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Compositional and Structural Identification of Natural Gas Hydrates Collected at Site 1249 on Ocean Drilling Program Leg 204

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Abstract−In contrast to the structural studies of laboratory-grown gas hydrate, this study has been performed on naturally grown clathrate hydrates from the sea floor. The PXRD pattern of natural gas hydrate shows that the sample had a structure I hydrate. The ^{13}C NMR spectrum was obtained for the natural gas hydrate sample in order to identify the cage occupancy of guest molecules and determine the hydration number. The NMR spectrum reveal that the natural gas hydrates used in this study contain only methane with no noticeable amount of other hydrocarbons. The existence of two peaks at different chemical shifts indicates that methane molecules are encapsulated in both large and small cages. In addition, Raman spectroscopic analysis is also carried out to identify natural hydrates and compared with the NMR results. Investigating the composition and structure of natural gas hydrates is essential for applying natural gas hydrates as a novel energy source.

Key words: Natural Gas Hydrates, Methane, ^{13}C NMR Analysis, X-ray Diffraction, Raman Spectroscopy, ODP Leg 204

INTRODUCTION

Clathrate hydrates or gas hydrates are crystalline compounds that are formed by physically stable interaction between water and relatively small guest molecules such as methane, nitrogen, and carbon dioxide. At high pressure and low temperature conditions water molecules are connected by hydrogen bonds and form various structures of cages. The low molecular weight gas molecules are encapsulated into these cages and finally transform to solid hydrates. These non-stoichiometric crystalline compounds are divided into three distinct structures I, II, and H, which differ in cage size and shape [Sloan, 1998]. One of the unique properties of gas hydrates is a change of the specific volume of hydrate formers during their transition from a free gas or liquid state into a solid hydrate state and vice versa. Because each volume of gas hydrates can contain about as much as 170 volumes of gas at standard temperature and pressure conditions, gas hydrates can be applied as storage and transportation media of natural gas [Gudmundsson et al., 1994]. The storage capability of each hydrate structure was investigated by Khokhar et al. [1998] and Seo and Lee [2003].

The most widely studied subject on gas hydrates is *in-situ* natural gas hydrates. Natural gas hydrates are powerful mineral energy resources [Milkov and Sassen, 2002] and are often considered as an important component of the global carbon cycle [Dickens, 2001]. Their use will significantly improve the energy balance of the world in the future. According to the estimates of many researchers, the potential resources of natural gases accumulated on earth in a hydrate state are from 1.4×10^{13} to 3.4×10^{16} cubic meters (m^3) for permafrost areas and from 3.1×10^{15} to 7.6×10^{18} m^3 for oceanic sediments [Kvenvolden, 1988; Makogon, 1988; Collett and Kuuskraa, 1998], which is at least twice as much as the energy contained in the total fossil fuel reserves. Natural gas hydrates, if dealt with trained mastering, can provide mankind with cheap energy for many decades. Although a huge amount of natural gas hydrates are deposited in the continental shelves, the attempts to analyze the physical properties of natural gas hydrates have not been done widely due to the dissociation of hydrates at atmospheric pressure and normal temperature. However, the measurements of fundamental properties and structural identification of natural gas hydrates should be the first consideration to utilize the natural gas hydrates as an energy source.

In the present study, as a microscopic approach, we report the composition and structure of natural gas hydrates mined from Site 1249 on ODP Leg 204 at Hydrate Ridge offshore Oregon (U.S.A.). Since the physical properties of natural gas hydrates relate to their composition and structure, we have focused our attention on these two points by using spectroscopic instruments such as powder X-ray diffraction (PXRD), NMR and Raman spectroscopy.

EXPERIMENTAL SECTION

1. Natural Gas Hydrate Samples

Clathrate hydrates of natural gases were collected during Ocean Drilling Program (ODP) Leg 204 at the Hydrate Ridge offshore Oregon. These samples were extracted from piston cores and placed in an insulated and pressure-tight container stored in liquid nitrogen to prevent the dissociation of hydrates. In order to analyze the natural gas hydrate samples as shown in the photograph of Fig. 1, the container was opened inside a refrigerator, and a lump of gas hydrate taken out from the container was quickly ground to fine powder.

2. X-ray Diffraction

The PXRD pattern was recorded at 123 K on a Rigaku Geiger-

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Fig. 1. A photograph of natural gas hydrate sample collected at Site 1249 on Leg 204 in Oregon offshore. The white parts represent natural gas hydrates.

flex goniometer diffractometer, using graphite monochromatized CuKα radiation (λ=1.5406 Å) in the $\theta/2\theta$ scan mode. The PXRD experiment was performed by step mode with a fixed time of 5 s and an increment of 0.05° in the 2θ range of 10-70°.

3. NMR Spectroscopic Measurements

To identify the hydrate structure and cage occupancy of guest molecules, a Bruker DSX400 NMR spectrometer was adopted in this study. Spectrum was recorded at 243 K by placing samples within 4 mm o.d. Zirconia rotor loaded into a variable temperature probe. The ^{13}C NMR spectrum was recorded at a Larmor frequency of 100.6 MHz with magic angle spinning (MAS) at about 3 kHZ. A pulse length of 2 μs and pulse repetition delay of 10-20 s under proton decoupling were employed when the radio frequency field strengths of 50 kHz corresponding to 5 μs 90° pulses were used. Cross-Polarization (CP) MAS spectra were also acquired for checking the signals from gas components. The down-field carbon resonance peak of adamantine, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference. The natural gas hydrate samples were crushed in a mortar and pestle.

4. Raman Spectroscopy

For the Raman spectrum of the natural gas hydrates, a high-pressure Raman cell, which has an internal volume of about 15 cm^3, was newly designed. It was made of 316 stainless steel and equipped with two sapphire windows at the front and back of the cell. The powdered natural gas hydrates were pressurized by pure methane gas to prevent dissociation of sample during the Raman measurement. The Raman spectrum was obtained by using a FT-Raman spectrometer (RFS-100/S, Bruker) with a highly sensitive InGaAs detector. The excitation source was a Nd : YAG laser emitting a 1,064 nm line. The laser intensity was typically 500 mV.

Table 1. Miler indices of structure I natural gas hydrate

h	k	l	2θ(obs)	2θ(Calc)	diff.
0	0	2	14.900	14.926	−.026
2	0	1	16.650	16.699	−.049
2	1	1	18.300	18.306	−.006
0	2	2	21.200	21.168	.032
1	0	3	23.700	23.701	−.001
2	2	2	26.000	26.001	−.001
3	0	2	27.100	27.083	.017
2	1	3	28.150	28.126	.024
0	0	4	30.150	30.112	.038
1	0	4	31.100	31.062	.038
4	1	1	32.000	31.986	.014
2	0	4	33.700	33.767	−.067
4	1	2	34.650	34.627	.023
2	3	3	35.450	35.468	−.018
3	2	4	41.000	40.940	.060
4	3	3	44.550	44.502	.048
5	1	3	45.200	45.188	.012
2	4	4	45.800	45.865	−.065
1	0	6	46.600	46.535	.065
3	2	5	47.250	47.197	.053
2	0	6	48.350	48.500	.150
1	2	6	49.200	49.143	.057
4	3	6	60.850	60.956	−.106
3	2	7	61.650	61.507	.143
2	5	6	63.100	63.144	−.044
5	4	5	63.800	63.685	.115
6	4	4	64.650	64.758	−.108
8	2	2	66.950	66.877	.073
1	5	7	68.300	68.445	−.145

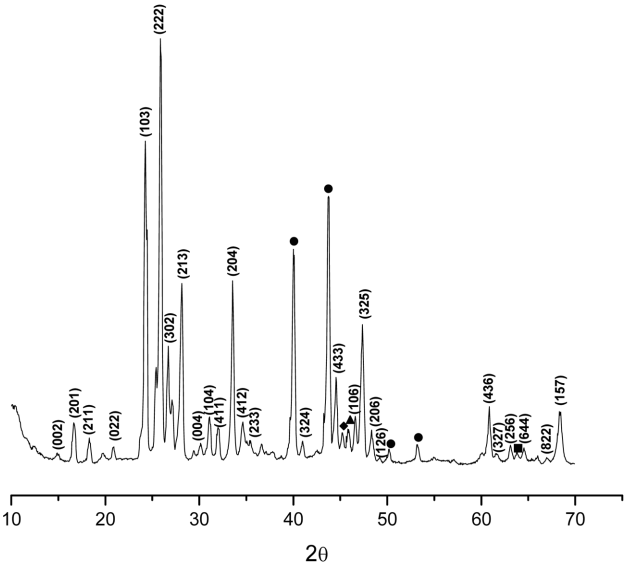

Fig. 2. The powder X-ray diffraction pattern of natural gas hydrates. The four peaks indicated by (●) come from ice and (◆), (▲) and (■) represent the (513), (244) and (545) planes, respectively.

RESULTS AND DISCUSSION

The structure of natural gas hydrate was determined by the PXRD, and 29 diffraction peaks were observed at 1 bar and 123.15 K (Table

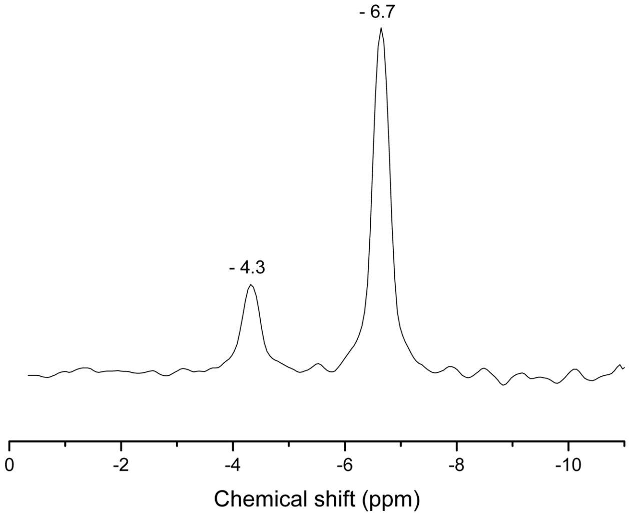

Fig. 3. ^{13}C NMR spectrum of natural gas hydrate (structure I) at 243 K. Methane molecules were represented by two peaks, small cages at −4.3 ppm and large cages at −6.7 ppm.

1). The PXRD pattern could be indexed by using the CheckCell program with the space group *Pm3n* and a unit cell edge of 11.8615 ±0.015 Å. The calculated unit cell parameter appeared to be in good agreement with that of pure methane hydrate of structure I determined by Kirchner et al. [2004]. After examination of the spectroscopic results of Table 1 and Fig. 2, the structure of natural gas hydrates was found to be a well-ordered cubic structure I hydrate.

NMR spectroscopy has been recognized as a powerful tool for the identification of clathrate hydrates. Particularly, the NMR technique can provide both qualitative and quantitative hydrate characteristics such as structure type, cage occupancies, and guest-component compositions [Ripmeester and Ratcliffe, 1988]. Cage-dependent ^{13}C NMR chemical shifts for the enclathrated guest molecules can be used to determine structure types of the formed hydrates. Fig. 3 is the ^{13}C MAS NMR spectrum of natural gas hydrates and indicates that methane molecules occupied in both small and large cages of structure showed peaks of small cages at −4.3 and large cages at −6.7 ppm. The peak representing large cage occupancy appeared to be higher than that for small cage occupancy, confirming the methane molecules in large cages were abundant in structure I.

The relative integrated intensities of ^{13}C MAS spectrum must be combined with the following statistical thermodynamic equation representing the chemical potential of water in structure I hydrate in order to determine the occupancies of methane in the small and large cages.

$$\mu_w(\mathrm{h})-\mu_w(\mathrm{h}^o)=\frac{\mathrm{RT}}{23}[3\ln(1-\theta_{L,CH_4})+\ln(1-\theta_{S,CH_4})] \qquad (1)$$

where $\mu_w(\mathrm{h}^o)$ is the chemical potential of water molecules of a hypothetical empty lattice and, θ_S and θ_L the fractional occupancy of small and large cages, respectively. When the hydrate is in equilibrium with ice, the left side of Eq. (1) becomes $\mu_w(\mathrm{ice})-\mu_w(\mathrm{h}^o)=-\Delta\mu_w^o$, where $\Delta\mu_w^o$ is the chemical potential of the empty lattice relative to ice and has been reported in the literature. The value of $\Delta\mu_w^o(\mathrm{h}^o)$ used in Eq. (1) was 1,297 J/mol, because this value corresponds to structure I hydrate [Davidson et al., 1986]. Integration of each peak enables us to determine the area ratio of the small to large cages. The cage occupancy ratio can be obtained by considering the facts that there are 3 times as many as large cages as small cages in structure I hydrate. The relative cage occupancy ratio, $\theta_{S,CH_4}/\theta_{L,CH_4}$, could be determined from peak areas in Fig. 3 and was found to be 0.8122. This value was substituted into Eq. (1) to obtain individual cage occupancies of θ_{S,CH_4}=0.8020 and θ_{L,CH_4}=0.9875. This value is higher than artificial methane hydrate.

The structure I hydrate is a unit cell consisting of 46 water molecules that form two small and six large cages. For hydrate composition, the hydration number is commonly used defined as (CH_4• $n$$H_2O$) for methane hydrate, where n represents the mole number of water reacted with a mole of methane. When the hydrate cages are fully occupied by methane molecules, n approaches the ideal value of 5.75. However, since actual occupancies of methane guest molecules into small and large cages, θ_{S,CH_4} and θ_{L,CH_4}, have the values smaller than unity, the hydration number at a specified condition must be calculated from $23/(\theta_{S,CH_4}+3\theta_{L,CH_4})$. The hydration number, n=6.11, obtained from Fig. 3 is slightly higher than the ideal value but agrees with other values (n=5.8-6.3) calculated from methane hydrate synthesized artificially [Ripmeester and Ratchliffe, 1988].

Besides the NMR, the Raman spectroscopy, known to be simpler and less resource intensive, was also used to examine the structural aspects of clathrate hydrate phase at *in-situ* temperature and pressure conditions. Fig. 4 shows the Raman spectrum of natural gas hydrates. The vibrational band of methane molecules captured in the clathrate hydrate is distinct from that of free methane gas molecules. Raman peaks of methane molecules in structure I were observed at 2905.0 and 2915.0 cm^{-1}, but for pure methane gas only one peak at 2918.0 cm^{-1} was observed. The splitting of the bands indicates that methane partitions between the small and large cages of structure I hydrate [Sum et al., 1997]. By considering the intensities of the bands of Raman spectrum, the smaller band at high wavenumber (2915.0 cm^{-1}) can be assigned to methane in the small cages and the larger band at low wavenumber (2905.0 cm^{-1}) to methane

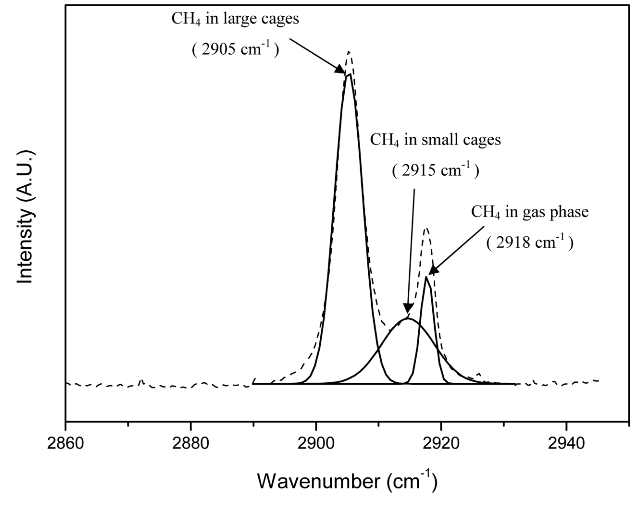

Fig. 4. Raman spectrum of natural gas hydrates. The dashed line represents original spectrum and the solid line is deconvoluted spectrum.

in the large cages, as identifiable with the values reported by other researchers [Sum et al., 1997; Seo and Lee, 2002]. The area ratio of the small to large bands is found to be almost the same as that of the NMR. The exact positions and areas of each peak were determined after deconvoluting two mixed bands using the curve-fitting routine in the commercial package Origin 6.0.

CONCLUSIONS

The natural gas hydrates collected from ODP Leg 204 were analyzed to identify the composition and structure by using spectroscopic measurements. Our PXRD result showed that the sample had cubic structure I hydrate with a=11.8615±0.015 Å. In order to measure hydrate composition and cage occupancies. The ^{13}C NMR spectrum was obtained for natural gas hydrates. The NMR results indicate that the examined natural gas hydrate contained only methane even though some traceable amount of other hydrocarbons was expected to exist in hydrate, and through proper calculation the cage occupancies was found to be about 99% for large cage and 80% for small cage. The hydration number of natural gas hydrates was found to be 6.11 via NMR spectroscopy. This measured hydration number was a little higher than the ideal one (5.75) that can be only attained under full occupancy of both small and large cages. However, the number directly determined from spectroscopic analysis must be considered as the corresponding equilibrium one at the specified temperature and pressure conditions. These NMR peaks were cross-checked by Raman spectra and both results agreed well. The composition and structure identification carried out in the present investigation will provide the fundamental guidelines for the exploitation of novel substitute energy sources.

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