

Synergistic promotion of CO₂ hydrate kinetics enabled by coupling magnesium with amino acid[#]

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ABSTRACT

In this study, we systematically investigated an environmental-benign kinetic promoter (*L*-leucine, *L*-Leu) coupling magnesium to enhance CO₂ hydrate formation at the pressure of 3.5 MPa and temperature of 275.2 K. The induction time (t_{ind}) of CO₂ hydrate was reduced to 696.65 minutes in the addition of 1.0 wt% *L*-leu. When magnesium was introduced to enhance CO₂ hydrate formation, it showed a superior promotion effect on reducing t_{ind} to less than 10 s. In pure water, the dense CO₂ hydrate film at the gas-liquid interface blocked the mass transfer and the CO₂ gas uptake was 10.44 V^g/V^w. Therefore, magnesium was applied to trig CO₂ hydrate nucleation coupling *L*-leu to realize rapid CO₂ hydrate formation, followed by rapid *P* drop with the CO₂ gas uptake of 78.77 V^g/V^w. In the coupling system, CO₂ hydrate formation rate was promoted effectively with the t_{90} of 85.08 min under the static condition. This work contributes to offering considerable enhancement in the kinetic process of CO₂ hydrate formation. which can be utilized for various hydrate-based technologies such as CO₂ sequestration.

Keywords: CO₂ hydrate, ultra-rapid nucleation, kinetics, amino acid, magnesium, hydrate-based CO₂ sequestration

NONMENCLATURE

Abbreviations	
C_{L-le}	<i>L</i> -leucine concentration (wt%)
Symbols	
n	number of moles (mol)
N_g	normalized CO ₂ gas uptake in CO ₂ hydrate (mol/mol)
P	pressure (MPa)
r	initial ratio of aqueous solution and CO ₂ gas (mol/mol)
T	temperature (K)

t_0	the time when CO ₂ reaches solubility equilibria
t_{90}	the time period of achieving 90% of CO ₂ gas uptake in CO ₂ hydrate (min)
t_c	the time point when CO ₂ was consumed rapidly
t_{ind}	induction time, the time period between CO ₂ reaching solubility equilibria (Mg triggering) and CO ₂ hydrate formation (min)
t_n	the time when the first CO ₂ hydrate crystal was observed
V	volume (mL)
X_{CO_2}	CO ₂ conversion rate (mol/mol)
X_{H_2O}	H ₂ O conversion rate (mol/mol)

1. INTRODUCTION

The global challenge of climate change has intensified the urgency to explore sustainable strategies for mitigating carbon dioxide (CO₂) emissions^[1]. Among various approaches, carbon capture utilization, and storage (CCUS) has emerged as a promising pathway to decrease CO₂ release into the atmosphere^[2]. One notable method within CCUS involves the utilization of gas hydrates, which offer a potentially efficient means of carbon sequestration^[3]. Gas hydrates are a kind of non-stoichiometric crystalline compounds in which light gas molecules (guest) such as carbon dioxide (CO₂), are captured by hydrogen-bonded water cages (host) at low temperature and high pressure^[4]. However, the practical application of CO₂ hydrates in large-scale CCUS operations faces significant challenges, particularly concerning the nucleation and growth kinetics of hydrate.

In recent years, the incorporation of magnesium (Mg) metal as a promoter in CO₂ hydrate formation processes has garnered considerable attention due to its

ability to enhance nucleation kinetics and promote hydrate formation^[5]. If Mg and amino acid are coupled together to achieve synergistic promotion, thereby offering potential improvements in the efficiency and feasibility of CO₂ sequestration technologies.

In this work, the effect of Mg coupled with amino acid on the kinetics and morphology of CO₂ hydrate were systematically investigated under static conditions. The purpose is to achieve on-demand formation of CO₂ hydrate and to reveal the synergistic promotion mechanism.

2. EXPERIMENTAL SECTION

2.1 Materials

All chemicals used in this study are of analytical grade. L-Leucine (L-leu, purity > 99.0%) was purchased from Aladdin Biochemical Technology Co., Ltd. CO₂ gas (purity > 99.8%) was purchased from Shenzhen Huatepeng Special Gas Co., Ltd. Ultra-pure deionized water made in the laboratory was used in all experiments. Pure magnesium metal (99.9% purity) was purchased from High Purity Metal Materials Co., Ltd. The Mg was mirror-polished with a surface roughness of 50 nm and was stored under vacuum before using it. The Mg sheets used in all experiments were 5 mm in width, 0.4 mm in thickness and 45.0 mm in length.

2.2 Experimental apparatus

Fig. 1 shows a schematic diagram of the experimental setup used for the CO₂ hydrate formation and dissociation experiments in this study. The experimental setup includes a high-pressure CO₂ hydrate reactor made of quartz glass and designed for a working pressure of 10.0 MPa. The reactor with full visualization is used to obtain the whole process of morphological evolution of the gaseous-aqueous-solid three phases in the system. The internal shape of the reactor is cylindrical with a diameter of 40.0 mm and a height of 78.0 mm. The total volume of the reactor is approximately 100.0 mL. The reactor is placed in a transparent water bath connected to a circulating cooler for temperature control. A high-resolution digital CCD camera is mounted on the side of the reactor to capture the CO₂ hydrate morphology.

The manual release device for Mg sheet is installed on the top of the reactor. The manual is retractable to ~2.5 cm. A 3 mm diameter hole is punched in the Mg sheet and connected to the manual trigger device. A needle valve is installed on the top of the reactor for CO₂ injection. The SENEX (DG2113-B-16/B) pressure sensor (P range of 0-16.0 MPa, accuracy of 0.25% F.S.) and a Pt-100-type thermocouple (T range of -20-200 °C with an accuracy of ± 0.1 K) are attached to measure the real-

time pressure and temperature data. The P and T are recorded using a data acquisition system that records the requisite data at intervals of 5 s. The real-time morphological evolution of the CO₂ hydrate is recorded every 60 s.

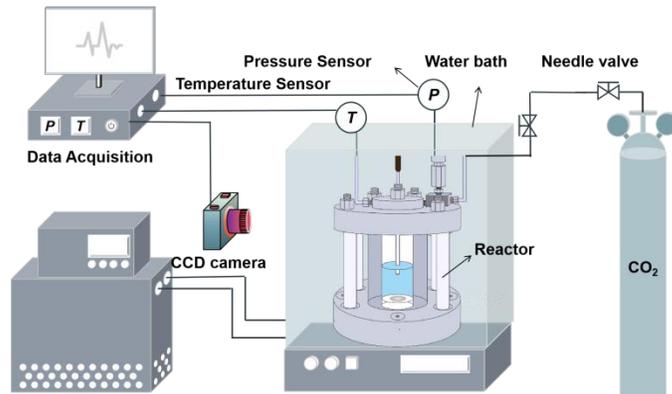


Fig. 1. Schematic diagram of the experimental setup for CO₂ hydrate formation and dissociation

2.3 Experimental procedure

The procedure of CO₂ hydrate formation and dissociation is shown in Fig. 2. Firstly, the reactor is dried after washing it with deionized water thrice. The pre-cooled amino acid solution (L-leucine) is injected to the reactor with a syringe. Then connect the Mg sheet and seal the reactor before submerging it into the water bath. The reactor is cooled to $T = 275.2$ K, and CO₂ gas is injected to $P = 3.5$ MPa after purging it three times with 0.5 MPa CO₂. The dissolution process of CO₂ gas into the aqueous solution is considered to be complete when the rate of pressure drop is less than 0.1 MPa/h. Mg sheet is stretched to the gas-liquid interface to induce CO₂ hydrate formation.

2.4 Calculation method

The calculation of CO₂ gas uptake during CO₂ hydrate formation should consider the solubility of CO₂ in aqueous solution. The volume-balance method is employed, following the work of Yin et al^[6]. The normalized CO₂ gas uptake (N_g , mol CO₂/mol H₂O) in CO₂ hydrate is used for analyzing the kinetics. Details of the calculation methods have been reported in our previous work^[7].

To better understand the gas capacity of CO₂ hydrate, CO₂ gas uptake (v/v) in hydrate is calculated as follows,

$$CO_2 \text{ gas uptake (v/v)} = \frac{22.4 \times 1000}{18.0} N_g \quad (1)$$

where 22.4 L/mol is the density of CO₂ gas, 18.0 is mL/mol is the density of H₂O.

The initial ratio of CO₂ gas / aqueous solution is calculated as follows,

$$r = \frac{n_0^{H_2O}}{n_0^{CO_2}} \quad (2)$$

where n_0^G is the initial number of moles of CO₂ gas, and $n_0^{H_2O}$ is the initial number of moles of aqueous solution.

The volume of Mg sheet of calculated as follows ,

$$0.5 \times 0.04 \times 4.5 = 0.09 \text{ cm}^3$$

The total volume of the reactor is 100 cm^3 . The volume of Mg sheet is only 0.9% of the reactor, therefore the effect of Mg addition on the CO_2 gas volume is negligible in this study.

3. RESULTS AND DISCUSSION

3.1 Effect of L -leu concentration on CO_2 hydrate formation in the static system

To better understand the mechanism of amino acid L -Leu on promoting CO_2 hydrate, we investigate the kinetics and morphology of CO_2 hydrate formation in L -Leu solution of 0.1, 0.3 and 1.0 wt% in the static system. At low concentration (below the kickoff concentration 0.3 wt%), dense CO_2 hydrate film formed at the gas-liquid interface. After ~ 10 h, only thin CO_2 hydrate film formation along the reactor wall was observed with limited pressure drop ($< 0.01 \text{ MPa}$). Results show that weak promotion effect of 0.1 wt% L -Leu on CO_2 hydrate formation kinetics in the static system. Similar promotion pattern was observed as in the stirring system in our previous study^[2].

Fig. 3 shows P - T trajectory and P , T evolution of CO_2 hydrate formation in 1.0 wt% L -Leu solution. After CO_2 gas injection, the dissolution stage commenced. After ~ 6 hours, the pressure change was less than 0.05 MPa/h , indicating the completion of dissolution, recorded as t_1 (point A). Following an extended induction period, CO_2 hydrate formation occurred, marked as t_n (point B), where a distinct temperature peak was observed, followed by a pressure drop as the hydrates grew. Approximately 6 hours later which is named deflection time^[8], a second significant temperature rise and rapid pressure were observed, indicating substantial hydrate formation and gas consumption.

Fig. 4 depicts the morphological evolution of the CO_2 hydrate formation process in a 1.0 wt% L -Leu solution under an unstirred system. After the initial gas injection, no hydrates were observed in the equilibrium region, and the solution remained clear (Fig. 4a). At time t_n , hydrate nucleation occurred, and turbidity changes were observed at the bottom of the reactor (Fig. 4b). As hydrate particles continuously formed from the dissolved gas, an increase in solution turbidity was visible (4b to 4g). This process was accompanied by a slow pressure decrease, attributed to the formation of hydrates from dissolved CO_2 , resulting in the dissolution of CO_2 from the gas phase and subsequent hydrate formation.

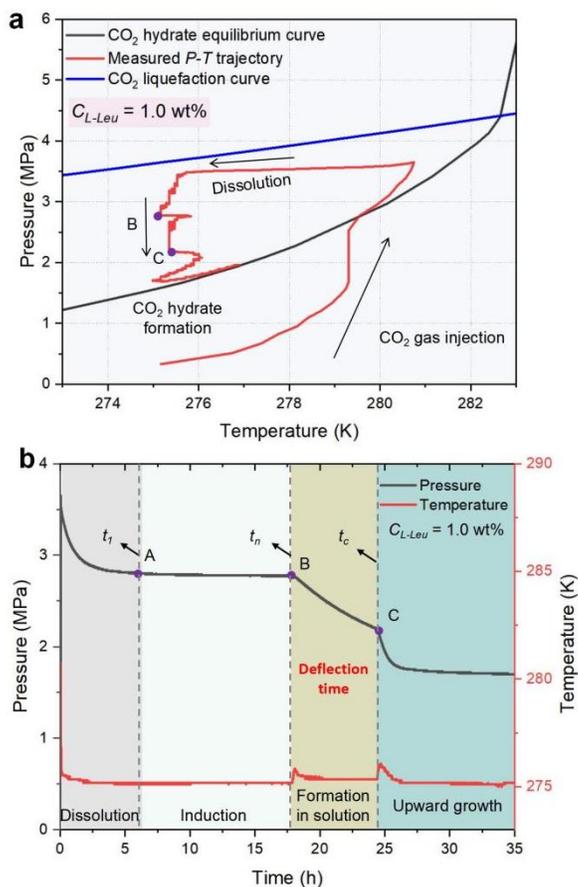


Fig. 3. (a) Experimental measured P - T trajectory in relation to the CO_2 hydrate phase equilibrium curve and the CO_2 liquefaction curve. (b) P , T evolution during CO_2 hydrate formation at $C_{L\text{-Leu}} = 1.0 \text{ wt\%}$ in the static system

CO_2 hydrate growth was observed at the gas-liquid interface (5 h) after more than 6 hours, which was 386 minutes after t_n . This time is referred to as the deflection time, representing the lag period before the amino acid exhibited a promoting effect on hydrate growth. It is evident that the formation of hydrates from dissolved CO_2 gas occurs at a relatively slow rate. The formation of hydrates in the solution induces the subsequent hydrate formation process at the interface. This phenomenon, characterized by the deflection time, is attributed to the amino acid's promoting effect. After t_c , substantial wall-climbing growth of hydrates in the gas phase was observed, accompanied by significant CO_2 gas uptake during this stage. This suggests that the primary factor influencing the growth rate is the mass transfer of CO_2 from the gas phase to the aqueous solution. Consequently, the deflection time is shorter in stirred systems compared to static systems, where the deflection time is prolonged. Therefore, narrowing the deflection time and enhancing the CO_2 hydrate formation kinetics are crucial for the amino acid L -Leu to

exhibit its promotion effect, which is also the key factor in realizing on-demand rapid CO₂ hydrate formation.

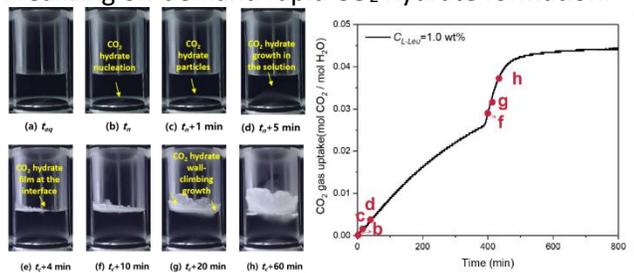


Fig. 4. Morphological evolution of CO₂ hydrate in 1.00 wt% L-Leu solution at $P_0 = 3.5$ MPa and $T = 275.2$ K

3.2 Addition of Mg on CO₂ hydrate formation kinetics and morphology in pure water

In this study, we firstly introduce Mg sheet to the realize the on-demand CO₂ hydrate formation. Fig 5 shows the morphological evolution of CO₂ hydrate formation in pure water triggered by Mg sheet. During the CO₂ gas dissolution period, Mg sheet was in the gas phase, then the Mg sheet was immersed into the solution about 4 mm as mentioned in the experimental procedure. Within 10 s, CO₂ hydrate nucleation was observed at the gas – solution interface near the Mg sheet (Fig. 5). In this regard, the t_{ind} was identified as 0. Therefore, the on-demand CO₂ hydrate formation was realized. When magnesium was introduced to enhance CO₂ hydrate formation, it showed a superior promotion effect on reducing t_{ind} to less than 10 s. In pure water, the dense CO₂ hydrate film at the gas-liquid interface blocked the mass transfer and the CO₂ gas uptake was 10.44 V^g/V^w.

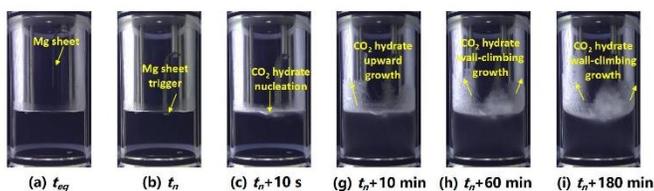


Fig. 5. Morphological evolution during CO₂ hydrate formation triggered by Mg sheet in pure water

3.3 Enhanced CO₂ hydrate formation kinetics and associated morphology coupled with L-leu

In this section, we perform experiments to examine if there is a synergistic enhancement of coupling Mg sheet and L-leu on CO₂ hydrate formation. The normalized CO₂ gas uptake and comparison of t_{90} are shown in Fig.6.

As reported in previous study, the induction time of CO₂ hydrate was not decreased as the increase of C_{L-leu} . L-leu showed limited promotion effect on CO₂ hydrate nucleation, weaker than the stochastic nature of hydrate nucleation. Even in the stirring condition, t_{ind} was higher to ~3 h. Therefore, magnesium was applied to trig CO₂ hydrate nucleation coupling L-leu to realize rapid CO₂

hydrate formation, followed by rapid P drop with the CO₂ gas uptake of ~0.055 mol/mol (78.77 V^g/V^w) (Fig. 6a). In the coupling system, CO₂ hydrate formation rate was promoted effectively with the t_{90} of 85.08 min under the static condition (Fig. 6b).

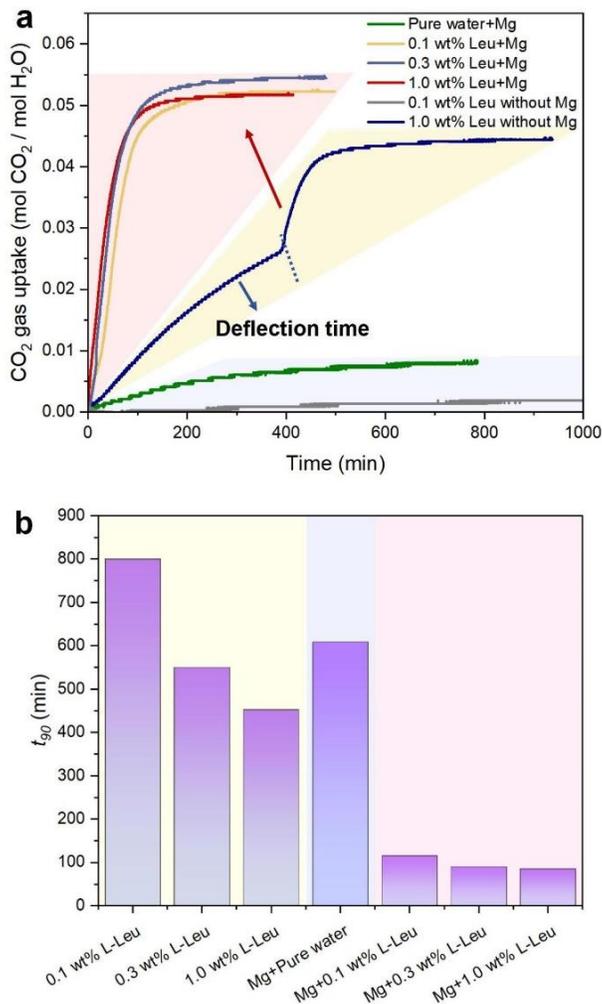


Fig. 6 (a) Normalized CO₂ gas uptake profiles during CO₂ hydrate formation with and without Mg sheet trigger for L-leu concentrations varying from 0.10-1.00 wt% at $T = 275.2$ K and $P_0 = 5.5$ MPa in the static system. (b) Comparison of t_{90} (time required to achieve 90% CO₂ final gas uptake in hydrate).

Fig. 7 depicts the morphology of CO₂ hydrate formation process in the coupling system. CO₂ hydrate nucleation was triggered by Mg sheet at the gas-liquid interface and the snow-like CO₂ hydrate growth along the wall. CO₂ hydrate growth in both directions was observed, along with superior CO₂ uptake.

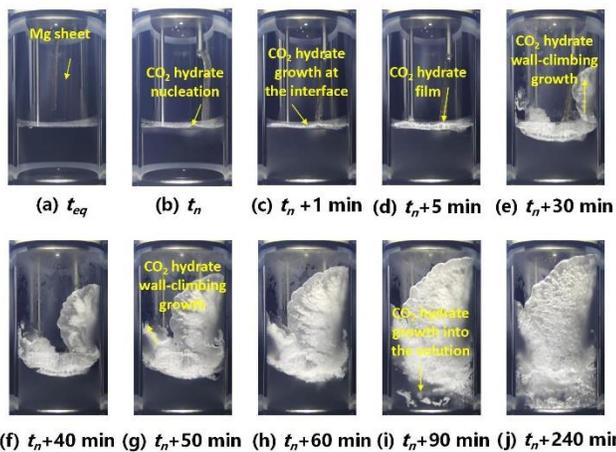


Fig. 7 Morphological evolution during CO₂ hydrate formation triggered by Mg sheet in 0.1 wt% L-leu

4. CONCLUSIONS

In this study, we systematically investigated an environmental-benign kinetic promoter (L-leucine, L-Leu) coupling magnesium to enhance CO₂ hydrate formation. The following conclusions can be drawn.

(a) L-Leu promotes CO₂ hydrate kinetics in the stationary system: the induction time is long (>10 h) and stochastic; there is still a limitation of the initiation concentration (0.3 wt%) of L-Leu; there is a lag time of the promotion effect (deflection time > 6 h), and the kinetic growth rate is slow ($t_{90} \sim 9$ h);

(b) A static enhancement method of magnesium-based metal-coupled amino acid L-Leu to promote the nucleation and growth of CO₂ hydrate is proposed to achieve controllable nucleation ($t_{ind} < 10$ s) and rapid growth ($t_{90} < 90$ min) in the stationary system.

(c) Magnesium metal achieves on-demand nucleation of CO₂ hydrate in the static regime with only limited CO₂ gas uptake (< 0.01 mol/mol) in pure water; Magnesium-based metal-coupled amino acid L-Leu system: magnesium metal triggers rapid nucleation of CO₂ hydrate with the CO₂ gas uptake of 78.77 V^g/V^w; CO₂ hydrate is able to grow rapidly after nucleation and exhibits significant wall-climbing growth. There is no limitation of the kickoff concentration, and the kinetic promotion effect is evident in 0.1 wt% L-Leu solution.

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