**In situ Raman spectroscopic investigation of flux-controlled crystal growth
under high pressure: A case study of carbon dioxide hydrate growth in aqueous
solution**

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ABSTRACT

We developed a high-pressure in-situ non-invasive technique to measure the solute concentration distribution in the solution around a growing crystal, in order to study the effect of increasing flux to the crystal surface on the growth process. Growth rates of carbon dioxide hydrate in pure water in a capillary high-pressure optical cell were determined at 20 and 40 MPa and 275.15, 278.15, 280.15, and 283.15 K. During the growth of the hydrate, CO₂ was supplied through diffusion in the aqueous phase from the liquid CO₂-aqueous solution interface, and the dissolved CO₂ concentrations along the diffusion path were monitored by Raman spectroscopy. We demonstrated that the hydrate growth rates could change a lot under constant driving force, such as under the same degrees of super-saturation, super-cooling or over-pressurization of the system, and that the growth rates depend on the mass transfer flux to the surface of the hydrate crystal; with the increasing flux to the crystal surface, the rate-dominant process changes from “diffusion controlled” to “interfacial reaction controlled” after the diffusion flux reaches a critical (maximum) value. The interfacial reaction coefficient k_r is estimated to be 1.31×10^{-6} m/s at 20 MPa and 280.15 K, and the molar volume and hydration number of CO₂ hydrate vary from 21.7 to 22.0 cm³/mol and 7.09 to 7.67, respectively. These observations and measurements could be useful for the design of crystal growth.

KEYWORDS: carbon dioxide hydrate; kinetics; concentration gradient; mass transfer; Raman spectroscopy

Nomenclature			
<i>List of symbols</i>		y	Hydration number
m_i	Molality of component i in liquid phase in mol/kg H ₂ O	n_i	Moles of component i
H_r	Peak height ratio	M_H	Molecular weight of hydrate in g/mol
D_i	Diffusion coefficient of component i in water in m ² /s	K'	Overall transfer coefficient in m/s
T	Absolute temperature in Kelvin	K	Reaction rate constant in mol/(m ² MPa s)
P	Pressure in MPa	k_d	Mass transfer coefficient
J	Diffusion flux	k_r	Reaction coefficient
ρ_i	Density of component i	k	Flux controlled coefficient
x_i	Mole fraction of component i in liquid phase	A_H	Crystal surface area in m ²
V_ϕ	Apparent molar volume of dissolved CO ₂	c	Bulk fluid concentration in mol/kg H ₂ O
V_i	Volume of component i in cm ³	c_{eq}	Concentration at equilibrium in the presence of hydrate
$V_{m,i}$	Molar volume of component i in cm ³ /mol	f_i	Fugacity
$L_{sol,t}$	Length of aqueous solution at time t in m	ϕ_i^L	Fugacity coefficient
$L_{H,t}$	Length of hydrate at time t in m	c_{tot}	constant total molar concentration
t	Time in s	<i>Subscripts</i>	
A	Cross-section area in m ²	sol	Solution
C	Constant of integration	H	Hydrate

1. INTRODUCTION

Natural gas components like methane, ethane, propane, carbon dioxide, nitrogen and hydrogen sulfide are known to form hydrates at high pressure and low temperature. The growth kinetics of crystal from solution under high pressure is of great interests in industrial and geological processes (e.g., geological CO₂ sequestration as a means to mitigate the global warming [1] and production of CH₄ from CH₄ hydrates with the injection of CO₂ [2]). However, only limited accurate data exist for the hydrate crystal growth rate [3]. The growth rate and the morphology of the crystal are controlled by the surface reaction as well as transport

of mass and heat, usually depend both on the diffusion rate and the reaction rate. To better understand the phenomena of crystal growth in solution under high pressure and improve the processes designed for the crystal growth under high pressure, it is necessary to develop high-pressure in-situ non-invasive techniques to measure the solute concentration distribution in the solution around a growing crystal and determine the ratio of surface flux to mass transport flux, because the rate-dominant process depends on the ratio of surface flux to mass transport flux. Furthermore, an accurate value for the reaction rate constant of hydrate formation is required for the design of proper reactor for a large-scale hydrate production [4].

Kinetic studies of hydrate growth are often carried out in a controlled environment using a semi-batch stirred tank reactor, where liquid water and hydrate former gas are in contact at suitable temperature and pressure to form gas hydrate. On the basis of experimental and theoretical analyses, models were established to describe the formation kinetics. For example, a fugacity model, proposed in the pioneering work of Englezos et al. [5], can be used to determine the reaction rate constant of hydrate formation. Skovborg and Rasmussen [6] limited hydrate growth to a mass-transfer problem and considered the transport of gas molecules from the gas phase to the liquid water phase as the rate-determining step in the overall hydrate formation process. Hashemi et al. [7] modified the gas hydrate growth model of Englezos et al. [5] based on a concentration driving force, where the equilibrium concentration at the hydrate surface was determined at the surface pressure and temperature. In most of these studies, heat and mass transfer resistances were designed to be negligible by

73 using high agitation rates in semi-batch stirred tank reactors, even though the growth
74 or dissolution of crystal may be controlled either by mass or heat transfer or by
75 interface reaction [8]. On the other hand, the role of hydrate intrinsic kinetics has
76 been more recently suggested to play a smaller role in hydrate growth in real systems
77 than heat and mass transfer effects [1]. In addition, although attempts have been
78 made to use particle size measurement techniques in recent studies, for example,
79 Herri et al. [9] used turbidimetry measurements to characterize kinetic inhibitors
80 during the crystallization of methane hydrate, and Clarke and Bishnoi [10] used a
81 focused beam reflectance method probe to measure the particle size distribution to
82 obtain the intrinsic rate constant, accurate measurement of the amount of hydrate
83 crystal is still a challenge for studying gas hydrate kinetics.

84 In the present study, a new reactor has been used for hydrate growth, in which the
85 size of crystal, the transfer of CO₂ and the consumption of CO₂ and water can be
86 accurately determined. CO₂ hydrates are formed in a capillary high-pressure optical
87 cell, a section of which can be fully filled by the crystal. The length of the sections
88 for hydrate crystal and solution were measured as a function of time. An in situ
89 measurement technique based on Raman spectroscopy was established to directly
90 measure the CO₂ concentration distribution in the solution around a growing hydrate
91 crystal, in order to determine the mass transfer rate and analyze the rate-determining
92 process. Growth rates of carbon dioxide hydrate in water were determined at 20 and
93 40 MPa and 275.15, 278.15, 280.15, and 283.15 K. The conversion of the
94 rate-determining step from mass transfer to interfacial reaction was observed.

2. EXPERIMENTAL SECTION

2.1. Experimental apparatus and procedures for growing single crystal

A capillary high-pressure optical cell (HPOC, [11, 12]) in combination with a Linkam CAP500 heating–cooling stage was used for the Raman spectroscopic study of mass transport flux in the aqueous solution during the hydrate growth at high pressure and low temperature (Fig. 1). The HPOC was constructed from a round cross-sectional flexible fused silica capillary tube with 375 μm OD, 50 μm ID and about 25 cm in length. One end of the tube was sealed with a hydrogen flame and the other end of the tube was epoxied inside a stainless steel high-pressure capillary tubing (1.59 mm OD, 0.5 mm ID and 4 cm long), which was connected to a pressure line by a sleeve-gland assembly and a high-pressure valve (HIP 15-15AF1). The cell was inserted into the sample chamber of the heating-cooling stage, its closed end was located near the center of the window of the heating-cooling stage, where the temperature could be maintained with accuracy of ± 0.2 K from 273 to 373 K [13].

A section of ultrapure water (about 1.85 cm long) with resistivity of 18.24 $\text{M}\Omega\cdot\text{cm}$ was loaded to the closed end of the capillary cell after the water was boiled for several minutes to expel possible dissolved air. Carbon dioxide (99.99%, Air Products) was loaded into the pressure line and the cell, after they were evacuated, and then [pressurized by using a pressure generator](#). One day was allowed to let the carbon dioxide diffuse into pure water. The pressure was read from a Setra 206 digital pressure transducer with a Datum 2000 manometer (9999 psi full scale; accurate to $\pm 0.14\%$). Hydrates were nucleated in the solution near the closed end of

the optical tube by placing about 5 mm section of the cell in the heating-cooling stage and adjusting the temperature to 238 K for a few minutes. The whole cell was then warmed to a target temperature to let a single crystal grow under a concentration gradient at a fixed temperature-pressure condition. After the crystal fully occupied a section of the HPOC (Fig. 2), we started to record the images of the sample continuously and perform Raman Spectroscopic measurements.

2.2. In situ monitoring of the concentration distribution of dissolved carbon dioxide

Quantitative Raman spectroscopy was used to measure the solute concentration distribution in the solution around the growing crystal. Raman spectra of dissolved carbon dioxide in solution were acquired by a JY/Horiba LabRam HR Raman system, using a 532.06 nm (Frequency doubled ND: YAG) laser excitation whose output laser power is 45 mW, a 50× long-work-distance Olympus objective with 0.5 numerical aperture, and a 300-groove/mm grating. The aperture of the confocal hole is 200 μm . Raman peak shifts were calibrated regularly with the $\sim 520.7\text{ cm}^{-1}$ band of a polished silicon wafer. Spectra were collected at each sample spot between 1200 and 4000 cm^{-1} , which covers the Fermi dyad of CO_2 between 1200 and 1400 cm^{-1} (the lower band at $\sim 1285\text{ cm}^{-1}$ and the upper band at $\sim 1390\text{ cm}^{-1}$), and the OH stretch of water between 3000 and 3700 cm^{-1} , for about 120 s with two accumulations per spectrum. The peak areas and heights for CO_2 are integrated from 1310 to 1440 cm^{-1} , and those for water, from 2650 to 3900 cm^{-1} , using GRAM32/AI software (Galactic Industries).

To obtain the carbon dioxide concentration profile between the liquid CO₂-aqueous solution interface and the hydrate-aqueous solution interface, several sample spots at specific positions were selected for Raman measurements (Fig. 1). The lengths of crystal, as well as the distance between the two interfaces, were measured with a screw micrometer (0.01 mm accuracy). The peak height ratio (H_r , stands for $(I_{\text{CO}_2}/I_{\text{H}_2\text{O}})$, in which the CO₂ peak near 1390 cm⁻¹ was used) was used directly as an indicator of relative concentration of dissolved carbon dioxide [14].

3. RESULTS AND DISCUSSION

3.1. Measured carbon dioxide hydrate growth rates in aqueous solution

The progresses for the growth of carbon dioxide hydrate in pure water at 20 MPa and 275.15, 278.15, 280.15 and 283.15 K, and at 40 MPa and 280.15 K were observed within the stability field of hydrate and water in the binary system CO₂-H₂O (Fig. 3).

As shown in Fig. 2, the single hydrate crystal fully filled a section of the HPOC, which gradually became longer with time. Fig. 4 shows the changes in length of the sections for the hydrate crystal and aqueous solution in capillary tubes during the hydrate crystal growth. It can be seen that, the changes of the lengths for hydrate and aqueous solution sections with time are linear when the aqueous solution sections are long enough (6~12 mm in our experiments; Fig. 4-a, b, c, d; 20 MPa, 275.15, 278.15, 280.15 K (1) and 40 MPa, 280.15 K), but these changes become faster when the hydrate-aqueous interface approaches the liquid CO₂-aqueous interface (<3 mm in our experiments; Fig. 4-e, f; 20 MPa, 280.15 K (2) and 283.15 K). This indicates that

the growth rates of CO₂ hydrate are constant under the former conditions and increase with the decreasing distance between the hydrate-aqueous interface and the liquid CO₂-aqueous interface in the latter.

3.2. Measured carbon dioxide concentration distributions in aqueous solution

Raman spectra were collected at spots 20 μm from the liquid CO₂-aqueous interface (LI), 20 μm from the hydrate-aqueous interface (HI), and two or three fixed positions (L1, L2, L3) between HI and LI in the aqueous phase, and also at 20 μm from the hydrate-aqueous interface near the closed end of tube (H0). Fig. 5 shows a set of raw spectra as an example.

Concentrations of CO₂ (mol/kg H₂O) were calculated through measured Raman peak intensity ratio between the upper band of CO₂ Fermi dyad, ν_u , to the OH stretching band of water in the CO₂-containing solution (H_r) at these points using the functional relationship among H_r , temperature (K), pressure, and concentration constructed by Guo et al. [16] as follow:

$$H_r/m_{\text{CO}_2} = -5.38 \times 10^{-5} T + 0.126, \text{ where } 273.15 \text{ K} \leq T < 404.45 \text{ K} \quad (1)$$

The error of such quantitative Raman spectroscopic measurement is within 3%.

The concentrations of CO₂ at the liquid CO₂-aqueous interface (c_{LI}) and hydrate-aqueous interface (c_{HI}) are essentially unchanged with time (Fig. 6, (a)-(d)) when the temperature and pressure are fixed, because they are defined by the solubility of CO₂ in water in the absence and presence of hydrate, respectively. However, the concentration gradients of CO₂ in aqueous solution increase slightly with time due to the distances between the two interfaces decrease slightly with time

(Fig. 6, (e)-(h)). The concentration differences between the two interfaces ($\Delta c = c_{LI} - c_{HI}$) decrease with temperature.

3.3. CO₂ flux to the crystal surface, molar volume of hydrate and its hydration number

The hydrate growth rate can be measured by the rate of CO₂ consumption when the pseudo-steady-state approximation is made. That is, at any instant the rate of CO₂ consumption by the formation of hydrate is assumed to be equal to the rate of CO₂ consumption from the liquid CO₂ phase [1]. In this study, the CO₂ consumption is accomplished by the continuous migration of carbon dioxide from the liquid CO₂ phase to the hydrate through the aqueous solution. According to Fick's law, the migration of CO₂ in fluid is determined by the concentration gradient and the diffusion coefficient. As the concentration difference between the liquid CO₂-aqueous interface and hydrate-aqueous interface (Δc) at fixed T and P is constant, the diffusion flux J of the CO₂ across a unit area perpendicular to the diffusion path to the growing surface of hydrate crystal can be described by Fick's first law:

$$J = -D_{CO_2} \frac{\rho_{sol} (c_{LI} - c_{HI})}{L_{sol,t}} = -D_{CO_2} \frac{\rho_{sol} \Delta c}{at+b} \quad (2)$$

where c_{LI} and c_{HI} are the concentrations of carbon dioxide at the liquid CO₂-aqueous interface and hydrate-aqueous interface, respectively in mol/kg H₂O, ρ_{sol} is the density of aqueous solution in kg/m³ and is calculated from Song et al. [17], $L_{sol,t}$ is the length of aqueous solution at time t , a and b are the coefficients of the linear relationships between $L_{sol,t}$ and t , the values of a and b for each set of experiments

are shown in Fig. 4, D_{CO_2} is the diffusion coefficient of carbon dioxide in water in m^2/s . The diffusion coefficients were calculated using the formula established by Lu et al. [14]:

$$D_{\text{CO}_2} = D_0 \left(\frac{T}{T_s} - 1 \right)^m \quad (3)$$

where D_{CO_2} is the diffusion coefficient of carbon dioxide in water in m^2/s , T is the absolute temperature in K, $D_0 = 13.942 \times 10^{-9} \text{ m}^2/\text{s}$, $T_s = 227.0 \text{ K}$, and $m = 1.7094$. At constant temperature, the pressure effect on the diffusion coefficients of carbon dioxide in water is rather small [14].

Thus the CO_2 flux through the cross-section (A) in a given time period can be expressed as follow:

$$\begin{aligned} \int J A dt &= -DA\rho_{\text{sol}}\Delta c \int \frac{l}{at+b} dt = -DA\rho_{\text{sol}}\Delta c \int \frac{l}{(at+b)(at+b)} (at+b)' dt = -\frac{DA\rho_{\text{sol}}\Delta c}{a} \int \frac{l}{L_{\text{sol},t}} dL_{\text{sol},t} \\ &= -\frac{DA\rho_{\text{sol}}\Delta c}{a} (\ln L_{\text{sol},t} + C) = -\frac{DA\rho_{\text{sol}}\Delta c}{a} (\ln(at+b) + C) \end{aligned} \quad (4)$$

where C is the constant of integration.

The carbon dioxide consumption amount (moles), i.e. the moles of hydrate formation, is given by:

$$n_{\text{CO}_2} = \int_{t_1}^{t_2} J A dt = -\frac{DA\rho_{\text{sol}}\Delta c}{a} \ln(at_2+b) - \left[-\frac{DA\rho_{\text{sol}}\Delta c}{a} \ln(at_1+b) \right] \quad (5)$$

The volume of hydrate generated during the same time interval can be estimated by:

$$V_{\text{H}} = \pi r^2 \Delta L_{\text{H},t} = \pi r^2 (L_{\text{H},t_2} - L_{\text{H},t_1}) \quad (6)$$

The volume of carbon dioxide hydrate per mole of carbon dioxide is given by:

$$V_{m,H} = \frac{V_H}{n_{CO_2}} \quad (7)$$

The volume of solution consumed is:

$$V_{sol} = \pi r^2 \Delta L = \pi r^2 (L_{sol, t_2} - L_{sol, t_1}) \quad (8)$$

The molar volume of the solution ($V_{m, sol}$) can be calculated with the apparent molar volume of dissolved carbon dioxide V_ϕ , the molar volume of water (V_{m, H_2O}) and the molar fractions of carbon dioxide (x_{CO_2}) and water (x_{H_2O}) at a certain temperature and pressure:

$$V_{m, sol} = x_{H_2O} V_{m, H_2O} + x_{CO_2} V_\phi \quad (9)$$

where V_{m, H_2O} was calculated from Duan et al. [18], V_ϕ was calculated from Enick and Klara [19].

The number of moles of water consumed n_{H_2O} can be estimated by:

$$n_{H_2O} = \frac{V_{sol}}{V_{m, sol}} x_{H_2O} \quad (10)$$

where V_{sol} is the volume of the consumed aqueous solution, the $V_{m, sol}$ is the molar volume of the aqueous solution.

Thus the hydration number y can be derived from

$$y = \frac{n_{H_2O}}{n_{CO_2}} \quad (11)$$

The volumes of carbon dioxide hydrate per mole of water ($V_{m, H}$) can be calculated from the molar volumes of the solution ($V_{m, sol}$) and the ratios (R) between the volume of hydrate formation and the volume of solution consumed, i.e. the slopes shown in Fig. 7.

$$V_{m, H} = R V_{m, sol} \quad (12)$$

Using the equation (2) to (12), we calculated the hydration numbers and molar volumes of CO₂ hydrate. The results are listed in Table 1. The hydration number y of structure I hydrate is 5.75 for the ideal hydrate, but always the cage occupancies are less than 100% and the actual value of y depends on the conditions under which the hydrates were formed [14]. Numerous techniques have been used to independently measure or infer the hydration number. As shown in Table 2, there is a large discrepancy among the previously reported values for the hydration number of CO₂ hydrate, varying from 5.82 to 7.8. Although Uchida [27] points out that techniques which attempt to measure the hydration number directly suffer from many problems concerning sample preparation and assumptions made in analysis, our values of y between 7.09 and 7.67 are in good agreement with the hydration number of 7.3 derived by Bozzo et al. [28] from thermodynamic measurements, 7.24 to 7.68 derived by Uchida et al. [20] from Raman spectroscopy, 7.23 derived by Kang et al. [24] from calorimetry, and ≥ 7 derived by Ripmeester and Ratcliffe [23] from NMR spectroscopy. Additionally, Larson [29], Yoon et al. [30], Anderson [26] derived the hydration number from the dissociation enthalpy of CO₂ hydrate based on the Clausius–Clapeyron equation. The results were summarized in Anderson [26] and mostly smaller than those from direct measurements. It is not surprising because the premise of these methods is under equilibrium condition, which has an extremely slow growth rate to let the guest molecules occupy the large and small cages more fully.

The molar volume of CO₂ hydrate has been rarely reported in the literature. Sun

and Duan [14] assumed it is the same as that of CH₄ hydrate at the same temperature and pressure. However, the molar volume of the CO₂ hydrate (per mole of water) can be calculated from CO₂ hydrate density and corresponding hydration number reported in the literature as:

$$V_{m,H} = \frac{M_H}{y\rho_H} \approx \frac{44.010 + 18.015y}{y\rho_H} \quad (13)$$

where M_H is the hydrate molecular weight in g/mol, ρ_H is the CO₂ hydrate density in g/m³, y is the hydration number. The results are summarized in table 2. Our values of molar volumes, in the range of 21.7–22.0 cm³ per mole of hydrate in the temperature range of 275.15–283.15 K at 20 MPa and 40 MPa, are smaller than most of the reported experimental values, but are in agreement with the values measured by Aya et al. [21].

3.4. Kinetic process coupled surface reaction and mass transport

On the molecular level, hydrate growth can be considered to be a combination of three factors: (1) the kinetics of crystal growth at the hydrate surface, (2) mass transfer of components to the growing crystal surface, and (3) heat transfer of the exothermic heat of hydrate formation away from the growing crystal surface (Sloan and Koh [1]). Previous studies have generally considered that the change in the rate of crystal growth (dn/dt) was controlled by two steps: (1) diffusion from the bulk concentration to the crystal (equilibrium) interface and (2) reaction at the interface. Hence the driving force can be expressed as:

$$\frac{dn_H}{dt} = K'A_H(c - c_{eq}) \quad (14)$$

where c is the bulk fluid concentration, c_{eq} is the solution concentration at equilibrium in the presence of hydrate, A_H is the crystal surface area. As seen in Fig. 2, the shape of the crystal-aqueous interface remains unchanged at constant temperature and pressure and can be considered to be a conical surface, thus we use the formula of fan-shape area to estimate A_H . K' is the overall transfer coefficient which is expressed in terms of the coefficients for diffusion k_d and reaction k_r as:

$$\frac{1}{K'} = \frac{1}{k_d} + \frac{1}{k_r} \quad (15)$$

The overall resistance can be controlled by a low value of either of these individual coefficients; the mass transfer coefficient (k_d) controls crystallization when the reaction is very rapid relative to diffusion, and the reaction coefficient (k_r) controls crystallization when diffusion is much more rapid than reaction. Modifications of the driving forces to quantitatively model the hydrate growth phenomenon are made to the basic Equation (14) as follow: the concentrations (c) are replaced with fugacities as in the kinetic model of Englezos et al. [5], and the controlling process is considered to be the diffusion through the boundary layer at the vapor–liquid interface – here it is the interface between the liquid CO₂ and the aqueous water-rich phases – as in the Skovborg–Rasmussen model [6].

Most of the experiments reported were carried out in stirred tank reactors under conditions that heat and mass transfer resistances around the particle are eliminated, such that $k_d \gg k_r$ and $K' \approx k_r$. In our experiments, as previously described, diffusional mass transfer of CO₂ from liquid CO₂ phase to hydrate interface in aqueous solution plays a significant role in dynamic process of hydrate growth. Fig. 8 was plotted in

order to investigate the effects of diffusion to the hydrate growth kinetics.

The dimensionless modulus Π_H defined as the ratio of J_H , the CO₂ flux at the hydrate crystal surface, to J , the diffusive CO₂ flux through the aqueous phase, is given by the time derivative of $L_{H,t} / V_{m,H} / (D\rho_{sol} \Delta c / L_{sol,t})$.

$$\Pi_H = \frac{J_H}{J} = \frac{d(L_{H,t} / V_{m,H} / (D\rho_{sol} \Delta c / L_{sol,t}))}{dt} \quad (16)$$

As shown in Fig. 8a and 8b, Π_H , the changing of the vertical parameter $L_{H,t} / V_{m,H} / (D\rho_{sol} \Delta c / L_{sol,t})$ with time, is equivalent to the growth rate of hydrate against the corresponding CO₂ diffusion flux. Fig. 8c and 8d are Π_H versus time diagrams showing how the mass transfer and hydrate-crystal growth processes progressed during each experiment. Π_H are identical when the growth rates are constant corresponding to experiments (a)-(d) in Fig. 4. (Fig. 8a and 8c). This shows that the growth rates are proportional to the diffusion fluxes of CO₂. The controlling process is considered to be diffusion, i.e. mass transfer, $k_d \ll k_r$ and $K' \approx k_d$ in this case. Hence, the rate of the CO₂ hydrate growth is given by:

$$\frac{dn_H}{dt} = \Pi_H JA \quad (17)$$

where Π_H is equivalent to flux controlled coefficient, and can be represented by the slope of the line shown in Fig. 8a. Combining Equations (2), (14), and (17) thus leads to the formula:

$$K' \approx k_d = \frac{\Pi_H DA}{L_{sol,t} A_H} \quad (18)$$

It can be seen that the mass transfer coefficient k_d is a function of diffusion distance $L_{sol,t}$ with the assumption of constant temperature and pressure, and it

gradually increases with the decrease of $L_{\text{sol}, t}$. If $L_{\text{sol}, t}$ remains constant or the changes of $L_{\text{sol}, t}$ are sufficiently small, k_d can be regarded as a constant, thus the growth rate is approximately constant. However, when k_d increases to approach the reaction coefficient k_r , k_r can't be ignored.

As shown in Fig. 4e and 4f, the growth rates of CO₂ hydrate are increase with the decreasing distance between the hydrate-aqueous interface and the liquid CO₂-aqueous interface when $L_{\text{H}, t} < 3$ mm. Meanwhile, the CO₂ concentration measured at the hydrate-aqueous interface of the two sets of experiments at 20 MPa and 280.15 K increased from 1.3 mol/kg H₂O (Fig. 4c, 20 MPa and 280.15 K (1)) to 1.4 mol/kg H₂O (Fig. 4e, 20 MPa and 280.15 K (2)) as $L_{\text{H}, t}$ decreased from 5.5–7 mm to less than 3mm. This increase can possibly be ascribed to (1) the limited rate of reaction kinetic at the hydrate crystal surface, or (2) the increase in the equilibrium concentration c_{HI} responding to the increase in the local temperature exceeding the experimental temperature T_{ex} due to the effect of heat release. The asymmetry of the Raman spectrum of water is a function of temperature. Comparing the spectra obtained at the hydrate-aqueous interface and the liquid CO₂-aqueous interface of the two sets of experiments at 20 MPa and 280.15 K, the O–H stretching bands at 2800–3800 cm⁻¹ show no significant difference. Thus we assumed that the experimental system was held isothermal at the prescribed temperature T_{ex} (= 280.15 K or 283.15 K) and the effect of heat release is negligibly small. Then the significant deviation of J_H from J ($J_H < J$) observed when $L_{\text{H}, t} < 3$ mm (Fig. 8b) can be ascribed to the limited rate of reaction kinetics at the

hydrate-crystal surface. The rates of diffusional mass transfer of CO₂ were greater than the consumption rates of CO₂ by hydrate growth, indicating that there were excess CO₂ unconsumed. The controlling process is considered to be converted into the interfacial reaction, and $K' \approx k_r$ at the inflection point where Π_H is equal to zero (Fig. 8b, 20 MPa and 280.15 K (2)). Then the values of Π_H become negative. This is because the actual diffusion fluxes are smaller than the calculated value due to the decreasing concentration differences. Thus we can obtain the reaction coefficient k_r by seeking the slope of dn_H/dt vs. $A_H(c-c_{eq})$ at the inflection point based on equation (15). The values of coefficients for diffusion k_d and reaction k_r obtained in the current study are listed in Table 3.

Numerous studies have been performed to determine the reaction rate constant of CO₂ hydrate formation in semi-batch stirred-tank reactors. The results are summarized in Table 4.

Chun and Lee [31], Malegoankar et al. [32], and Clark and Bishnoi [10] used the fugacity to express the driving force and gave the reaction rate constant in mol/(m² MPa s). Sloan and Koh [1] noted that with the assumptions (a) constant temperature and pressure, (b) ideal liquid solutions, and (c) constant total molar concentration (c_{tot}), the fugacity is related to the concentration by the expression:

$$f_i = \left(\frac{\Phi_i^L P}{c_{tot}} \right) c_i \quad (19)$$

where Φ_i^L is the fugacity coefficient. So that the coefficient K in mol/ (m² MPa s) can be calculated as:

$$K = \left(\frac{c_{\text{tot}}}{\Phi_i^L P} \right) K' \quad (20)$$

It can be seen that, when the rate-determining step for the hydrate growth is interfacial reaction, both the concentration model and the fugacity model well describe the growth kinetics of hydrate, and they can be converted to each other. This is consistent with the models of Englezos et al. [5] and Hashemi et al. [7]. However, when the rate-determining step is mass transfer, the overall transfer coefficient K' or K is still a variable, such that the concentration or fugacity model cannot completely express the driving force, but our results show that it can be well described by the flux controlled model. Therefore, the classical models should be further modified to better reveal the whole process of hydrate growth kinetics, and a critical (maximum) value of diffusion flux separates the rate-determining steps, where the growth of hydrate is diffusion controlled when diffusion flux is low and interfacial reaction controlled after the diffusion flux reaches that critical value. The calculated coefficient K values are listed in Table 3. Compared to the previous studies, the value obtained in the current study for the reaction rate constant of CO_2 hydrate formation at 280.15 K and 20 MPa, 1.31×10^{-6} m/s or 5.76×10^{-4} mol/(m² MPa s), is in relative agreement with the value reported by Malegoankar et al. [32], but is an order of magnitude smaller than those obtained by Clark and Bishnoi [10] and four orders of magnitude larger than those obtained by Hashemi et al. [7] and Bergeron and Servio [33]. These discrepancies could be due to three major factors. Firstly, accurate estimation of the particle size and surface area of hydrate crystal is difficult in previous studies. Hashemi and Macchi [7] reevaluated the intrinsic

kinetic rate constant K_r of the experimental of Clark and Bishnoi [10] using the modified model based on a concentration driving force. The resulting K_r at 277.15 K and 21.87 bar is 1.20×10^{-8} m/s with the particle surface area obtained by the simplified population balance, while it is 4.25×10^{-5} m/s with the measured particle surface area. Secondly, some of them do not correct the Englezos et al. [5] model for the particle size inconsistency. Malegoankar et al. [32] noted that Englezos et al. [5] represented particle size by its radius in deriving the model equations, but defined the initial conditions using the particle size as the particle diameter. They re-determined the intrinsic kinetic rate constants, K^* , for methane hydrate formation using the experimental data from Bishnoi et al. [34, 35] by considering the particle size as the particle diameter consistently in deriving the model equations, and they are about 5 times of those values reported by Englezos et al. [5]. Furthermore, previous works were carried out in isochoric semi-batch stirred tank reactors. The increase in solution temperature and the decrease in pressure during the hydrate formation should be taken into account in order to accurately calculate f_{eq} for the kinetic model.

4. CONCLUSIONS

We developed a high-pressure in-situ non-invasive technique to measure the solute concentration distribution in the solution around a growing crystal, in order to study the rate-dominant process of crystal growth coupled surface reaction and mass transport. Carbon dioxide hydrate growth in water were observed at 20 and 40 MPa and 275.15, 278.15, 280.15 and 283.15 K. The growth rate is diffusion controlled

when diffusion flux is low, and becomes interfacial reaction controlled after the diffusion flux reaches a critical value. It was seen that the mass transfer coefficient k_d varied with diffusion distance, which affected the concentration gradient in the solution between the hydrate-aqueous interface and the liquid CO₂-aqueous interface. We demonstrated that, the hydrate growth rates could change a lot under constant driving force, such as under the same degrees of super-saturation, super-cooling or over-pressurization of the system; however the growth rates depend on the mass transfer (diffusion) flux to the surface of the hydrate crystal. We believe that the technique for single crystal kinetic study presented here is useful for the investigation of the effect of additives on hydrate crystal growth and morphology.

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Fig. 1. A schematic diagram showing the distribution of the growing hydrate crystal, the aqueous solution, and the carbon dioxide rich section in the capillary high-pressure optical cell. The initial length of the aqueous solution between its interface with carbon dioxide section and the closed end of the tube is about 1.85 cm. Raman spectra were collected at the sample spots LI (20 μm from the liquid CO₂-aqueous solution interface), L1, L2, L3 (fixed positions between LI and HI), HI (20 μm from the hydrate-aqueous solution interface) and H0 (20 μm from hydrate-aqueous solution interface near the closed end of tube) during hydrate growth.

Fig. 2. Photos showing a section the HPOC fully filled with hydrate crystal, which grew gradually with time and pushed both of the interfaces between hydrate and aqueous solution (right diagram; HI shown in Fig. 1) and between aqueous solution and liquid CO₂ section (left diagram; LI shown in Fig. 1) toward left in the hydrate-aqueous solution-liquid CO₂ system. No movement was observed for the hydrate-aqueous solution interface near the closed end of tube (H0 shown in Fig. 1) after reaching equilibrium during the experiment. The internal diameter of the capillary cell is 50μm.

Fig. 3. P–T diagram of the three–phase equilibria in the system carbon dioxide–water. H, CO₂ hydrate; L_w, liquid water, L_{CO₂}, liquid CO₂; V_{CO₂}, vapor CO₂; Q, Quadruple point; —, Sun and Duan [15]; $\blacklozenge$, Experimental conditions of this study.

Fig. 4. Increase in length of the section in the HPOC occupied by hydrate crystal and the change in length of the section in the HPOC occupied by aqueous solution during the growth of hydrate crystal at 20 and 40 MPa and fixed temperatures. They were measured using a screw micrometer with an accuracy of 0.01 mm.

Fig. 5. Raman spectra of dissolved carbon dioxide (CO_2 , around 1390 cm^{-1}) and water (H_2O , around 3486 cm^{-1}), the dashed lines between 1200 and 1430 cm^{-1} and between 2650 and 3900 cm^{-1} showing the base lines for calculating the Raman peak heights of CO_2 and H_2O .

Fig. 6. (a)-(d): Concentrations of CO₂ at various sample spots of the aqueous solution (m_{CO_2} , mol/kg H₂O) during the growth of carbon dioxide hydrate at 20 and 40 MPa and fixed temperatures. $\square$ LI, liquid CO₂-aqueous solution interface; $*$ L1; Δ L2; $\times$ L3; $\diamond$ HI, hydrate-aqueous solution interface; $+$ H0, hydrate-aqueous

589 solution interface near the closed end of tube. LI and HI were moving during the
590 growth of hydrate, whereas L1, L2 and L3 were fixed positions. (e)-(h): The right
591 side diagrams show the linear concentration gradients in the aqueous solution
592 between the two interfaces at fixed times (*t*). The spectral acquisition positions were
593 read from the micrometer screw scale.

Fig. 7. Experimental results showing the linear relationship between hydrate formation and aqueous solution consumption. Plotted are the data measured by the screw micrometer. The slopes are equivalent to the ratios between the molar volumes of hydrate and aqueous solution.

Fig. 8. (a)-(b): The changing of the vertical parameter $L_{H,t} / (V_{m,H} / (D\rho_{sol}\Delta c / L_{sol,t}))$ with time, is equivalent to the growth rate of hydrate against the corresponding CO_2 diffusion flux. The slopes of the trend lines are the time derivative of $L_{H,t} / (V_{m,H} / (D\rho_{sol}\Delta c / L_{sol,t}))$, defined as Π_H . (a) shows that the growth rates of CO_2 hydrate crystal was controlled by CO_2 diffusion flux. (b) shows that the rates of diffusional mass transfer of CO_2 were greater than the consumption rates of CO_2 by hydrate growth. (c)-(d): Π_H versus time diagrams showing how the mass transfer and hydrate crystal growth processes progressed during each experiment. (c) and (d) are the values of Π_H corresponding to the four groups of experiments in (a) and the two groups of experiments in (b) respectively.

Table 1

Calculated molar volume, density and hydration number of CO₂ hydrate

T (K)	P (MPa)	V_{ϕ} (cm ³ /mol)	x_{CO_2}	$V_{\text{m, sol}}$ (cm ³ /mol)	$V_{\text{m, H}}$ (cm ³ /mol)	y	ρ_{H} (kg/m ³)
275.15	20	38.74	0.0169	18.20	21.74	7.67	1072
278.15	20	37.59	0.0195	18.23	21.94	7.09	1081
280.15 (1)	20	36.90	0.0231	18.29	21.91	7.10	1078
280.15	40	36.90	0.0233	18.14	21.72	7.42	1077
280.15 (2)	20	36.90	0.0231	18.29	21.98	–	–
283.15	20	35.94	0.0277	18.35	21.82	–	–

Notes: V_{ϕ} is the apparent molar volume of dissolved carbon dioxide in cm³/mol; x_{CO_2} is the molar fractions of carbon dioxide; $V_{\text{m, sol}}$ is the molar volume of the aqueous solution in cm³/mol; $V_{\text{m, H}}$ is the volumes of carbon dioxide hydrate per mole of water in cm³/mol; y is the hydration number; ρ_{H} is the CO₂ hydrate density in kg/m³.

Table 2

Reported values of the density/molar volume and hydration number y for carbon dioxide hydrate

Reference	Technique	T, P	density (kg/m ³)	y	molar volume (cm ³ /mol)
Uchida [20]	Raman	282.2 K, 4.56 MPa	1040	7.68	22.8
		276.2 K, 3.93 MPa	1060	7.24	22.7
Aya et al. [21]	Pressure drop	30 MPa	1090–1110	6–7.8	21.7–22.8
Ohmura and Mori [22]	crystallographic prediction		1046–1130	5.82–7.8	22.6
Ripmeester and Ratcliffe [23]	NMR			≥ 7.0	
Kang et al. [24]	Calorimetry	273.65 K		7.23	
Udachin et al. [25]	X-ray diffraction	276 K, 3.8 MPa	1120	6.2	± 22.4
Anderson [26]	Clapeyron equation	272–283 K		6.6	to 5.6
Sun and Duan [15]	Model	268–283 K 1–6.2 MPa		6.09	to 22.4 to 6.55 22.6

Table 3

The overall transfer coefficient and reaction rate constant of CO₂ hydrate formation determined in this work

T (K)	P (MPa)	K' (m/s)	K (mol/(m ² MPa s))
275.15	20	$7.69 \times 10^{-8} \sim 8.93 \times 10^{-7}$	$3.98 \times 10^{-5} \sim 4.63 \times 10^{-5}$
278.15	20	$9.66 \times 10^{-8} \sim 1.35 \times 10^{-7}$	$4.50 \times 10^{-5} \sim 6.29 \times 10^{-5}$
280.15 (1)	20	$1.24 \times 10^{-7} \sim 1.58 \times 10^{-7}$	$5.46 \times 10^{-5} \sim 6.95 \times 10^{-5}$
280.15 (2)	20	$4.02 \times 10^{-7} \sim 1.31 \times 10^{-6a}$	$1.77 \times 10^{-4} \sim 5.76 \times 10^{-4a}$
283.15	20	$3.79 \times 10^{-7} \sim 6.23 \times 10^{-7}$	$1.55 \times 10^{-4} \sim 2.95 \times 10^{-4}$
280.15	40	$\sim 1.15 \times 10^{-7}$	$3.86 \times 10^{-5} \sim 3.88 \times 10^{-5}$

^a $K' = 1.31 \times 10^{-6}$ m/s or $K = 5.76 \times 10^{-4}$ mol/(m² MPa s) is the coefficient at the inflection point equivalent to the reaction coefficient k_r .

624 **Table 4**

625 Reported values of reaction rate constant (K^*) for CO₂ hydrate formation

Reference	T (K)	K^*
Chun and Lee [31]	275.2 ~ 279.2	$0.69 \times 10^{-5} \sim 0.71 \times 10^{-5} \text{ mol/m}^2$ MPa s
Malegoankar et al. [32]	274 ~ 278	$1.90 \times 10^{-4} \sim 4.90 \times 10^{-4} \text{ mol/m}^2$ MPa s
Clark and Bishnoi [10]	274.15 ~ 279.65	$3.214 \times 10^{-3} \sim 6.423 \times 10^{-3}$ $\text{mol/m}^2 \text{ MPa s}$
Hashemi et al. [7]	277.15	$1.20 \times 10^{-8} \text{ m/s}$
Bergeron and Servio [33]	275.5 ~ 279.3	$1.8 \times 10^{-8} \sim 1.8 \times 10^{-7} \text{ m/s}$

626