Effect of sodium montmorillonite on the kinetics of CO₂ hydrate: A kinetic and morphology study

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ABSTRACT

The influence of clay minerals in marine sediments strong interactions between clay particles, water and CO₂ hydrate - on hydrate-based carbon sequestration has long been a controversial topic, hampered in part by a lack of experimental evidence. In this study, we investigated experimentally and morphologically the effect of clay minerals on the nucleation and growth kinetics of CO₂ hydrate in sodium montmorillonite (Na-MMT) suspensions with mass fractions ranging from 0 wt% - 10.0 wt%. The results indicated that Na-MMT greatly reduced the induction time t_{ind} by ~77%. While, the average growth rate (NR_{20}) of CO₂ hydrate was reduced by ~70% in high Na-MMT mass fraction systems (>5.0 wt%). Furthermore, significant morphological changes were identified, which were in accordance with the growth kinetics. The flakes-corolla lobes-like hydrate rapidly rises up toward spreading growth across the gasliquid interface to the gas phase space and then extends down into bulk suspension. The clay induces significant changes in hydrate morphology, which results in the upward water migration, hydrate-clay stratification and the growth of densely packed hydrate particles.

Keywords: CO₂ hydrate, montmorillonite clay, formation kinetics, gas uptake, hydrate-clay morphology

NONMENCLATURE

Abbreviations	
Na-MMT	Sodium montmorillonite
CDH	Carbon dioxide hydrate

1. INTRODUCTION

Hydrate-based CO_2 storage/sequestration (HBCS) was considered a potential CCS technology and the pathway toward decarbonization.[1, 2] At STP conditions, 1 m³ of CO_2 hydrate (CDH) can theoretically hold up to 184 m³ of gas.[3, 4] In addition, considering the negative buoyancy effect [5, 6], relatively mild *P* and *T* conditions [1], stable cementing effect [7], the technical feasibility of the hydrate-based carbon sequestration was proposed.

However, in deep-sea environments, unconsolidated sands and clay sediments are widely identified. Clay minerals such as, montmorillonite, illite, Kaolinite and chlorite possess special characteristics, such as small particle size (<5 μ m) [8], low permeability (0.001-1.0 mDarcys), large specific surface area (15-800 m²/g), and strong interface reaction activity that could potentially affect the kinetic behavior of gas hydrate formation kinetics. Sodium-montmorillonite (Na-MMT) is widely distributed in sea sedimentary environment was chosen as a representative clay mineral.

In previous studies [9, 10], although some experimental studies have been conducted to investigate the kinetics of CDH formation in the presence of clay minerals, the most of them were conducted in porous media with a specified clay content through a thermodynamic perspective and did not show kinetic consistency in CDH formation. Lee et al.[11] investigated the induction time through the one-way analysis of variance (ANOVA) of CDH in the presence of Na-MMT and found that the clay surface provides potential nucleation sites thus promoting the growth kinetics of hydrate. Lamorena et al.[12] investigated the effect of bentonite and kaolinite on the induction time and the kinetics of CDH and found that the clay minerals promoted the formation of CDH. Lee et al.[13] reported the dual effect of clay particles for the promotion in nucleation and retardation in hydrate growth kinetics, but they did not explain this remarkable behavior any further. Given the similarities in the crystal structures and physicochemical characteristics between CDH and methane hydrate, several kinetic investigations on methane systems may provide some reference. Kumar et al.[14] reported that bentonite delay the growth kinetics of hydrate. Clennell et al.[15] found that the sufficiently low water activity near the negatively charged clay surface may retard the gas hydrate kinetics.

A controversial topic still remains what is the mechanism underlying the complicated role of clay minerals on the kinetics of CDH. In this study, we designed a series experiments along with morphological observations to investigate the kinetic behavior of CDH formation with varying Na-MMT mass fraction (0 wt% - 10.0 wt%). Based the acquired experimental data (*P*, *T* and morphology), the induction time, the gas uptake over time and the morphology of CDH in clay suspensions were analyzed in detail and compared to elucidate the effect of clay particles on the CDH kinetics. The experimental results from this study have implications in understanding the mechanisms of clay particle affect the CO_2 sequestration and designing effective storage strategy in them.

2. EXPERIMENTAL SECTION

2.1 Experimental apparatus and materials

A schematic of the experimental setup is provided in Fig. 1. A reactor (V = 153.3 mL) with two viewing windows is immersed in a cooling water tank and coupled with a magnetic stirrer. An external water tank was used to adjust the reactor temperature through a circulating chiller. One pressure sensor (±0.01 MPa) and two temperature sensors (one in liquid phase inner the cell and one in the water tank with an accuracy of ±0.1 K) were used to obtain P and T. A CCD camera was employed to record the morphology images.



Fig. 1. Schematic of the experimental apparatus.

Sodium montmorillonite (Na-MMT, \geq 98%, Wande Chem Co., Ltd) and CO₂ gas (\geq 99.99%, Shenzhen Huatepeng Special Gas Co., Ltd.) was procured. Ultrapure water (18.2 M Ω cm) was made in house and used to prepare the Na-MMT suspensions.

2.2 Experimental procedure

The following experimental procedure is used to determine the formation and dissociation of CDH in Na-MMT suspension: (a) the reactor was cleaned and dried; (b) dry Na-MMT clay was added to the cell and then sealed at T = 288.2 K; (c) residual air was removed and the reactor was pressurized to 3.65 MPa with CO₂ gas and then stabilized for 30 min at T = 288.2 K; (d) water (the quantity of water required to prepare a 50 g suspension) injected into the cell through the high pressure pump and then stabilized for 60 min with a constant stirring speed of 600 rpm at T = 288.2 K; (e) CDH formation was induced by cooling the reactor to T = 275.2 K at a rate of 6.0 K/hr; (f) at the end of the formation process, CDH was dissociated by increasing the reactor temperature back to T = 288.2 K at a rate of



Fig. 2. Evolution of (a) experimental *P*, *T* over time and (b) *P* and *T* trace during CDH formation and dissociation in pure water.



Fig. 3. Kinetics of CO₂ hydrate formation characterized by (a) induction time; (b) gas uptake and (c) the partition of CO₂ in hydrate.

6.0 K/hr; (g) a CCD camera capture CDH morphology images. The P and T data were recorded every 20s.

2.3 Calculation method

A volume-balance method was used in this study followed Yin et al. [16]. The solubility of CO_2 in water was took into account in our experiments. The reaction of CDH formation is described as,

$$CO_2 + N_H H_2 O \rightleftharpoons CO_2 \bullet N_H H_2 O \tag{1}$$

where the hydrate number, $N_H = 6.0$ is assumed. The volume balance method is presented as,

$$V_{cell} = V_{G,t} + V_{W,t} + V_{H,t} + V_{Clay,t}$$

= $n_{G,t}\rho_{G,t} + n_{W,t}\rho_{W,t} + n_{H,t}\rho_{G,t} + V_{Clay,t}$ (2)

Where $n_{i,t}$ presents the number of mole at at time t and $\rho_{i,t}$ is the mole volume of the i^{th} phase (i = gas, water, hydrate) at time t.

$$n_{G,t} = n_{G,init} \left(1 - X_{CO_2,t}^H \right)$$
(3)

$$n_{H,t} = n_{G,init} \times X_{CO_2,t}^H \tag{4}$$

$$n_{W,t} = n_{W,init} - N_H \times n_{G,init} \times X^H_{CO_2,t}$$
(5)

where $X_{CO_{>t}}^{H}$ represents the partition of CO₂ in hydrate and the subscript "init" refers to the initial condition before CDH formation. The molar volume of H₂O and CDH is 18.0 cm³/mol and 138.2 cm³/mol [6], respectively. The molar volume of CO₂ at time *t* was estimated using the SRK-EOS.

Hydrate productivity is defined as the normalized rate of hydrate formation computed for the first couple of hours from nucleation (the start of hydrate growth) or the typical deflection point (the start of stable hydrate growth) and is given by Eq. (6).

$$NR_{t} = \frac{R_{t}}{V_{water}} \tag{6}$$

where V_{water} is the volume of water (m³) injected to the reactor, and R_t is the rate of hydrate growth (mol/hr)

calculated by the gas uptake due to hydrate growth versus time.

3. RESULTS AND DISCUSSION

3.1 Effect of the Na-MMT mass fraction on CO₂ hydrate formation kinetics

CDH formation was induced by cooling the reactor to 275.2 K with the Na-MMT suspension (0 - 10.0 wt%). The induction time (t_{ind}) in this study was estimated based on the time when *P*-*T* first enters the CDH stable region to the time that hydrate particles was identified from visual observation. Table 1 summarizes t_{ind} in all experimental cases. *NR*_t was introduced to determine the average CDH growth rate. By comparing t_{ind} in different cases, it was found that t_{ind} decreases with the addition of Na-MMT. As the clay content increase, t_{ind} was reduced by 45% in Case-1.0, 77% in Case-5.0 and 17% in Case-10.0 (see Fig. 3a), respectively.

		t _{ind} (min) -	Rate of CDH formation,	
Case No.	Clay conc. (wt%)		NRt	
			$(mol m^{-3} hr^{-1})$	
			Stage I ^a ,	Stage II ^b ,
			NR_4	NR_{20}
Case-	Pure	47	256	42
0	water	47		
Case-	1.0 wt%	26	253	36
1.0	Na-MMT	20		
Case-	5.0 wt%	11	150	10
5.0	Na-MMT	11	152	19
Case- 10.0	10.0		282	13
	wt% Na-	39		
	MMT			

Table 1 The kinetic parameters in different systems.

^a Rate of CDH formation (NR_4) calculated form nucleation.

^b Rate of CDH formation (NR_{20}) calculated form the deflection point.

In our early study, we found that the nucleation of methane hydrate was induced by the electric field near the negatively charged clay surface (DDL theory) resulting in the shorted t_{ind} . This could explain that even a small Na-MMT mass fraction (1.0 wt%) reduce the t_{ind} by 45% in our experiments.

Fig. 3b presents the gas uptake profiles in the Na-MMT suspension with different mass fractions. Compared with pure water system (Case-0), a slow growth of CDH was observed in Na-MMT suspensions. The hydrate fast growth stage I and the hydrate steady growth stage II are two stages of CDH growth process that can be observed. The deflection points occurred at 585 minutes, 580 minutes, 284 minutes and 214 minutes, respectively. The failure of magnetic stirring due to the increased viscosity of the liquid phase system, according to our observations and analysis, is the main reason of the deflection point. On the one hand, as the amount of water consumed increases, the mass fraction of clay in the suspension increases, increasing the viscosity of the suspension; on the other hand, the aggregation of hydrate particles and clay agglomerates increases the viscosity sharply, causing magnetic stirring to fail.

The explanation can be made from the classical diffuse double layer (DDL) theory for the delayed CDH growth kinetics in Na-MMT suspension. When water is added, the initially dry clay particle absorbs water molecules strongly and forms a DDL with the released cations (e.g., Na^+). The DDL continues to develop as the water content increases, eventually becoming fully developed DDL. The water in the DDL has a higher electrical conductivity (the surface conductivity) and a lower activity than the surrounding free water. [17, 18] Thus, when the clay particles were present in the water, the electric field induces hydrate nucleation, as mentioned in the previous section. It should note that the electric field induces hydrate nucleation mainly occurs outside of the DDL (electric field strength is approximately 10⁵-10⁶ V/m). [17, 19] While in the whole interior of the DDL, the strong polarization effect and the low activity of water lead to the unfavorable conversion of water into CDH. Therefore, although there is a promotion effect on CDH nucleation but the retardation of hydrate growth is very significant as well.

In addition, when the clay particles in water are raised in large amounts (>5.0 wt%), the clay particles are well dispersed in water and are continually exfoliated



Fig. 4. Morphology of CO₂ hydrate formation in 5.0 wt% Na-MMT suspension.

resulting in a vast distribution of monolayers clay in water. Because of this, a huge amount of water around the clay particles is promoted to nucleation that is evidenced by the shorted t_{ind} in Na-MMT suspension. Moreover, the slowing effect of low activity water on CDH growth in the interior of the DDL is gradually apparent, indicating that the growth kinetics of hydrates in general is delaying that are evidenced by the gradual flattening of the gas uptake profiles in stable hydrate growth stage with increasing Na-MMT mass fraction (see Fig. 3b) and by the decreasing final partition of CO_2 in hydrate (see Fig. 3c). More specific theoretical calculations and analysis of DDL will be discussed in our full paper.

3.2 Morphology evaluation of CDH formation

Fig. 4 presents a comprehensive visual observation of the nucleation, growth process of CDH in 5.0 wt% Na-MMT suspension. t_n (hydrate particles were first observed) was introduced to determine the evolution of CDH morphology so that to illustrate the relationship between the morphology changes and the kinetics.

It was found that CDH nucleation occurs on the gasliquid interface (see Fig. 4a). Then the large amount of needle-like CDH was growth along the viewing window and growth towards to the gas phase space (see Fig. 4bc). After 30 min growth of CDH, the hydrate crystal morphology is predominantly dendritic vein-like on the observation window (see Fig. 4e), while the flakes-corolla lobes-like hydrate rapidly rises up across the gas-liquid interface to the gas phase space and then extends down into bulk suspension (see Fig. 4d-f). This rapid spreading growth behavior carried part of the water into the gasphase space, increasing the contact area between gas and liquid and thus accelerating the growth of CDH. This phenomenon is evidenced by the basically the same growth trend during stage I in Case-5.0 compared with pure water system as shown in Fig. 4b. Considering the delay effect in growth kinetics of Na-MMT.

As illustrated in Fig. 4A, a large number of hydrate particles formed in the bulk suspension and thereafter grew in size. Additionally, the rapid growth of hydrate was followed by a rapid water consumption, resulting in the formation of a gas cavity (see Fig. 4g). This evidence also demonstrates water migration during the CDH growth process. Furthermore, as the hydrate grows, the clay particles aggregate and deposit in the reactor's bottom while the CDH particles densely packed upside, resulting in hydrate-clay stratification (see Fig. 4h-j). The increased mass transfer resistance of the dense hydrate layer is attributed for the decrease in CDH growth kinetics. The initial fine dendritic hydrate crystals (see Fig. 4e) progressively convert into stocky dendritic crystals along the observing window (see Fig. 4B). Additionally, the initial thin flakes-corolla lobes-like hydrate eventually thickened, revealing two distinct hydrate morphologies in the reactor: (I) flakes-corolla lobes-like hydrate and (II) dendritic vein-like hydrate. Corroboration for the slow change in hydrate morphology comes from the slow rate of hydrate growth (see Fig. 3b).

3.3 Implication for CO₂ sequestration

As discussed previously, the wide spread of clay minerals in marine sediments necessitates elucidating the role of clays in the formation of CDH. The type of clay, clay content, and the P and T conditions under which clay-bearing sediments are deposited have major implications for both the location of storage sites and the design/optimization of the operation. Thus, representative Na-MMT clay suspensions were used in this study to evaluate the kinetic effects of clay content on CO₂ hydrate and to elucidate its intrinsic mechanism of action. Na-MMT, the most swelling and watersensitive clay mineral present in sediment was used to revealed the effect of clay on the hydrate-based ocean carbon sequestration. The formation of CO2 hydrate is slowed by a higher clay concentration. After a relatively long time (50 hours), the storage capacity of clay suspension is smaller than that of pure water (see Fig. 3c). Given that pumping CO2 into subsea sediments is an energy-intensive process, and given the inevitable loss in storage volume due to leakage and dissolution during storage, the slower hydrates can be stored, the less costeffective the process design becomes. Our findings set the groundwork for choosing the best location for CO2 storage as well as achieving speedy and consistent storage.

CONCLUSION

The following conclusions can be drawn from this study:

a. Na-MMT facilitates the nucleation of CDH, the presence of Na-MMT reduce the t_{ind} by ~77%.

b. Na-MMT delayed the growth kinetics of CDH by \sim 70% (*NR*₂₀) at high clay mass fraction (>5.0wt%). The clay induces significant changes in hydrate morphology, which results in the upward water migration, hydrate-clay stratification and the growth of densely packed CDH particles.

c. The effect of Na-MMT on the kinetics of CHD with varying mass fraction have implications on site and process selection for CO_2 sequestration.

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