are in agreement with those reported on synthetic and natural methane hydrate samples (~ 6.0).^{17–19}

Raman Spectroscopic Observation of Hydrate Dissociation in Silica Sands. Figure 2 shows a representative dissociation process of methane hydrate in silica sands. It is noteworthy that several spurious peaks, jumping high in a general trend of

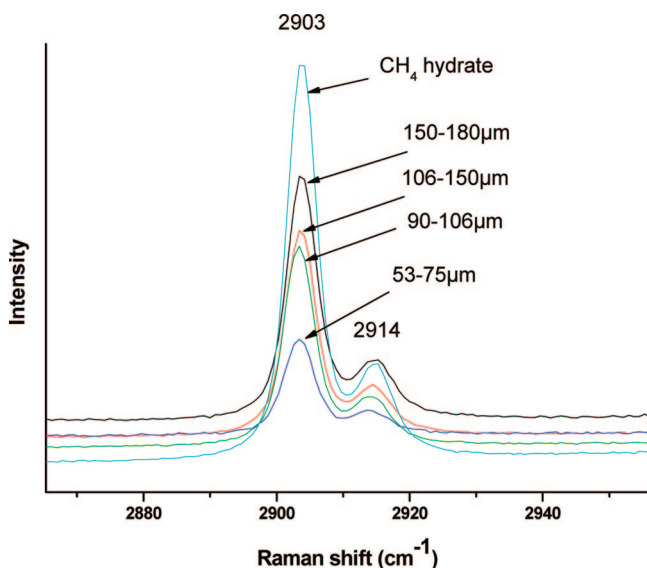


Figure 1. Raman spectra of methane hydrates synthesized in sand with various sizes.

(17) Ripmeester, J. A.; Ratcliffe, C. I. Low-temperature cross-polarization/magic angle spinning ¹³C NMR of solid methane hydrates: Structure, cage occupancy, and hydration number. *J. Phys. Chem.* **1988**, *92*, 337–339.

(18) Lu, H.; Moudrakovski, I.; Riedel, M.; Spence, G.; Dutrisac, R.; Ripmeester, J. A.; Wright, F.; Dallimore, S. Occurrence and structural characterization of gas hydrates association with a cold vent field, offshore Vancouver Island. *J. Geophys. Res.* **2005**, *110*, B10204, doi: 10.1029/2005JB003900.

(19) Uchida, T.; Hirano, T.; Ebinuma, T.; Narita, H.; Gohara, K.; Mae, S.; Matsumoto, R. Raman spectroscopic determination of hydration number of methane hydrates. *AIChE J.* **1999**, *45*, 2641–2645.

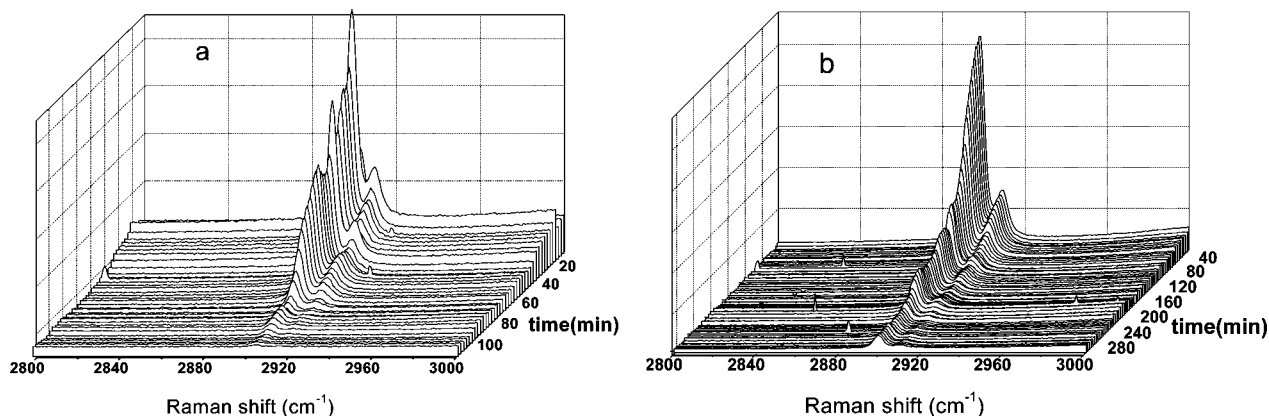


Figure 2. In situ Raman spectroscopic observation on the dissociation process of methane hydrate (a) in silica sands with a particle size of 53–75 μm and (b) in pure methane hydrate.

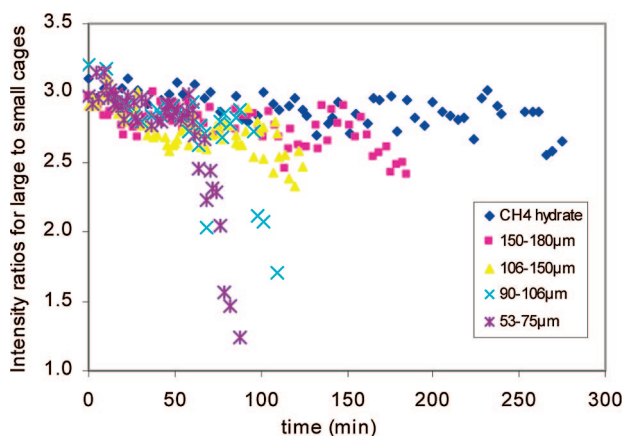


Figure 3. Variations of intensity ratios of large to small cages through hydrate dissociation in silica sands.

intensity decreasing, appeared during hydrate dissociation. These peaks were caused because of focus improvement, because focus adjustment became necessary sometimes in the dissociation process. It can be seen that the dissociation of methane hydrate in silica sands is similar to bulk hydrate, with the intensities of both large and small cages decreasing during the course of hydrate dissociation. As shown in Figure 3, methane hydrate dissociation was completed in a shorter time period in finer silica sands, indicating a particle-size-dependent trend. It is reported that the effective thermal conductivity of porous materials increases with increasing grain size;^{20,21} therefore, the particle-size-dependent dissociation trend should not be caused by powdered sand itself but by something related to it. With regard to the study by Lu et al.,²² the saturation of methane hydrate in silica sands is particle-size-dependent, decreasing from 94% (pore space) in 150–180 μm sand to 54% (pore space) in 53–75 μm sand. As a result, the faster completion of methane hydrate in finer sands might be caused by less hydrate available. Although the intensities of both large and small cages decrease

in the hydrate dissociation process, the intensity ratio of the large cage to small cage behaved in different ways for the bulk hydrate and for that in silica sands, especially for the sands of 53–75 and 90–106 μm . In comparison to the nearly linear trend in bulk hydrate, the ratio dropped dramatically after a certain point of dissociation. This may suggest that, in silica sands, the large cage loses methane faster than the small cage.

Preferential disappearance of the large cage guests of gas hydrate has been reported by Dec et al.¹⁰ for a mixed methane–ethane hydrate. It was explained as the result of the lower stability of hydrate containing exclusively ethane. Our results on bulk methane hydrate are consistent with the previously reported observation of Gupta et al.,¹¹ in that the unit cell decomposes as a single entity. However, for the hydrate in silica sand, the timing of the dramatic drop in the ratio is particle-size dependent: it is not obvious in sands larger than 106 μm , and it comes earlier in the finer silica sands. For example, it was about 80 min after the experiment started in silica sands of 90–106 μm but only about 50 min for silica sands of 53–75 μm . Although further study is needed to elucidate the mechanism of the change of the large/small cage ratio, one possible explanation is that the nature of the hydrate changes with the pore sizes present in the silica sands and that hydrate in some pores decomposes more rapidly than hydrate in other pores.

Conclusion

Through studies on methane hydrates synthesized in a series of silica sands, both the characteristics and the dissociation of methane hydrate in silica sands are found to be generally similar to those in bulk methane hydrate. However, the dissociation behavior of hydrate in fine sands was found different from bulk hydrate; the average ratio of the large to small cage of methane hydrates in silica sands dropped dramatically in fine sands after a certain time, whereas it changed linearly with time in bulk methane hydrate.

Acknowledgment. We appreciate the comments of three anonymous reviewers. C. Liu is grateful for the financial support from the government of Shandong Province and Qingdao Institute of Marine Geology and for his stay at the National Research Council Canada.

EF800440S

(20) Tavman, I. H. Effective thermal conductivity of granular porous materials. *Int. Commun. Heat Mass Transfer* **1996**, *23*, 169–176.

(21) Rosenbaum, E. J.; English, N. J.; Johnson, J. K.; Shaw, D. W.; Warzinski, R. P. Thermal conductivity of methane hydrate from experiment and molecular simulation. *J. Phys. Chem. B* **2007**, *111*, 13194–13205.

(22) Lu, H.; Kawasaki, T.; Zeng, H.; Fujii, T.; Nakamizu, M.; Ripmeester, J. A. Sediment control on the saturation level of gas hydrate in natural environment. 6th International Conference on Gas Hydrates, Vancouver, Canada, July 6–10, 2008.