Raman Spectroscopy Study on Ternary Model Coal Mine Methane Hydrates

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ABSTRACT: The microfeatures of coal mine methane (CMM) hydrates, synthesized with three gas samples (CH4/C2H6/N2, G1 = 43 : 47 : 10, G2 = 60 : 30 : 10, and G3 = 74 : 16 : 10) in a self-made transparent high-pressure cell at 275.15 K and 5 MPa were investigated using Raman spectroscopy. As a discriminator, the vibrational band frequencies in the C–C regions of the recorded hydrate Raman spectra for C2H6 show that G1–G3 hydrates are structure I. The three principal parameters used to study the microfeatures of the model CMM hydrates, including cavity occupancies, hydrate guest compositions, and hydration numbers, were calculated. The large cavity occupancies for C2H6 constantly decrease from 85.12 to 79.32%, while the small cavity occupancies for CH4 have a continuous increase from 73.75 to 96.42%. However, CH4 competes with C2H6 on entering the large cavities for their large cavity occupancies of 12.79–17.31%. The cavity occupancies of N2 are less than 1.2%. The hydrate composition calculations show that the molar fractions of C2H6 are the maximum. The hydration numbers range from 6.221 to 6.00. Based on the hydrate guest compositions and hydration numbers, the molecular formulas of the three CMM hydrates are presented.

INTRODUCTION

Coal mine methane (CMM) is a type of unconventional natural gas and is usually mixed with air during the process of coal mining. The reduction of CMM emissions and CH4 recovery are the two main issues that have currently attracted researchers’ efforts worldwide. CMM has been a notable part of the U.S. natural gas market for decades, while Australia, China, India, and Indonesia are poised to embark on coal be methane (CBM) development that will establish CBM industries of a similar scale. However, discharged CMM is usually emitted straight into the atmosphere, because most of the discharged CMM has a CH4 concentration of less than 30%, which not only represents the loss of a valuable energy resource but also threatens the environment when released into the atmosphere. CH4 is one of five greenhouse gases in addition to carbon dioxide, water vapor, nitrous oxide, and ozone. Considering that the global warming potential (GWP) of CH4 is 21 times higher than that of carbon dioxide, several techniques, such as membrane separation,1 pressure-swing adsorption (PSA),2 and low-temperature liquefaction,3 have been developed over the last few decades to separate the two gases. Hydrate-based gas separation (HBGS) is a more recently proposed method for low-concentration CMM.4

Gas hydrates are crystalline solids consisting of a hydrogen-bonded network of host water molecules and encaging guest molecules. The most common structures of clathrate hydrates, which are generally determined by the size of the guest molecules, include structure I (sI), structure II (sII), and structure H (sH). sI hydrates consist of two small (s12) cages and six large (s1262) cages; sII hydrates consist of sixteen small (s12) cages and eight large (s1264) cages; and sH hydrates consist of three small (s12) cages, two medium (s35663) cages, and one large (s1268) cage.5 For the industrial application of HBGS hydration technology, the most likely breakthrough points are improving the thermodynamic condition (P–T), accelerating the kinetic process (induction time6 and formation rate7), and increasing gas storage (hydration number8). To determine the stability and storage of a gas hydrate, the hydrate structure type, cage occupancies, and hydration number are crucial parameters. Raman spectroscopy is a widely used, powerful tool to observe changes in the symmetry of a system and microscopic motions of target molecules and to analyze the structural information of hydrates. Recently, dynamic motions of the guest molecule in the host cage have attracted much research attention so as to understand the formation/dissociation process. In Raman spectra, peaks in the hydrate
phase change compared to peaks in the vapor phase. Cage occupancies and hydration numbers of a single gas component hydrate can be calculated using the van der Waals-Platteeuw model. Related studies on two-component gas hydrates, such as CH$_4$–CO$_2$, CH$_4$–C$_2$H$_6$, and CH$_4$–C$_3$H$_8$, suggest that Raman shifts in the characteristic peaks of guest molecules are related to the hydrate crystal structure and type of the cavity. Other researches have shown that the structure type of a hydrate is determined by gas components and have reported hydrate structural transitions for CH$_4$ + C$_2$H$_6$. $s_I$ and $s_{II}$ hydrates were both found to exist for 0.12 to 0.22 molar fractions. The binary gas mixtures of CH$_4$ and C$_2$H$_6$ form $s_{II}$ hydrates at certain compositions, showing a structural transition from $s_I$ to $s_{II}$ depending on their gas composition range, while pure CH$_4$ and C$_2$H$_6$ form $s_I$ hydrates. The structure of CH$_4$ + C$_2$H$_6$ mixed-gas hydrates changes from $s_I$ to $s_{II}$ when CH$_4$ ranges 72.2–75.0 mol % in the vapor phase and then reverts to $s_I$ from $s_{II}$ between 99.2 and 99.4 mol % CH$_4$. The transition from $s_I$ to $s_{II}$ has attracted much attention since it can increase the storage capacity of CH$_4$ in $s_{II}$ hydrates compared with that in $s_I$ hydrates.

For the coal mine gas main ingredients such as CH$_4$, C$_2$H$_6$, and N$_2$, the structures of CMM hydrates vary due to their complex gas compositions (such as CH$_4$, C$_2$H$_6$, N$_2$, and O$_2$). However, the micromechanisms and hydrate structures in the CMM separation process remain unclear. To better understand and apply CMM hydrate storage and transportation, accurate characterization of hydrate crystal structures is particularly important. In this work, Raman spectroscopy was used to characterize the occupancy and probe vibrational modes of guest molecules in clathrate hydrates. The effects of CMM components on the hydrate crystal structure, cage occupancies, and hydration number from the microscopic view were also analyzed as a means to establish a data foundation for elucidating the microscopic characteristics of CMM hydrates.

**EXPERIMENTAL SECTION**

**Materials.** Three model CMM hydrates with compositions of 43 mol % CH$_4$ + 47 mol % C$_2$H$_6$ + 10 mol % N$_2$ (G1), 60 mol % CH$_4$ + 30 mol % C$_2$H$_6$ + 10 mol % N$_2$ (G2), and 74 mol % CH$_4$ + 16 mol % C$_2$H$_6$ + 10 mol % N$_2$ (G3) were supplied by Harbin Liming Gas Ltd., with a reported uncertainty of ±0.05 mol %. We set the initial experimental conditions to 275.15 K and 5 MPa and used homemade distilled water in all experimental runs. The model CMM hydrates were formed after 3 days and then tested on a Raman spectrometer.

**Apparatus and Procedure.** The model CMM hydrates were prepared and investigated in a self-developed online Raman test system for gas hydrates (as shown in Figure 1). We first injected 1.5 mL distilled water in a stainless-steel high-pressure cell designed with a 3 mL inner volume and a sapphire window. The cell was sealed and put into a thick plastic jacket, which was supplied with recirculated cooled water using a low-temperature thermostat to regulate and maintain the temperature at 275.15 K. After the air in the cell was exchanged with the model CMM hydrates 3–4 times, the model CMMs were pressurized to 5 MPa and then the Raman spectra of the gas phase were collected by a Raman spectrometer. The spectrometer (LabRAM HR800, Jobin Yvon Ltd. France), containing a 200 μm wide slit and a 400 μm diameter confocal hole, was equipped with an air–iron laser excitation source of 532 nm. A 50× long working distance objective was used to focus the laser on the sample. The scattered radiation was collected at 90° with spectral positions calibrated repeatedly against the Raman mode of a Si-wafer (520.7 cm$^{-1}$) before and after measurements.

**RESULTS AND DISCUSSION**

Figure 2 shows the Raman spectra for CH$_4$, C$_2$H$_6$, and N$_2$ of the three gas mixtures as well as the related vibrational modes and ball-and-stand models. Due to their simple compositions and structures, CH$_4$ and N$_2$ have only one definite vibrational mode: frequency at 2916.9 cm$^{-1}$ (designated to the $\nu_1$ C–H symmetric stretch vibration for CH$_4$ gas) and frequency at 2326.9 cm$^{-1}$ ($\nu_1$ N–N symmetric stretch vibration for N$_2$ gas). Because C$_2$H$_6$ has a relatively complex structure, it has several vibrational modes; the $\nu_3$ C–C stretching vibration at 993.1 cm$^{-1}$, $\nu_4$ C–H symmetric stretching vibration at 993.1 cm$^{-1}$, $\nu_3$ C–H symmetric stretching vibration at 993.1 cm$^{-1}$, and $\nu_4$ C–H symmetric stretching vibration at 993.1 cm$^{-1}$.
the characteristic Raman signatures of CH4, N2, and CO2 C4 hydrocarbons (methane through butanes). 20 CH4/N2 bands in the C hydrates are divided into several individual peaks. Raman shows that the collected Raman spectra of the model CMM and 1.0 MPa for about 10 h.22 However, the relationship between the crystalline structure and guest molecule size is not strict, for example, in a CH4 + C2H6 system, transitions of the gas hydrate structure from sI to sII can be observed23,24 Figure formed from CH4, C2H6, or their mixtures. sII hydrates, having 512 cages and six large 51262 cages per unit cell, are often depending on the gas species involved, gas hydrates with sI structure by a guest molecule (cage occupancy) is one of the estimation of the guest molecule density, stability of clathrate structure. The Raman vibrational bands of the sI hydrate bands were deconvoluted into Gaussian + Lorentzian bands using PeakFit software (Systat Software, Inc.). The spectral deconvolutions were conducted to obtain the areas of the Raman vibrational bands for CH4, C2H6, and N2. Ratios of areas under the bands for guest molecules in the gas phase. The vibrational bands of C2H6 in the hydrates are much stronger than those of CH4 in the gas mixtures, and the intensity of the Raman bands for CH4 is much stronger than those of CH4 in the hydrate phase. Compared to the vibrational bands of C2H6 gas, the frequencies of the ν1 C–H symmetric stretching vibrations and 2ν1 CH4 deformation vibrations bands for C2H6 in the hydrates shifted to lower frequencies of 2888.8 and 2943.9 cm−1, respectively. Conversely, the ν3 C–C symmetric stretching vibrations for C2H6 shifted to a higher frequency with a difference of 5.6 cm−1. The ν1 C–H symmetric stretching vibration of CH4 in the hydrate will shift to a higher frequency if the hydrate is sI and will shift to a lower frequency if the hydrate is sII. Therefore, the ν3 C–C symmetric stretching vibration is considered the discriminator of hydrate structures. In addition, the frequency at 998.7 cm−1 for ν3 C–C symmetric stretching vibration of C2H6 in our experiments demonstrates that the formed hydrates are sI if the size of the C2H6 molecule is large enough, C2H6 can only be encased in the large cavity of sl or sII, meaning C2H6 in the model CMM hydrates is trapped in the large (51262) cavities of sl. The ν1 C–H symmetric stretching vibration bands for CH4 shown in Figure 3 are split into two bands, where the higher bands are shifted to 2914.7 cm−1 and the lower bands are shifted to 2902.6 cm−1. The split bands result from CH4 being encaged in two different cavities of the hydrates. Frequencies of 2914.7 cm−1 and 2902.6 cm−1 were designated to the ν1 C–H symmetric stretching for CH4 in the small (512) and large (51262) cavities of sl hydrates, respectively. The weak vibrational bands of the hydrates at 2323.5 cm−1 are attributed to the ν1 N–N symmetric stretching vibrations of N2 encaged in small cavities of sl. Duringhydrate formation, the cage in the formation (large in 2902.6 cm−1 and small in 2914.7 cm−1) was detected by the in situ Raman signals. It was also observed that at the beginning of the hydrate growth step, the Raman peak intensity of CH4 occupying the large cage (51262) and small cage (512). The encapsulation rate of large cages was faster than that of small cages throughout the hydrate formation process. Gas hydrate is a notable nonstoichiometric compound; because the gas molecules are randomly trapped in cavities, the cavities cannot be completely occupied by gas molecules. In order to study the microstructure of the model CMM hydrates, quantitative calculations of the cavity occupancy, hydration number, and hydrate guest composition were performed. It is worth noting that the occupation of each cage of the clathrate structure by a guest molecule (cage occupancy) is one of the most interesting properties because it is related to the estimation of the guest molecule density, stability of clathrate hydrates, etc.25 Cavity Occupancy. The absolute cavity occupancy of a guest molecule in a certain cavity type is the ratio of the amounts of cavities occupied by guest molecules to all of the same type of cavities. The Raman vibrational bands of the sl model CMM hydrates can be used to determine the absolute occupancies of CH4 in both large and small cavities, C2H6 in the large cavities, and N2 in the small cavities. The individual peaks of the hydrate bands were deconvoluted into Gaussian + Lorentzian bands using PeakFit software (Systat Software, Inc.). The spectral deconvolutions were conducted to obtain the areas of the Raman vibrational bands for CH4, C2H6, and N2. Ratios of areas under the bands for guest molecules in cavities (Ai/A) are equal to the amounts of guest molecules encased in the corresponding cavities. sl hydrates contain three
times more large cavities than small cavities. Therefore, the cavity occupancy ratio of guest molecules in large and small cavities \( \theta_L/\theta_S \) is equal to the ratio of the large cavity area and three times that of the small cavity area \( A_L/3A_S \). As known before, the large cavities of the model CMM hydrates were partly occupied by CH\(_4\) and C\(_2\)H\(_6\), and the small cavities were partially occupied by CH\(_4\) and N\(_2\). Therefore, the total large cavity occupancy \( \theta_L \) is the sum of the absolute occupancy of CH\(_4\) and C\(_2\)H\(_6\) in the large cavities \( \theta_{L,CH_4} \) and \( \theta_{L,C_2H_6} \), and the total small cavity occupancy is the absolute occupancy of CH\(_4\) \( \theta_S,CH_4 \) plus the absolute occupancy of N\(_2\) \( \theta_S,N_2 \). To obtain the values of the \( \theta_{L,CH_4} \), \( \theta_{L,C_2H_6} \), \( \theta_S,CH_4 \), and \( \theta_S,N_2 \) for the sl hydrates, a statistical thermodynamic expression from the van der Waals-Platteeuw model is considered.\(^5\) The expression is approved on the basis of five assumptions: (1) The hydrate-free energy is unacted on cavity occupation. (2) Only one guest molecule can be engaged into each cavity, and the guests cannot disperse from the cavity. (3) The guests have no interactions with each other, and the host lattice cannot distort. (4) The quantum effects are not considered. (5) The classical statistics are effective. The expression involving chemical potentials of water in the hydrate \( \Delta \mu_w(h) \), ice \( \Delta \mu_w(h^0) \), and hypothetical empty hydrate lattice is given as follows:

\[
\Delta \mu_{w,H} = \Delta \mu_w(h) - \Delta \mu_w(h^0)
= -\frac{RT}{23} \left[ \ln(1 - \theta_S,CH_4 - \theta_S,N_2) \right]
+ 3\ln(1 - \theta_{L,CH_4} - \theta_{L,C_2H_6}) \right]
\]

where \( \Delta \mu_{w,H} \) is the chemical potential of an empty hydrate lattice, and its value for sl hydrates is confirmed to be 1297 J/mol.\(^{26}\) The results are displayed in Figure 4.

Figure 4 shows that the cavities of gas mixture hydrates are composed of four portions: one part being unoccupied cavities and three others are the cavities occupied by CH\(_4\), C\(_2\)H\(_6\), and N\(_2\). For the occupied portions, the small and large cavities are mostly occupied by CH\(_4\) and C\(_2\)H\(_6\), respectively, while a very small fraction of small cavities and about a quarter of large cavities accommodate N\(_2\) and CH\(_4\), respectively. Although the molar fractions of C\(_2\)H\(_6\) gas decrease by 62.8%, the large cavity occupancy of C\(_2\)H\(_6\) decreases only by 6.8%. The molar fractions of gas CH\(_4\) increase by 37.0%, where the maximum increment of large cavity occupancy for CH\(_4\) is 35.3%. Therefore, we can deduce that C\(_2\)H\(_6\) has a higher priority to enter large cavities over CH\(_4\) and N\(_2\). Observations also show that the amounts of CH\(_4\) occupying large cavities in the G2 hydrate are greater than the other two gases, which is followed by the amounts of CH\(_4\) occupying small cavities in the G3 hydrate. It should be also noted that the number of small cavities capturing CH\(_4\) successively increases from G1 hydrate to G3 hydrate, and the extent of increase between the G3 hydrate and G2 hydrate is much larger than that between G2 and G1. This difference can be explained by the increase in CH\(_4\) that accelerates the amount of CH\(_4\) entering small cavities, and this acceleration effect becomes stronger from G2 to G3. Moreover, the amount of CH\(_4\) engaged in the small cavities is much greater than CH\(_4\) occupying the large cavities, indicating that CH\(_4\) has a greater ability to occupy small cavities than large cavities. Only a small amount of N\(_2\) is enclathrated in the G1–G3 hydrates due to the low partial pressure and adsorption constant. In addition, a relative increment of 23.3% of CH\(_4\) in the G1–G3 hydrates results in an increase by 26.6 and 96.42% small cavities are occupied by CH\(_4\), so it is obvious that the higher competitiveness of being captured in small cavities belong to CH\(_4\). While G1 and G2 hydrates contain numerous vacant small cavities, there are only a few unoccupied small cavities in the G3 hydrate. However, very few large cavities in the G1–G3 hydrates did not trap guest molecules, which may be due to the competition of CH\(_4\) with C\(_2\)H\(_6\) and N\(_2\).

According to Sloan’s work,\(^5\) the stability of cavities is related to the guest-to-cavity diameter ratio. The ratios for most stable cavities are in the range of 0.76–1.0, where the cavities will be more stable when the ratios are closer to 1.0. If the ratio is below 0.76, the molecular attractive forces contribute less to cavity stability, and if the ratio is above 1.0, the cavity cannot accommodate the guest molecule without distortion. As shown in Table 1, all of the size ratios of the methane diameter/small-cavity diameter, ethane diameter/large-cavity diameter, and nitrogen diameter/large-cavity diameter are within the range 0.76–1.0. Therefore, methane, ethane, and nitrogen in the
Table 1. Three Guest Molecule Sizes and Molecular Diameter to Cavity Diameter Ratios

| molecule | diameter/nm | \( \frac{\text{molecular diameter}}{\text{cavity diameter}} \) | 5\( \theta \)4(a) | 5\( \theta \)6(a) |
|----------|-------------|----------------|-------------|-------------|
| CH\(_4\)  | 0.436       | 0.855          | 0.744       |
| C\(_2\)H\(_6\)  | 0.550       | 1.080          | 0.939       |
| N\(_2\)  | 0.410       | 1.040          | 0.947       |

model CMM hydrates can form stable hydrates and can be detected, and methane has a higher priority to enter small cavities. The size ratio of the methane diameter/large-cavity diameter is slightly below 0.76, suggesting that most methane molecules cannot stabilize the large cavities and the competitiveness of methane is weaker than ethane.

**Hydrate Guest Compositions and Hydration Numbers.** As previously discussed, a gas hydrate is composed of guest molecules and water frameworks. The formula of a hydrate can be expressed as M\(n\)H\(_2\)O, where M stands for the molar fraction of guest molecules and \(n\) is the hydration number. The molar fraction of the guest molecules is the hydrate guest composition, and the hydration number refers to each \(n\) moles of water molecules encompassing one mole guest molecules on average. The ideal formula of the sI hydrate for which there is no vacant cavity can be expressed as M\(5.75\)H\(_2\)O. In fact, as it is random for the gas molecules to get into cavities, there is no hydrate that can be fully occupied; also, the occupation condition of all the hydrates are different from each other, suggesting that the hydrate guest compositions and hydration numbers of each hydrate formula are different. In addition, the hydration number has a negative correlation with the gas storage of the hydrate, i.e., a real hydration number is closer to the ideal one, and the gas storage of the hydrate is higher. Based on the cavity occupancies of CH\(_4\), C\(_2\)H\(_6\), and N\(_2\), the hydrate guest compositions (see CH\(_4\) for example) and the real hydration numbers of sI can be calculated using the following equations, respectively:

\[
n = \frac{23}{3(\theta_{l,CH_4} + \theta_{l,C_2H_6}) + \theta_{s,CH_4} + \theta_{s,N_2}}
\]

\[
x_{CH_4} = \frac{3\theta_{l,CH_4} + \theta_{s,CH_4}}{3(\theta_{l,CH_4} + \theta_{l,C_2H_6}) + \theta_{s,CH_4} + \theta_{s,N_2}}
\]

Table 2 contains the calculation results, which reveal that the hydrate guest compositions for C\(_2\)H\(_6\) are always higher than the molar fractions of C\(_2\)H\(_6\) in the gas phase, it can be inferred that the increase of CH\(_4\) in the gas mixture can improve the gas storage capacity in the hydrate.

| hydrate guest composition | CH\(_4\) | C\(_2\)H\(_6\) | N\(_2\) | hydration number |
|--------------------------|--------|-------------|--------|----------------|
| G1                       | 0.304  | 0.690       | 0.006  | 6.221          |
| G2                       | 0.343  | 0.646       | 0.012  | 6.152          |
| G3                       | 0.374  | 0.621       | 0.005  | 6.001          |

60% but show a downturn, whereas the hydrate guest compositions for CH\(_4\) increase from about 30 to 40% from the G1 to G3 hydrate. It is notable that the three hydrates contain very few N\(_2\). Although the molar fractions of C\(_2\)H\(_6\) in the gas phase only range 16–47% and the large-to-small cavity ratio is 0.5, C\(_2\)H\(_6\) has the largest hydrate guest compositions and thus is the most competitive to enter cavities. The tendency of CH\(_4\) and C\(_2\)H\(_6\) may be due to the change in their molar fractions from the vapor to gas phase. The very few hydrate guest compositions for N\(_2\) means that it is difficult for N\(_2\) to form hydrates under these conditions. Table 2 also shows that the hydration numbers continually decrease from the G1 to G3 hydrate, and the absolute slope of the curve from the G2 to G3 hydrate is higher than the slope from the G1 to G2 hydrate. This suggests that gas storage increases from the G1 to G3 hydrate, and the increment of gas storage for the G3 to G2 hydrate is greater than that for the G2 to G1 hydrate. Because the molar fraction of CH\(_4\) increases in the gas phase, it can be inferred that the increase of CH\(_4\) in the gas mixture can improve the gas storage capacity in the hydrate.

**CONCLUSIONS**

C\(_2\)H\(_6\) and CH\(_4\) are mainly encased in large and small cavities of model CMM hydrates, respectively, where CH\(_4\) has the highest priority in entering large cavities and CH\(_4\) has the highest priority in entering small cavities. Overall, CH\(_4\) has more competitiveness to occupy cavities compared to CH\(_4\) and N\(_2\). Moreover, increasing CH\(_4\) in the gas mixture can improve the gas storage capacity of the formed hydrate. The molecular formulas of the three model CMM hydrates were determined to be 0.304CH\(_4\)-0.690C\(_2\)H\(_6\)-0.006N\(_2\)-6.221H\(_2\)O, 0.343CH\(_4\)-0.646C\(_2\)H\(_6\)-0.012N\(_2\)-6.152H\(_2\)O, and 0.374CH\(_4\)-0.621C\(_2\)H\(_6\)-0.005N\(_2\)-6.001H\(_2\)O, respectively, based on the hydration numbers and hydrate guest compositions.

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The authors declare no competing financial interest.

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