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GAS HYDRATE INHIBITION AND ITS UNIQUE THERMODYNAMIC BEHAVIORS WITHIN THE POROUS CLAY SEDIMENT

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ABSTRACT

The fundamental understanding of gas and water system in geological sediments is necessary for greenhouse gas sequestration and future energy production. Depending on the surrounding environments that water, gas, and other substrate material coexist, several unique phases such as supercritical, dissolved gas, gas oversaturated, and hydrate could be formed. Especially, gas hydrates which are composed of water frameworks and several gaseous guest molecules have drawn people's attention for its application such as methane production with carbon dioxide sequestration. For these reasons, to produce methane from natural gas hydrate and store carbon dioxide by replacement reaction, the thermodynamic behaviors of gas hydrate and its stability have become an important issue. Therefore, in this study, we investigated the physicochemical behaviors of intercalated gas hydrate such as unique dissociation patterns, cage occupancy, and phase equilibria in depth. Moreover, we suggested the precise location where gas hydrates are formed within the clay sediment considering the effect of unique surroundings and pore dimension. To analyze the effect of interlayered structure and pore dimension of clay on properties of gas hydrate, Na-montmorillonite and aluminum pillared clay (aluminum pillared montmorillonite) were used and compared.

INTRODUCTION

The fundamental understanding of gas and water system in geological sediments is necessary for greenhouse gas sequestration and future energy production. Depending on the surrounding environments that water, gas, and other substrate material coexist, several unique phases such as supercritical, dissolved gas, gas oversaturated, and hydrate could be formed. Gas hydrate, one of various water-gas coexisting systems, has recently drawn people's attention in both scientific and industrial fields as a new future energy resource and CO₂ sequestration material. Lee et al. suggested the method to replace CH₄ by using CO₂ and N₂ gas mixture. This method attributes to both energy production from the methane

hydrate and CO₂ sequestration within the hydrate[1]. By the way, for the CH₄ production and CO₂ sequestration, basic physical and chemical properties of gas hydrate should be studied much precisely to be realized in the real engineering field. Until today, many researchers performed and characterized well about the properties of gas hydrate in the pure and bulk state. However, the properties of gas hydrate which exists in nature could be somewhat changed due to the unique surroundings. Actually, there are a lot of types of clathrate hydrate existed in nature [2]. Therefore, in order to do successful field test by adopting replacement of CH₄ and sequestration of CO₂, we have to consider the unique properties of gas hydrate located in our targeting site. Most of natural gas hydrates exist in the form of intercalated methane hydrate within the mud, sand, and clay, etc. Moreover, some of gas hydrates bearing layers are located near the sea or under the deep-sea sediment. Therefore, we have to consider the effect of ions in seawater or natural sediment on the properties of hydrate. Actually, we are experiencing the lack of information about the gas hydrate behavior in the natural sediment. Therefore, in this study, we investigated the physicochemical behaviors of intercalated gas hydrate such as unique dissociation patterns, cage occupancy, and phase equilibria in depth. Moreover, we suggested the precise location where gas hydrates are formed within the clay sediment considering the effect of unique surroundings and pore dimension. To analyze the effect of interlayered structure and pore dimension of clay on properties of gas hydrate, Na-montmorillonite and aluminum pillared clay (aluminum pillared montmorillonite) were used and compared. In general, montmorillonite includes members of the dioctahedral and trioctahedral series with various tetrahedral Si/Al ratios and with different interlayer compositions. The generic chemical formula of Na-montmorillonite is Na_{0.32}[Al_{3.01}Fe(III)_{0.41}-Mn_{0.01}Mg_{0.54}Ti_{0.02}][Si_{7.98}Al_{0.02}]O₂₀(OH)₄[3]. These series structure forms aluminosilicate layers and they are stacked in the perpendicular direction. There are also various metal cations and Na is the dominant element.

Water and other gaseous molecules can be introduced in the interlayer of montmorillonite.

By the way, the distance between each interlayer in Na-montmorillonite could be changed with the introduction of guest molecule. Depending on the types of substituents, molecular shape or symmetry, and degree of intercalation, the interlayer spacing is changed differently. However, in the other type of clay, there are some synthetic aluminum oxide pillars between its interlayer, so we call it as aluminum pillared clay. Due to the existence of pillar, the interlayer space does not change. Based on these different physical properties, both types of clay have different pore properties such as pore size distribution. By using the spectroscopic methods such as X-ray diffraction patterns and solid state NMR, detailed information regarding geometrical constraints on gas hydrate behavior could be obtained. Moreover, these physical differences cause the unique dissociation patterns compared to the normal gas hydrate.

1 Experimental Procedures

Na-montmorillonite and aluminium pillared clay were purchased from the Clay Minerals Society (USA) and Sigma Aldrich, respectively. Without any additional treatment, the purchased clays were evacuated at 353.15K for at least 1 day in a vacuum oven to remove the residual waters within the interlayer of clays before the sorption. The water sorption of clay was conducted by following the previous vaporization method[4]. The schematic diagram of the vaporization method is shown in Figure 1. The dried clay was put in the desiccator with distilled water and evacuation followed. Distilled water with ultrahigh purity was obtained from a Millipore purification unit. The clay interlayers slowly absorbed the water vapor. After 5 days, which can be assumed to sufficient time to reach the equilibrium inside the interlayer, the amount of water absorbed in the clay interlayer could be calculated by weighing clay before and after sorption of water vapor. The dispersion method which is also shown in Figure 1 has disadvantages that water molecule cannot perfectly diffuse inside the interlayer since they contact the surface of clay in bulk state[4].

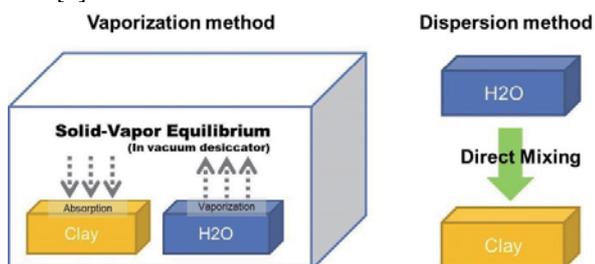


Figure 1 Schematic illustration of vaporization method and dispersion method

After making water - saturated clay sample, intercalated CH_4 and CO_2 hydrate was formed. Water - saturated clay was loaded to high - pressure reactor and CH_4 and CO_2 gas was injected to different reactor respectively.

After gas injection, reactors were cooled in the circulating bath (Jeio Tech, RW-2025G) by following step - by - step with decrement of 1K per hour. After hydrate formation, the sample was kept in liquid N_2 to maintain its structure.

The XRD pattern of dried and water - saturated clays was measured by X-ray radiation with CuK_α radiation ($\lambda=1.5406 \text{ \AA}$) at a generator voltage of 40 kV and generator current of 100 mA with 1 %/min of scan speed. The diffraction of clays including gas hydrate was also measured by using Low Temperature XRD (D/MAX, Rigaku) with CuK_α radiation ($\lambda=1.5406 \text{ \AA}$), step width (0.02) and two times of scan at a generator voltage of 40 kV and generator current of 300 mA, where the measuring temperature was controlled by low temperature accessories equipped with XRD. Dissociation pressure - temperature trace curve was measured by following procedure. Water saturated clays, around 20~22 wt% of water, were loaded in the high - pressure reactor. After that, the reactors were placed in the circulating bath at 283K and pressurized CH_4 and CO_2 gas up to certain pressure. The reactor was equipped with pressure and temperature monitoring system. A four-wired type Pt-100 Ω probe was used for the temperature sensing device which has a full scale accuracy of $\pm 0.05\%$. The digitalized-temperature was calibrated using an ASTM 63C nitrogen-filled thermometer with 0.1 K precision. The pressure transducer (Druck, PMP5073) was used for the pressure sensing device which has accuracy to 0.20% of full scale with a range of 0–70 MPa sealed gauge. All temperature and pressure log were recorded automatically by a data acquisition system at every 20 second. The circulating bath cool the reactor with temperature decrement of 1K per hour to form gas hydrate and heat the reactor with temperature increment of 0.1K per hour to dissociate hydrate.

2 Results

Before investigating the unique behavior of gas hydrate within the two clay sediments, we have to know the critical boundaries of water contents that can sufficiently cause swelling of clay interlayer. From the previous research, for Na-montmorillonite, around 20 wt% of water was saturated inside the interlayer. That amount was sufficient to make hydrate and fully swelled clay. To determine appropriate water amounts for hydrate formation within pillared clay system, several pillared clay samples with various water contents from 0 to 22.3 wt% were prepared. Each sample loaded in high - pressure reactor was pressurized to ~ 150 bar with CH_4 at 243K in the circulating bath for 2 days. Then, prepared samples were analyzed by low temperature XRD. As shown in Figure 2, as the amount of water increases, the CH_4 hydrate peaks appeared at water contents higher than 20 wt%. This tendency and amount of saturated water are very similar to Na-montmorillonite case. Therefore, we performed all the experiment with aluminum pillared clay samples containing water around

20-22 wt%. The structural changes of Na-montmorillonite and pillared clay after water sorption and hydrate formation were analyzed by XRD shown in Figure 3, respectively. In XRD results, the lowest peak below 10 ° corresponds to diffraction from (001) basal planes of clay, where the d spacing of peak indicates the distance between two neighbor interlayers (also called as interlayer distance).

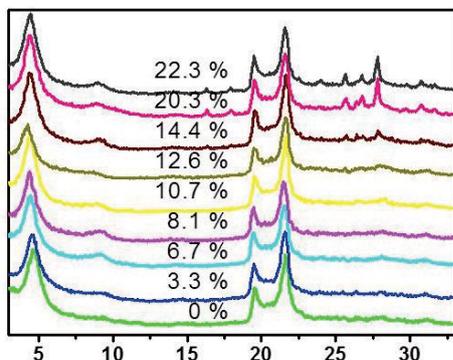


Figure 2 XRD patterns of Al-pillared clay with various water contents + CH₄ exposure at 150 bar

As shown in Figure 3.a, interlayer distance of the Na-montmorillonite is 11.5 Å and increases to 16.7 Å when the clay contains water about 20 wt%, and then is extracted to 15.9 Å with gas hydrate formation. On the contrary, the interlayer distance of pillared clay is 17.4 Å, which is higher than that of Na-montmorillonite due to the incorporated pillars making permanent interlayer opening. The distance slightly increases to 18.8 Å with water swelling and slightly decreases to 18.6 Å after hydrate formation. We note that swelling and hydrate formation significantly affect the interlayer spacing of Na-montmorillonite, however the effect is insignificant for the pillared clay due to the pillars. The structure analysis verifies the successful synthesis of gas hydrate in the swelled clays that we prepared and also guarantees its use for further study.

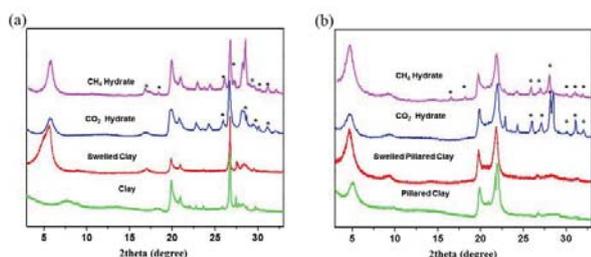


Figure 3 XRD patterns of clay various with various environments (* indicates diffraction from sI gas hydrate): (a) within the Na-montmorillonite; (b) within the aluminum pillared clay

Contrary to pure and bulk water system, the influence of surrounding environments on the properties of gas hydrate is important. The representative difference between two systems is phase equilibria behavior; a few inhibition effect of gas hydrate in mesoporous material were reported [5-8]. Since two clays have both

micropores and mesopores region, the gas hydrate could be formed in the both pores. So, it is crucial to elucidate the exact place where gas hydrate forms. Even though many previous studies on gas hydrate in clay sediment were performed, there was no clear explanation about how the gas hydrate exists in the sediment. Based on our experiments, we performed the analysis and discussed about the possible location of gas hydrate.

First of all, the most possible candidate of location where hydrate form possibly is the interlayer of clay. There were a few studies that suggested the hydrate formation in interlayer of clay and explained the unusual properties of gas hydrate related with the confining of hydrate in interlayer. But there was no clear and direct evidence to support these ideas. In this study, the possibility is discussed in terms of size of hydrate structure and clay (see Figure 4). The interlayer distance of Na-Montmorillonite is 15.9 Å, however the actual space that molecules can be intercalated in about 6 Å considering the thickness of a clay layer. In the case of sI hydrate, the lattice parameter is about 12 Å and the size of small cage (5¹²) is somewhat bigger than 8 Å. We note that formation of gas hydrate structure in interlayer is physically difficult.

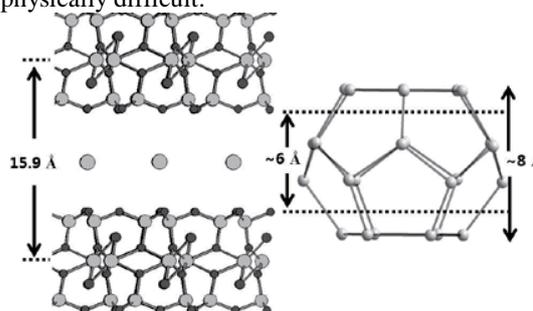


Figure 4 Schematic illustration of the structure of clay and 5¹² cage with their dimensions

To verify these ideas, XRD analysis is performed on the both clays containing gas hydrate. If gas hydrate forms in the interlayer where the space is smaller than hydrate structure, its cage structure should be distorted and the limited repetition of hydrate lattice in [001] direction perpendicular to clay layers is inevitable, which should be reflected in the XRD result in the way of peak broadening and change of diffraction result. According to the XRD result shown in Figure 3, the appearing hydrate peaks corresponds to that of well-known bulk sI gas hydrate.

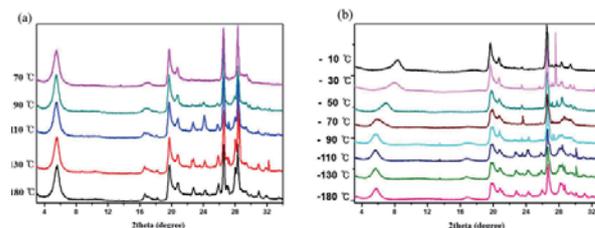


Figure 5 Low Temperature XRD patterns of Na-montmorillonite containing (a) CH₄ hydrate; (b) CO₂ hydrate

To cross-check our idea, Na-montmorillonite samples containing CH₄ hydrate, CO₂ hydrate and hexagonal ice were prepared and their structural changes were observed by LT-XRD with the temperature increment from -180 °C to -10 °C as shown in Figure 5.

We note that interlayer distance depends on the state of intercalation and should be changed when the structure of intercalated solids are though hydrate, hexagonal ice and water due to the difference of density of each form (Hydrate : 0.79 g/ml, Ice: 0.91 g/ml, Water: 1.0 g/ml). As shown in Figure 5, gas hydrate peak disappeared at -110 °C and hexagonal ice melted at -70 °C completely. During the structure transition of water structure, there was no shift of (001) peak of clay, which means that the water structure forms outside of the interlayer. Therefore, we suggest that gas hydrate can be formed in mesopore, macropore and excess bulk water except the interlayer.

Next, to investigate the effect of the confinement of hydrate in clay sediment, phase equilibrium measurement was performed. Figure 6 represents the Pressure - Temperature trace curve of CO₂ and CH₄ with Na-montmorillonite and pillared clay. During the formation and dissociation of hydrate, two noticeable phenomena were detected that cannot happen in bulk water phase: 1) while all the gases recover to their initial pressure after a cycle of cooling and heating procedure in bulk water, the CO₂ cannot recover its initial pressure with the presence of both clays, 2) Two distinct equilibrium points appear, which are dominant in Na-montmorillonite and insignificant in pillared clay. These two phenomena indicate that the CO₂ and CH₄ exist at 3 and 2 different states in clay sediment, respectively. Contrary to CH₄, CO₂ can be stored in clay interlayer revealed by other group[9], which is in agreement with the early interlayer contraction of CO₂ sample than CH₄ at Figure 5. We suspected that the unrecovered pressure is caused by the isolation of CO₂ stored in the hydrate after dissociation.

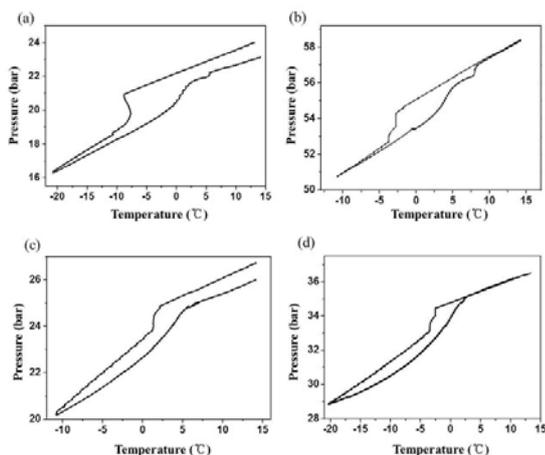


Figure 6 Pressure - Temperature trace curve of (a) CO₂ + Na-montmorillonite; (b) CH₄ + Na-montmorillonite; (c) CO₂ + Al pillared clay; (d) CH₄ + Al pillared clay

To understand and explain the appearance of two distinct phase equilibrium points, we measured Pressure -

Temperature trace at various pressures and temperatures with CO₂ and CH₄ gas. Two points were observed at every cycle with the Na-montmorillonite, and the one point with higher temperature and pressure corresponds to bulk hydrate. Considering the fact that the hydrate could be formed from bulk water or confined water in pore of clay, it is apparent that the inhibited phase equilibrium point corresponds to that of confined gas hydrate in the pore of clay. Specifically, the latter one is an equilibrium point at the pore size where boundary of confined and bulk state. Based on our observation, we suggest the generalized model explaining Pressure - Temperature curve during dissociation trace measurement of gas hydrate in porous materials shown in Figure 7.

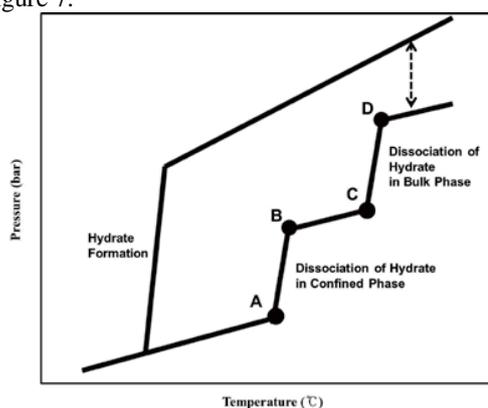


Figure 7 General Pressure - Temperature trace curve of gas hydrate within the porous material

Cooling of system leads to abrupt hydrate formation in the clay sediment like as bulk water, however noticeable changes can be observed during heating process. As the temperature of hydrate system increases, the gas hydrate formed in smaller pore starts to dissociate in advance due to the higher inhibition effect in much smaller pore [5-8]. The shape of dissociation curve reflects the characteristic of pore structure such as pore size distribution. The slope of dissociation curve is increased suddenly from point (A) which means the dissociation process is rapid. With the end of dissociation of the hydrates affected by confining geometry at (B), the gas in system experience thermal expansion due to heating (between point (B) and (C)). We note that the point B corresponds to the equilibrium point of hydrate that existing at the boundary of nano-confined space and bulk phase. Continuous heating leads to the dissociation of bulk hydrate phase (between point (C) and (D)). Region (E) is observed when the porous materials have micropores that hydrate cannot be formed and the applied gas has high affinity to water like CO₂, where gas is stored in terms of gas oversolubility [10-13]. The pressure change ratio between A-B and C-D region implies the ratio between confined and bulk phase and the length of B-C region represents the degree of inhibition related with pore size, shape and surface of pore, which should be dependent on the types of porous materials. Those factors determine the shape of dissociation curve of hydrate in porous materials. Based

on our model, we measured the phase diagram of CH₄ and CO₂ in Na-montmorillonite (Figure 8.a) and pillared clay (Figure 8.b). Phase equilibrium points of CH₄ and CO₂ at the boundary of confining effect and bulk is represented.

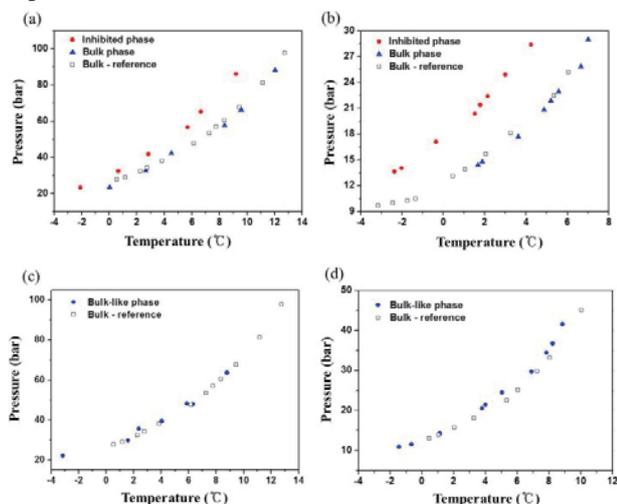


Figure 8 Phase equilibrium diagram of (a) CH₄ hydrate within Na-montmorillonite; (b) CO₂ hydrate within Na-montmorillonite; (c) CH₄ hydrate within Al pillared clay; (d) CO₂ hydrate within Al pillared clay

CONCLUSIONS

We investigated the behavior of gas hydrate in clay sediment starting from the location where gas hydrate forms. Moreover, we elucidated the effect of confining on physicochemical properties of gas hydrate. Instead of hydrate formation, the stable storage of CO₂ in swelled interlayer was observed, where acts as storing niche for hydrophilic molecules. The formation of two different hydrate phase in Na-montmorillonite were observed, one is formed in macropores and outer space of clay, and the other one is confined hydrate in mesopore. We developed the model to explain the hydrate dissociation behavior during measurement of phase equilibrium point of gas hydrate in porous materials. Based on model, we distinguished the phase equilibria of confined and bulk phase, where strong inhibition effect was observed by confining effect. Furthermore, the confining of hydrate in nanopores causes the abnormal cage occupancy of CH₄ hydrate. We expect our result broaden the understanding of the hydrate in confining system and pore materials as well as provide firstly the precise and specific explanation about behavior of hydrate in clay as well.

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