Study on dissociation characteristics of CO_2 hydrate with THF for cooling application

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HIGHLIGHTS

- A kinetic model is developed to predict the activation energy for CO_2-THF hydrate.
- An experimental correlation for CO_2-THF hydrate dissociation rate is developed.
- The activation energy for CO_2 hydrate with THF is estimated as 193.6 kJ/mol.
- The enthalpy of the CO_2-THF hydrate is measured to be 263.5 kJ/kg-H_2O.
- The COP of the CO_2–THF hydrate cooling system is estimated as 14.26.

ARTICLE INFO

ABSTRACT

The CO_2 hydrate with tetrahydrofuran (THF) is used to study the kinetics of CO_2 hydrate dissociation. The experiments are conducted at temperature (279–280) K and moderate pressures (0.3, 0.4 and 0.5 MPa), which are suitable for the cooling application. These experimental conditions can also make sure that there is no dissociation of the THF hydrate. No kinetic model and experimental correlation to calculate the activation energy and dissociation rate of the CO_2 hydrate with THF has been found. From this study, it is found that the dissociation rate strongly depends on the temperature. A kinetic model is developed to predict the activation energy for CO_2-THF (5.56 mol%) hydrate, which fits well the experimental data with the error bands of ±8.2%. An experimental correlation for CO_2-THF hydrate dissociation rate is developed with the error bands of ±26.0%, which can be used to calculate the dissociation rate for estimation of cooling load for district cooling application. It is found that the activation energy ΔE for CO_2 hydrate with THF is estimated as 193.6 kJ/mol and the enthalpy of the CO_2-THF hydrate is measured to be 263.5 kJ/kg-H_2O. Based on the results, the CO_2 hydrate district cooling system with CO_2–THF hydrate slurry is simulated for 5000 RT, and the COP is estimated as 14.3.

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1. Introduction

The CCS (Carbon Capture and Storage) has gained wide attention all over the world. One of the most novel technologies among the CCS is hydrate. Gas hydrates are ice-looking solid in which the guest gas molecules are trapped in the cavities of the lattice provided by host water molecules [1]. The common structures for gas hydrates are SI, SII, and SH. CO_2 hydrate is SI, however, after adding some additives such as tetrahydrofuran (THF), the structure of the mixture changes into SII [2].

For studying the CO_2 hydrate, both kinetics and thermodynamics of CO_2 hydrate formation and dissociation are required for a

better understanding. Gas hydrate should be formed at the suitable thermodynamic conditions, normally at high pressure and low temperature, which can be lower by adding some additives. For example, it was found that adding THF could give optimal thermodynamic conditions [3,4]. In the case of the CO_2 hydrate thermodynamics, the equilibrium conditions [5–8] and the dissociation enthalpy [9–12] have been well studied.

Most of the kinetic studies have focused on the hydrate formation, such as the induction time [13,14] and the formation rate [15–18]. However, relatively little attention has been paid to the kinetic study of hydrate dissociation. In the case of experimental study, Xu and Li [19] and Song et al. [20] used warm water injection, depressurization, and the combination of the two methods to study the percentage of gas production, gas production rate and energy efficiency, and they found that the combined method resulted in the best performance. Yang et al. [21] calculated the

Nomenclature

A_s	surface area of a particle, m^2
B_ε	bias error, %
C	number of components in hydrate phase
D_0	the diameter of the particle, μm
f_{eg}	fugacity of THF-CO$_2$ hydrate at three-phase equilibrium pressure, Pa
f_g	fugacity of CO$_2$ in gas phase, Pa
HEX	heat exchanger
J	gas component
k	rate constant, s^{-1}
k_0	intrinsic dissociation rate coefficient, 1/(MPa·s)
k'	rate coefficient, 1/(MPa·s)
K_d	dissociation rate coefficient, mol/m^2·MPa·s
M_{WJ}	molecular weight of component J
Mw_{H2O}	molecular weight of water
n_0	number of moles in the hydrate phase before dissociation, mol
n_H	number of moles remaining in the hydrate phase during dissociation, mol
N	number of cavity types in unit cell
N'	finite value
N_w	number of water molecules per unit cell
N_{Ava}	Avagadro's number, 6.023×10^{23} molecules/mol
P	pressure, MPa
P_ε	standard deviation, %
R	universal gas constant (8.214 J/mol·K)
RT	refrigeration tons (3.5 kW)
t	time, s
T	temperature, K
vi	number of type i cavities per water molecule in unit cell
V_{cell}	volume of unit cell
X	measurement value
$\bar{X}$	measurement mean value

Greek symbols

η	efficiency
ΔE	activation energy for gas hydrate dissociation, J/mol
$\theta_i j$	fractional occupation of cavity i by component J
ρ	density of combined hydrate, g/cm^3
ρ_H	density of mole CO$_2$-THF per unit volume, mol/m^3

formation and dissociation rate of CO$_2$ hydrate in porous media at two different temperature driving forces by experiments. They reported that three stages of CO$_2$ regeneration were observed for all experiments and the dissociation rate of CO$_2$ hydrate was accelerated under a higher temperature driving force. In case of kinetic model study, compared with the old axial dissociation, the radial dissociation seemed to be more acceptable, and the concept was also verified by Gupta [22], who used the X-ray computed tomography (CT) to capture images of the methane hydrae hole. Several kinds of numerical models have been proposed. The model for the intrinsic rate of hydrate dissociation was initially developed by Kim et al. [23]. The same amount of hydrate was required to be formed and then during the dissociation process, the experiment process was divided into two stages: (1) stabilizing the hydrate by maintaining the pressure 0.05 MPa above the equilibrium pressure, (2) decreasing the pressure to the desired experimental pressure. The suitable stirring speed was also studied to eliminate the mass transfer effect. In their model assumption, all the particles were assumed to have the same size and the Stokes law was used to estimate the initial particle size. Clarke and Bishnoi et al. [16,24–28]. They did a series of kinetic study on the methane, ethane, CO$_2$ hydrate, including the experimental work and analytical model. The analytical model was deducted based on the Kim et al. [23]. However they calculated the total surface area by measuring the hydrate particle size distribution instead of using Stoke's law. The experimental data were used to regress the activation energy and the intrinsic rate for gas hydrate dissociation in their model. Recently, Windmeier and Oellrich [29] conducted the theoretical study of gas hydrate decomposition kinetics to provide an estimate for the order of magnitude of isothermal gas hydrate dissolution and dissociation. They proposed the consecutive desorption and melting (CDM) model including the dynamic description of phase equilibrium and the specific phase change kinetics.

The CO$_2$ hydrate application has gained increasing attention instead of being studied to prevent the blocking problem in the pipelines. The positive applications include the cooling system, sequestration, gas storage and so on. For applying in the cooling system, CO$_2$ hydrate is considered as secondary refrigeration, which is environment-friendly, and has a high phase change enthalpy [30]. It has been proven that the energy efficiency is improved significantly by using the phase change materials

[31,32]. Hence, many researchers has investigated the dissociation enthalpy of gas hydrate for cooling application [12,33–35]. Compared with the traditional refrigeration used in the cooling application, R11 (334 kJ/kg) and R141b (344 kJ/kg), the dissociation enthalpy of CO$_2$ hydrate is high enough (500 kJ/kg) [36]. Choi et al. [37] studied the cost of using CO$_2$ hydrate as the secondary refrigeration in the cooling system and found that the CO$_2$ hydrate cooling system was an economic alternative solution to the conventional district cooling system. Sun and Kang [38] investigated the CO$_2$ hydrate formation rate at the conditions suitable for cooling system, and developed the experimental correlation for the CO$_2$ hydrate formation rate.

As mentioned above, many researches about CO$_2$ hydrate have focused on the formation phenomenon, and there are little researches on the dissociation process. Moreover, there were experimental and analytical works about the kinetic model of methane, ethane and CO$_2$ hydrate dissociation for the natural gas production [39]. But, there was no kinetic model which could be used to calculate the dissociation rate of the CO$_2$ hydrate with THF. In the fields of the cooling application and the CO$_2$ gas separation of post-combustion capture using the hydrate technology, THF is needed to lower the phase equilibrium conditions (such as the working pressure) of CO$_2$ hydrate for operating the proposed system. Especially, it is important to develop the kinetic model of CO$_2$-THF hydrate dissociation to predict the performance of the cooling system using the hydrate slurry as a secondary refrigerant. In the present study, the experiments are conducted by depressurization process, and the kinetic data of CO$_2$ hydrate dissociation rate in the presence of THF for the cooling system are presented. Hydrate dissociation is an endothermic process, which is driven by the difference between the equilibrium and vapor fugacities. There are three main methods for dissociation; depressurization, inhibitor injection, and thermal injection. Among these three common methods, depressurization is the most economic in terms of energy consumption. In the previous studies, the purpose of developing the kinetic model of hydrate dissociation was to produce the natural gas from the natural gas hydrate. Therefore, the kinetic models were developed at high pressure conditions. However, this study investigates the kinetic model of CO$_2$ hydrate dissociation at moderate pressure below 0.5 MPa for the application of hydrate technology in CO$_2$ capture and district cooling systems. The kinetic