



Semiclathrate based CO₂ capture from fuel gas mixture at ambient temperature: Effect of concentrations of tetra-n-butylammonium fluoride (TBAF) and kinetic additives[☆]



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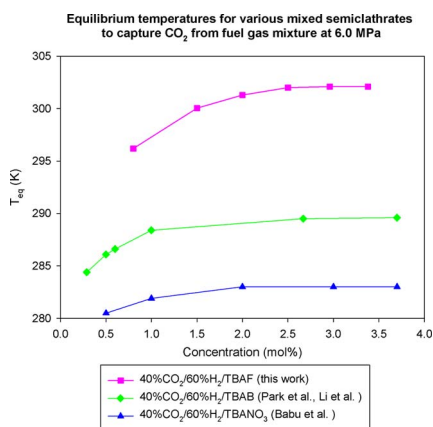
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HIGHLIGHTS

- CO₂/H₂/TBAF hydrate was formed with various concentrations at ambient temperatures.
- 0.8 and 1.5 mol% TBAF showed better kinetics than stoichiometric concentrations.
- SDS, leucine and tryptophan enhanced hydrate formation rate.
- Long induction time with leucine/tryptophan caused a special hydrate growth style.
- Challenge for semiclathrate-based CO₂ capture is to significantly enhance the rate and capture capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrate-based gas separation (HBGS) for pre-combustion CO₂ capture from fuel gas is one of the attractive methods to reduce carbon emission. To further advance the HBGS technology, there is a need to identify promoters that can moderate the operating conditions and enhance the kinetics and separation efficiency. Tetra-n-butylammonium fluoride (TBAF) is a semiclathrate former that can enable the HBGS process to be operated at ambient temperatures. In this study, the kinetic performance of CO₂/H₂/TBAF semiclathrate formation was evaluated under various TBAF concentrations in a stirred tank reactor at 6.0 MPa with a temperature driving force of 4.1 K. Compared with other concentrations, 0.8 and 1.5 mol% solutions exhibited higher gas uptake (normalized by the solution volume), hydrate formation rate, and CO₂ composition in the captured gas. In addition, the effects of three kinetic additives on hydrate formation were tested, including sodium dodecyl sulfate (SDS), leucine, and tryptophan. All additives could reduce the induction time and increase the hydrate

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formation rate. The visual images of hydrate formation indicated two morphology styles, with the occurrence of style II identified to be highly related to the long induction time and the presence of leucine or tryptophan.

1. Introduction

Global warming is an international issue caused by the increasing greenhouse gas emissions. Among various anthropogenic greenhouse gases emitted into the atmosphere, CO₂ accounts for the largest percentage due to human induced activities [1,2]. In order to control the CO₂ emission in the short term, Carbon Capture and Storage (CCS) has been proposed as one of the major strategies that has an immediate effect on the mitigation of global warming [3]. The pre-combustion CO₂ capture through an integrated gasification combined cycle (IGCC) is one of the possible approaches to equip power plants with CCS [4,5]. The typical fuel gas composition coming out from the IGCC is around 40% CO₂ and 60% H₂ with its pressure between 2.0 and 7.0 MPa [5]. Hydrate-based gas separation (HBGS) is one of the attractive methods to capture CO₂ from fuel gas mixtures [6–9]. Clathrate hydrates are inclusion crystals in which water molecules form the framework through hydrogen bonding and guest molecules of suitable size like CO₂, CH₄, etc. are trapped inside [10,11]. When a fuel gas mixture is subjected to hydrate formation with high pressure and low temperature, CO₂ has more preference over H₂ to occupy the cages in hydrate, thus making the separation of CO₂ from fuel gas mixture feasible [7].

The equilibrium temperature of hydrate formation from fuel gas mixture is around 274.6 K at 6.0 MPa [12]. In order to reduce the operating cost, various thermodynamic promoters have been identified to mitigate the equilibrium conditions of hydrate formation, such as propane [12–14], tetrahydrofuran (THF) [15–19], cyclopentane [20–23], cyclohexane [24], and neohexane [25]. The performance of thermodynamic promoters on hydrate formation from fuel gas has been reviewed in detail by Babu et al. [6]. They reported that the best hydrate formation rate and gas uptake were achieved by the addition of 2.5% propane in the gas phase with the hydrate formation carried out in a silica sand bed reactor. The equilibrium temperature of this system (38.1%CO₂/59.4%H₂/2.5%C₃H₈) is around 281.4 K at 6.0 MPa [26]. At the same pressure (6.0 MPa), the equilibrium temperature of hydrate formation from fuel gas was found to be 289.9 K and 290.7 K in the presence of 5.6 mol% THF [18] and cyclopentane [22] respectively. With the help of these thermodynamic promoters, the equilibrium temperature for hydrate formation is increased significantly. However, in order to have a large driving force for hydrate formation, an operating temperature much lower than the equilibrium is still required.

Recently, another promoter, tetra-*n*-butylammonium fluoride (TBAF), was tested for hydrate formation from fuel gas mixture [27,28]. The hydrate formation process was proved to be feasible at ambient temperature (298.0 K) by the addition of TBAF [27]. The equilibrium temperature of this system (40%CO₂ /60% H₂/3.38 mol% TBAF) is around 302.1 K at 6.0 MPa [28]. With a significantly higher equilibrium temperature than the thermodynamic promoters mentioned above, TBAF is classified as another type of promoters, which are known as quaternary ammonium/phosphonium salts, or semiclathrate formers/promoters. Different with THF, propane, and cyclopentane, they form semiclathrates in which the promoter molecules not only occupy the cages but also constitute a part of the host framework [29]. Many semiclathrate promoters have been investigated for CO₂ hydrate formation, such as tetra-*n*-butyl ammonium bromide (TBAB) [30–35], tetra-*n*-butyl ammonium nitrate (TBANO₃) [36,37], tetra-*n*-butyl ammonium fluoride (TBAF) [27,38], tetra-*n*-butyl ammonium chloride (TBAC) [39–41], tetra-*n*-butyl phosphonium chloride (TBPC) [42,43], tetra-*n*-butyl phosphonium bromide (TBPB) [44–47], and tetra-*iso*-amyl ammonium bromide (TiAAB) [48]. Among these various semiclathrate promoters, only TBAB [49–53], TBANO₃ [36,37,53], and

TBAF [27,28,53] have been studied in detail for hydrate formation from fuel gas.

The phase equilibrium data for CO₂/H₂/TBAB hydrate formation are available in the literature [28,54,55], and the most evident alleviation of formation condition is achieved by the stoichiometric concentration (3.7 mol%). On the other hand, different optimal TBAB concentrations to enhance the hydrate formation kinetics were reported in the literature [28,54,56,57]. From a recent study conducted in a stirred tank reactor at 6.0 MPa and 279.2 K [31], it was found that lower TBAB concentration could give better kinetics. Out of the five concentrations studied, 0.3 mol% TBAB achieved the highest gas uptake and separation efficiency, while the shortest induction time and the highest hydrate formation rate were given by 1.0 mol%. The performance of TBANO₃ was also evaluated in a stirred tank reactor [36,37]. Similar to TBAB, a TBANO₃ concentration (1.0 mol%) lower than the stoichiometric concentration was reported for the best kinetic performance [37]. In terms of TBAF, the stoichiometric concentration (3.38 mol%) was reported to have the most evident effect to alleviate the hydrate formation conditions, which was even more significant compared with TBAB and TBANO₃ [28]. The kinetic performance of TBAF on hydrate formation from fuel gas was tested for two concentrations (0.8 mol% and 3.3 mol%) at 8.0 MPa with a temperature driving force of 4.0 K [28]. 3.3 mol% TBAF solution exhibited a much higher gas uptake than the 0.8 mol% TBAF solution. Both were lower than the TBAB systems at comparable concentrations. Our previous study [27] investigated the kinetic performance of CO₂/H₂/TBAF hydrate process with stoichiometric concentration (3.38 mol% TBAF) at different temperatures and pressures. The highest gas uptake was achieved by experiments conducted at 6.0 MPa and 298.0 K. Given that for both TBAB and TBANO₃ system, the optimal concentrations were found to be lower than the stoichiometric concentrations [31,37], it is of great interest to investigate the kinetics of CO₂/H₂/TBAF system with lower TBAF concentrations and determine the optimal concentration.

While the addition of thermodynamic promoters can moderate the hydrate formation conditions, there is another category of promoters known as the kinetic promoters, which can enhance the hydrate formation kinetics without affecting the equilibrium. Some surfactants such as sodium dodecyl sulfate (SDS) were found to be excellent kinetic promoters [58,59]. It is suggested that the kinetic improvement in presence of a surfactant is due to the enhancement of gas dissolution, improvement of gas-water contact by lower interfacial tension, and the capillarity-driven supply of water into the porous hydrate phase [58,60,61]. Among various kinetic promoters, SDS is the most extensively studied. It was shown in many studies that the addition of SDS could enhance the formation of CO₂ hydrate in a fixed bed reactor [59,62,63]. The combination of SDS with THF was found to increase both the formation rate and final gas consumption for CO₂ system [64]. Apart from the surfactants, recently some amino acids were also found to be effective kinetic promoters for the methane hydrate system [65,66]. In a methane/water system in presence of leucine, the hydrates formed were observed to be very flexible and expandable, resulting in a promotion in the gas uptake similar to SDS [65]. The optimal concentrations to promote methane hydrate formation were found to be 3000 ppm for both leucine and tryptophan [65,66]. Although only few studies have worked on the performance of kinetic promoters on CO₂/semiclathrate systems [67], the great promotion effect of SDS, leucine, and tryptophan mentioned above arouses the interest of testing the performance of these kinetic additives in this work for the CO₂/H₂/TBAF system.

In this study, we investigated the kinetics of CO₂/H₂/TBAF hydrate

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