Kinetics of Methane Hydrate Formation Catalyzed by Iron Oxide and Carbon under Intense Stirring Conditions

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As an active surface can be a nucleation site for some reactions, the possibility of iron and carbon acting as a catalyst for methane hydrate formation has been examined in the previous study. If iron oxide and carbon can be used as a catalyst, they would have a low environmental influence and a relatively low cost. It has previously been shown that carbon and iron oxide can be used as a catalyst under weak stirring conditions. In the present study, experiments involving intense stirring were conducted for the establishment of the basis for a high production system.

The proposed reaction model consisted of the mass transfers of CH4 in the liquid films both at the gas-liquid and the liquid-solid interfaces and the diffusion in liquid water, and a chemical reaction at the liquid-solid interface. The kinetic analysis was performed using the model and the following results were obtained.

The reaction was a mixed control between the mass transfer and the chemical reaction at 277 K, which was closed to the maximum temperature of methane hydrate formation thermodynamically. While in the lower temperature region lower than 275 K, the mass transfer including the diffusion of CH4 and the apparent mass transfers in the liquid films, K was dominant.

The addition of catalysts (hematite, graphite and its mixture) had acceleration effects on hydrate formation, but to varying degrees. The catalyst “Mix” (mixture of hematite and graphite) had the largest effect on hydrate formation over the whole stirring range. From the results of kinetic analysis, the existence of catalyst had a relatively large influence on the chemical reaction of the formation of methane hydrate.

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1. Introduction

Methane gas hydrate (MH, MGH) consists of methane gas trapped inside the cage-like ice crystal of water molecules. Under atmospheric pressure and around 273 K, the amount of methane gas contained in methane hydrate is equivalent to 170 times the volume of methane gas hydrate. As the dissociation reaction of methane hydrate is an endothermic reaction, the dissociation is delayed by heat transfer from the surroundings.1,2) This feature of methane hydrate is known as the self-preservation effect. Presently, many researchers are planning to develop storage and transportation systems for natural gas (methane) using gas hydrate according to this property.3–6) Recently, the effects of liquid additives of some kind of surfactants (sodium dodecyl sulfate, linear alkyl benzene sulfonate and cetyl trimethyl ammonium bromide,7) alkylypolyglucoside, sodium dodecyl benzene sulfonate and potassium oxalate monohydrate8) on the hydrate formation and the storage capacity have been studied. In the case of solid catalyst, an activated carbon for the storage capacity has been studied by A. Celzard et al.9) and H. Najibi et al.10) In this study, we are working on the development of a catalyst for hydrate formation. The goal of this study was to develop the technology for the collection and transportation of methane gas from small-scale methane sources. In addition, there is a lot of snow in winter in Hokkaido prefecture in Japan, which can be used as a coolant in summer, and also there are many biomass production regions from the fishing and forestry industries and from agriculture. Thus, the results of this study can be applied to the utilization of the locally available resources in Hokkaido.

There is also a possibility that the development of a catalyst for methane hydrate formation will promote the reaction and cause a decrease in the total energy required. Other experiments in our laboratory found that a mixture of iron oxide and carbon becomes extremely activated by mechanical milling. As the active surface can be a nucleation site for some reactions, the possibility of iron and carbon acting as a catalyst was examined in a previous study.11) If iron oxide and carbon can be used as a catalyst, they will have a low environmental influence and a relatively low cost. In the previous study,11) it was shown that carbon and iron oxide can act as a catalyst even under weak stirring conditions. Thus, in the present study, an experiment involving intense stirring was conducted to determine the feasibility of establishing a high production system.

2. Experimental

Schematics of the experimental apparatus for the intense stirring conditions are shown in Fig. 1. Stirring must be performed within the chamber, isolated from the ambient atmosphere. Therefore, the stirring of water was carried out by an impeller with a shaft attached with permanent magnets. The outside magnet was independently rotated by a motor through a belt and pulley. This rotation was transferred to the rotation of the inside magnet attached to the impeller. Using this mechanism, stirring under high pressure was possible. The volume of reaction vessel made of the stainless steel was 200 cm³. A gas inlet tube was attached to the top of the shaft holder, which was located at the cap of the vessel. Pressure and temperature variations were monitored continuously by a
Diffusion stirring with a temperature control accuracy of density (1.77 g/cm$^3$) with a temperature control accuracy of ±0.01°C. The cooling medium was ethylene glycol, and the top of the bath was covered and insulated by a foamed styrene board to obtain stable temperature control.

Experimental conditions such as temperature and the pressure were almost identical to previous experiment. In this study, the reaction temperature was cooled from 293 to 273 K, selected based on the typical temperature of snow. The stirring conditions were changed from 300 to 1200 rpm, and the effect of stirring on the reaction rate was examined. We define the present stirring conditions as intense, in contrast to the previous stirring mechanism, which used a magnetic stirrer and which was stopped by blockage from hydrate formation.

The same catalysts as previous study were used, specifically hematite, graphite and a hematite and graphite mixture. The notations “Hem”, “Gra” and “Mix” refer to these respectively hematite, graphite and a hematite and graphite mixture. The milling conditions and the details of the phenomena during milling have been discussed in previous papers.

Distilled water (70 cm$^3$) and catalyst (iron oxide and/or carbon 0.1 g) were put into a stainless steel reaction vessel (5 cm in diameter). Then, the vessel was evacuated with a vacuum pump, and methane gas was pressurized up to 6.0 MPa. Before the experiment, the temperature was stabilized at 297 K, then the chamber was cooled to 273 K at a rate of 0.35 K/min. Stirring was continuously performed until the end of experiment. The experimental conditions for hydrate formation in this study are summarized in Table 1.

The iron oxide used for the catalyst was a high purity (ash content <100 ppm) and high density (1.77 g/cm$^3$) graphite for electrodes. The iron oxide and the carbon were crushed roughly into the range of 75 μm to 500 μm, respectively. In this study, iron oxide and carbon were mixed and milled using a high purity alumina (>99%) vessel and balls. For mixed milling, the weight of iron oxide was 50.0 g and that of the carbon was 14.3 g. The ratio of the reducible oxygen in the iron oxide and the fixed carbon in the graphite was equal to O/C = 1.0. The rotation speed of milling was constant at 200 rpm, and the number of balls was 10. The atmosphere during milling was Ar for all catalysts.

### 3. Kinetic Analysis

Figure 2 illustrates the reaction model in this experiment. Figure 2(a) shows the stirring condition and Fig. 2(b) shows the condition without stirring. Stirring will change the macroscopic reaction mechanism (mass transfer of CH$_4$ from the surface of water to the reaction interface). The solubility of CH$_4$ obeys Henry’s law for less than 10 MPa:

$$K_H = \frac{P_{CH_4}^b}{X_{CH_4}}$$ (Pa) (1)

where $K_H$ is Henry’s constant (Pa), $X_{CH_4}^M$ is the solubility in mole fraction (–) and $P_{CH_4}$ is pressure (Pa). In high pressure situations (more than 1.0 MPa), the gas film mass transfer can be ignored and the surface concentration of CH$_4$ in water can be assumed to be the same as the solubility, $X_{CH_4}^M$.
When stirring was not performed (Fig. 2(b)), the mass transfer process could be considered as shown in Fig. 3. The liquid film mass transfer $n_{d}$ (mol/s) can be expressed by eq. (2)' using molar concentrations of CH$_4$, $C_{M}^{CH_4}$, $C_{f}^{CH_4}$ at both ends of the liquid film. In this study, using Henry’s constant, $K_H$, eq. (2)' can be rewritten to eq. (2) using mole fractions of CH$_4$, $X_{M}^{CH_4}$, $X_{f}^{CH_4}$, 

$$n_{s} = A \cdot k_s (C_{M}^{CH_4} - C_{f}^{CH_4})$$

(2)'

where $k_s$ is the mass transfer coefficient (cm/s) in liquid film at the gas-liquid interface. $A$ is surface area ($cm^2$), $X_{M}^{CH_4}$ is the mole fraction of CH$_4$ at the end surface of liquid film, the dimension of $X_{M}^{CH_4}$, $\frac{A}{RT}$ is equal to mol/cm$^3$, and $R$ is the gas constant $8.314 \times 10^5$ (Pa·cm$^3$/mol·K).

The diffusion of CH$_4$ in water is expressed as eq. (3).

$$n_{d} = A \cdot \frac{D_{CH_4}}{\Delta Z} (X_{M}^{CH_4} - X_{f}^{CH_4}) \frac{K_{H}}{RT}$$

(3)

where $D_{CH_4}$ is the diffusion coefficient (cm$^2$/s) of CH$_4$ in water, $\Delta Z$ (cm) is the distance from the end of the liquid film at the gas-liquid interface to the top of the liquid film at the liquid-solid (hydrate) interface.

Similarly, the mass transfer in the liquid film at liquid-solid interface is

$$n_{l} = A \cdot k_{l} (X_{M}^{CH_4} - X_{f}^{CH_4}) \frac{K_{H}}{RT}$$

(4)

where $k_{l}$ is the mass transfer coefficient (cm/s) in the liquid film at the liquid-solid interface.

Finally, the hydrate formation reaction can be expressed as eq. (5).

$$n_{c} = A \cdot k_{c} (X_{M}^{CH_4} - X_{f}^{CH_4}) \frac{K_{H}}{RT}$$

(5)

where $k_{c}$ is the reaction constant (cm/s) and $X_{f}^{CH_4}$ is the mole fraction of CH$_4$ at equilibrium for the hydrate formation reaction.

Under steady state conditions, the overall reaction rate $n$ is equal to the respective rates of each step.

$$n = \frac{1}{n_{s} + n_{d} + n_{l} + n_{c}}$$

(6)

For the stirring condition (Fig. 2(a)), the formed hydrate was broken and moved with agitated water. Hence, the two cases will be considered that the diffusion term at the liquid-solid interface are negligible (eq. (8)), or only the diffusion term is negligible (eq. (8)'). In addition, the solid (formed hydrate) is broken by the energy of stirring and the situation caused to minimize the resistance of mass transfer between solid and liquid ($\frac{A}{K} \rightarrow 0$). The situation expressed in Fig. 3 will be applied to an fragment of moving hydrate with stirred water.

$$\frac{\Delta Z}{A \cdot D_{CH_4}} \rightarrow 0, \frac{1}{A \cdot k_{l}} \rightarrow 0$$

(8)

or

$$\frac{\Delta Z}{A \cdot D_{CH_4}} \rightarrow 0$$

(8)'

However, since it is difficult to clarify the respective effects of the diffusion and the mass transfer at the liquid-solid interface, separately, we adopt the assumption of eq. (8). Then, eq. (7) can be rewritten as eq. (9), where $k'_{s}$ is an apparent mass transfer coefficient. Actually, the term of $\frac{1}{A}$ includes the other effects such as the diffusion and the mass transfer at the liquid film and is expressed as eq. (9a).

$$n = \frac{1}{\left(\frac{A}{A \cdot k_{s}} + \frac{1}{A \cdot k_{c}}\right)} \frac{(X_{M}^{CH_4} - X_{f}^{CH_4})}{RT} \frac{K_{H}}{RT}$$

(9)

$$\frac{1}{A \cdot k_{s}} = \frac{1}{A \cdot k_{c}} + \frac{\Delta Z}{A \cdot D_{CH_4}} + \frac{1}{A \cdot k_{l}}$$

(9a)

In the present study, for the calculation of the reaction rate using eq. (9), Henry’s constant $K_{H}$ was expressed as a function of temperature ($K$) as follows;\(^{16}\)

$$K_{H} = -2.33 \times 10^{-4} \cdot T^2 + 0.206 \cdot T + 36.7$$

($r^2 = 0.99999$)\(^{10}\)

Fittings of the apparent mass transfer coefficient $k'_{s}$ and the reaction rate constant of hydrate formation $k_{c}$ were carried out in accordance with a comparison with the observed data. For our experiment, the reaction degree, $R$ (–) was determined by eq. (11), as shown in the previous paper.$^{11}$

$$R = \frac{(P_{cal} - P_{obs})}{(P_{cal} - P_{eq})} = \frac{\Delta P_{obs}}{\Delta P_{max}}$$

(11)

The reaction rate in experiment, $r$ (1/s) was then obtained by differentiation of eq. (11).
In eq. (11), $P_{eq}$ can be estimated by the following eqs.\(^1\)

$$
P_{eq}(kPa) = \exp(38.980 - 8533.8/T) \\
\quad \text{for } T = 273 K - 298 K, \ \text{Lw-H-V} \\
P_{eq}(kPa) = \exp(14.717 - 1886.79/T) \\
\quad \text{for } T = 248 K - 273 K, \ \text{I-I-H-V}
$$

These pressures express the equilibriums among liquid water(Lw)-Hydrate(H)-vapor(V) and Ice(I)-Hydrate(H)-Vapor(V), respectively.

Since the experimental values (reaction degree, $R$ and reaction rate, $r$) are expressed as mole fractions, the calculated reaction degree and rate were normalized by maximum reaction degree, which is equal to $(\Delta P_{max} \cdot V)/RT$ (mol), and can be determined only as a function of temperature. Thus, eq. (9) can be rewritten as follows.

$$
r(1/s) = \frac{1}{(A \cdot k_c + A \cdot k_s)} \left( X_{CH_4}^{M} - X_{CH_4}^{c} \right) \frac{K_{H}}{\Delta P_{max}}
$$

Using eq. (9), the specific reaction rate constant $\frac{A \cdot k_c}{V}$ and the specific mass transfer coefficient $\frac{A \cdot k_s}{V}$ were determined. As mentioned above, the particle size of the formed hydrate, $d_D$ will decrease and the $A/V$ will increase with the stirring speed, $d_D$ and $A/V$ are estimated to obtain the adequate $k_c$ and $k_s$ for determining the curves observed. The details are shown in the following section.

4. Results and Discussions

4.1 Effect of stirring speed without catalyst (no-add.)

Figure 4 shows the reaction rate of hydrate formation for different stirring speeds in comparison with the results of calculations in this study. The reaction rate increased with stirring speed, meaning that the hydrate crystal size is affected by the stirring speed; this will be discussed in detail below. The results of the calculations are in good agreement with the observations. In the slowest stirring experiment (300 rpm), the experimental reaction rate could hardly be measured due to relatively large scattering.

In Fig. 4 at 300rpm were estimated with a calculation in which the mass transfer coefficient and reaction constant were extrapolated from the experiments at higher stirring speeds.

The meanings of “$V$” and $A$ in $A/V$ as a specific surface area are very difficult to understand in this study. Inherently, “$V$” might be a volume of CH$_4$ in the liquid, which is changed with the stirring condition. “$A$” might be a surface area of hydrate particle or an interface area of gas-liquid interface, which are also changed with the stirring condition. In this paper, “$A$” and “$V$” are assumed using the particle size of hydrate.

Figure 5 shows the variation of $d_D$ and $A/V$ in terms of the stirring speed. The $A/V$ was estimated using following equations.

$$
\text{Volume of hydrate particle: } V_D = \pi/6(d_D)^3
$$

$$
\text{Surface of hydrate particle: } A_D = \pi(d_D)^2
$$

$$
A/V = A_D/V_D = 6/d_D
$$

It was found that the value of $d_D$ decreased with the increase of the stirring speed from 300 rpm (30 $\mu$m) to 1200 rpm (0.5 $\mu$m).

The observed value of $\frac{A/V}{V}$ is shown in Fig. 6. The chemical reaction constant, $k_c$ was also obtained using $A/V$ estimated from eqs. (16)–(18). As shown in Fig. 6, the constant value of $k_c$ for the all stirring conditions in the present study was obtained and the value was $5 \times 10^{-6}$ (cm/s).

Similarly, $k_s'$ was estimated from $\frac{A/V}{V}$ which obtained from the experiment and shown in Fig. 7.
The equilibrium pressure calculated from eq. (13) is 3.5 MPa at 277 K and 4.4 MPa at 279 K. In the present experiment, 277 K is close to the maximum temperature at which the hydrate formation reaction occurs.

On the other hand, the diffusion coefficient of CH\(_4\) (g) in H\(_2\)O(l) can be estimated by the Wilke-Chang equation: 17)

\[
D_e = \frac{7.4 \times 10^{-10} \phi M_{H_2O}^{1/2} T}{\mu_{H_2O} V_{CH_4}^{0.6}}
\]  

(19)

where \(\phi\) is the Thiele modulus and is equal to 2.26, \(M_{H_2O}\) is the molecular weight of H\(_2\)O, \(\mu_{H_2O}\) is the viscosity of H\(_2\)O, and \(V_{CH_4}\) is equal to 37.7 cm\(^3\)/mol (the volume of CH\(_4\) at boiling).

At 273 K, as \(\mu_{H_2O}\) is equal to 0.01 g/cm-s, \(D_e\) is equal to 1.46 \(\times 10^{-5}\) cm\(^2\)/s. The order of \(D_e\) is almost the same as \(k'_s\) obtained at 277 K. However, the calculated value of \(D_e\) is almost the same in this temperature range from 273 K to 277 K.

The value of \(k'_s\) at 273 K is significantly smaller than that in other conditions. As mentioned above, the value of diffusion of CH\(_4\) in H\(_2\)O was almost equal to the \(k'_s\) at 1200 rpm, 277 K. In the lower temperature, a contribution of mass transfer in the liquid film at the liquid-solid (hydrate) interface must be quite large.

As a result, the order of \(k'_s\) and \(k_e\) are almost the same at 277 K, it could be concluded that the reaction would be a mixed control between the mass transfer and the chemical reaction. While in the lower temperature at 275 K and 273 K, the mass transfer, \(k'_s\) could be dominant, however, it was not clear which effect among the diffusion and the mass transfers at the liquid-solid and liquid-gas film were dominant.

### 4.2 Effects of catalysts

#### 4.2.1 Without milling

Figure 8, Figure 9 and Figure 10 show the effects of catalysts on the reaction of hydrate formation. The maximum reaction rates in terms of stirring speed for each catalyst are summarized in Fig. 11. Those catalysts were not milled and were only roughly crushed into 75 \(\mu\)m to 500 \(\mu\)m particles.

In the case of hematite catalyst (Fig. 11, Hem), the reaction rate was almost the same as the result of the “no-addition” experiment for stirring speeds less than 900 rpm. However, the reaction rate at 1200 rpm was significantly higher than the other conditions (except ‘Mix’), especially at the beginning of experiment. As shown in Fig. 11, the reaction rates with the Graphite catalyst (Gra) were slightly slower than the “no-addition” rates. The results from the hematite and graphite catalysts show a continuous increase in reaction rate with increasing stirring speeds. However, the reaction rate for the mixture catalyst (Mix) showed different tendency (Fig. 10 and Fig. 11, Mix): reaction rates were very high, even with lower stirring speeds (600 and 900 rpm). Also, while the reaction rate at 1200 rpm was relatively low in comparison with the slower stirring speed, the value was still higher than those of “Gra” and “no-add”.

**Fig. 7** \(k'_s\) v.s. stirring speed with different temperatures.

**Fig. 8** Comparison of observed reaction rates with calculated ones for hematite catalyst.

**Fig. 9** Comparison of observed reaction rates with calculated ones for graphite catalyst.

**Fig. 10** Comparison of observed reaction rates with calculated ones for a mixture of hematite and graphite (Mix catalyst).
Figure 12 shows the obtained specific chemical reaction rate, \( \frac{A}{C_1}k_cV \), for different catalysts. Trends in this figure resemble the relationship of the maximum reaction rate shown in Fig. 11. As shown in Fig. 12, the values of “no-add” and “Gra” were almost the same over the total range of stirring speeds. The result of “Hem” was slightly larger than those of “no-add” and “Gra” at stirring speeds less than 900 rpm, but was extremely high at 1200 rpm. The “Mix” catalyst showed the largest values for mass transfer coefficients, especially at 600 rpm and 900 rpm. However, at 1200 rpm, the value decreased drastically and was close to those of “no-add” and “Gra”.

Figure 13 shows the comparison of specific mass transfer coefficients, \( \frac{A}{C_1}k_s'V \), for different catalysts at three temperature levels (273, 275 and 277 K). In Fig. 13(c), the values of “Mix” are compared with the results of “no-addition”. It was found that when catalysts (Hem, Gra and Mix) were added, most values of \( \frac{A}{C_1}k_s'V \) (except at 273 K) were smaller than that of “no-addition”. The results indicated that the effect of catalyst addition was mainly working on the chemical reaction of hydrate formation, which meant that the surface of catalyst would provide a reaction site.

The reaction of methane hydrate formation was quite a complicated reaction. The presence of the catalyst might have an effect on the flow of water by stirring. Furthermore, the catalyst itself has a different effect on gas adsorption. From the results of kinetic analysis, it was found that the presence of the catalyst had an influence on the chemical reaction, mainly, which meant those fine particles affected the nucleation of methane hydrate.

Whereas the solubility change of gas in the presence of fine particles has not yet been clarified, it is very important to determine not only for hydrate formation but also for the absorption of gases into water.

4.2.2 Effects of milling of catalysts

The effect of milling of catalysts on the reaction rate was examined. In this experiment, the maximum milling time was 48 h (except “Gra”; 24 h) under an argon atmosphere. Then, the hydrate formation experiment was performed under stirring conditions of 1200 rpm as shown in Table 1. Figure 14 shows the variations in the reaction rate of hydrate formation for the different experiments using the three kinds of catalyst (“Hem”, “Gra” and “Mix”). The profiles of the reaction rates were almost the same among three catalysts for
was found that the specific reaction rate Figure 16 represents the specific chemical reaction constant from the rate constants, from the observed one. The calculation results were obtained

![Fig. 15](image)

**Fig. 15** Maximum reaction rates of methane hydrate formation for three kinds of catalyst (hematite, graphite and mixture) prepared with different milling times.

24 h of milling. The result of “Gra” was relatively separated from the observed one. The calculation results were obtained from the rate constants, $k_1$ and $k_2$. The details are mentioned below.

Figure 15 shows a comparison of maximum reaction rates at the beginning of reactions among different kinds of catalyst after 24 h of milling. In comparison with the “no-addition” experiment, all catalysts had some acceleration effect on hydrate formation. The maximum effect on the reaction rate was obtained at 6 h of milling for “Hem” and “Mix”. For the catalysts with longer milling times, the acceleration effect was not so significant, which can be explained by deactivation from gas adsorption on the catalyst because of the highly activated surface just after milling.\(^{(1)}\)

Figure 16 represents the specific chemical reaction constant $\frac{A_k}{V}$ for three kinds of catalysts with different milling times. It was found that the specific reaction rate $\frac{A_k}{V}$ increased with the milling time. The values of Hem for all milling times were the highest compared with the results for Mix and Gra. However, the difference between 6 h and 48 h was small, which means that the short time milling was sufficient for methane hydrate formation.

![Fig. 16](image)

**Fig. 16** Variation of the $A_k/V$ of methane hydrate formation for three kinds of catalyst (hematite, graphite and mixture) prepared with different milling times.

In Fig. 17, the apparent mass transfer coefficient $\frac{A_k}{V}$ for Hem, Gra and Mix at 273 K, 275 K and 277 K were compared with the milling time. As shown in Fig. 17, those values at 0 h were smaller than that of the “no-addition” experiment, which means that the rate-determining step was in the mass transfer in the liquid water. There was little difference in the $\frac{A_k}{V}$ among the different catalysts (Hem, Gra and Mix).

![Fig. 17](image)

**Fig. 17** Variation of the $A_k/V$ of methane hydrate formation at 1200 rpm vs. milling time.

From these results, it can be concluded that the presence of a catalyst increased the chemical reaction of the hydrate formation. In this study, it was assumed that the reaction site will exist at the surface of the catalyst such that the nucleation of methane hydrate will become easier. Unfortunately, there is no evidence that the nucleation site is related to the catalyst directly. For this, it would be necessary to directly observe methane hydrate formation on the surface of a fine particle. This will be incorporated into a future study. Moreover, for the “no-addition” experiment, the starting time of the reaction (incubation time) was quite unstable, which suggests that nucleation is difficult in highly pure water. We assume that the nucleation of methane hydrate will be also related to the structure of water (Appendix, Fig. A-1).

5. Conclusion

The effects of intense stirring and catalyst addition on the formation of methane hydrate were examined. A reaction model for methane hydrate formation was proposed, including the mass transfer of CH\(_4\) and the chemical reaction at the surface of the hydrate. The following results were obtained.

Results for no-addition (without catalyst):

1. The reaction was a mixed control between the mass transfer and the chemical reaction at 277 K. While in the lower temperature region lower than 275 K, the mass transfer including the diffusion of CH\(_4\) and the mass transfers in the liquid films, $k_1'$ could be dominant, however, it was not clear which effect among the diffusion and the mass transfers at the liquid-solid and liquid-gas film were dominant.
Effects of catalysts with 0 h of milling:
(2) The addition of catalysts (hematite, graphite and its mixture) had acceleration effects on hydrate formation, but to varying degrees. The catalyst “Mix” (mixture of hematite and graphite) had the largest effect on hydrate formation over the whole stirring range, while at the maximum stirring speed of 1200 rpm, “Hem” (hematite) had the highest effect.
(3) From the results of kinetic analysis, the existence of catalyst had a relatively large influence on the chemical reaction of the formation of methane hydrate.

Effects of milling of catalysts:
(4) After milling, all catalysts had a larger effect on the reaction acceleration than that of 0 h of milling.
(5) Catalysts undergoing longer milling times did not show higher acceleration effects after more than 6 h. It was determined that this result was caused by deactivation through the adsorption of other gases during handling of the catalysts, which means that a short milling time is sufficient for methane hydrate formation.

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Appendix

Figure A-1 shows the change in the starting time of the reaction when the same water was used repeatedly. It was found that the starting time of the reaction became earlier with repetition of experiment. This result would be related to the change in the liquid structure of water, which was confirmed by measurements with Raman spectroscopy.18)

REFERENCES