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Review

A comprehensive review of semi-clathrate hydrates for CO_2 capture: Characterizations, mechanism and role of promoters

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ABSTRACT

Recently, clathrate hydrate-based CO_2 separation is considered as one of the most attractive processes for reducing CO_2 emissions because of its effective energy utilization, environmental friendliness, and economic viability. The ionic semi-clathrate hydrate, a quaternary salt used to facilitate hydrate formation, is particularly shown interest because it can boost CO_2 capture by improving the physical and chemical interactions between host lattice and guest molecules for hydrate formation. A reduced pressure of 1 MPa or less is high enough for effective gas trapping at 280 K using a semi-clathrate hydrate. The operating parameters, ionic hydrate structure, and promoter concentration affect CO_2 capture. The efficiency of the CO_2 separation process can be significantly reduced by inhibitory effects at a particular salt concentration. Research has been conducted using tetra-n-butyl-ammonium and phosphonium salts because their crystal structure and morphology are favorable to form semi-clathrate hydrates. However, only a few lookups on environment-friendly and appropriate characterization strategies of the hydrates and novel promoters, and their design, and operability have been performed. This review addresses the mechanisms involving the size of CO_2 molecules in an ionic hydrate network, the characterization methods of the hydrates, promoter integration and their overall performance analysis. In addition to that, operational strategies of the semi-clathrate hydrate-based CO_2 capture processes, the drawbacks and future routes to research CO_2 capture using semi-clathrate hydrates have been addressed.

1. Introduction

The excessive emissions of CO_2 in the surroundings for an extended period of time have created drastic climatic changes, including droughts, heat waves, tropical storms, wildfires, and the melting of ice. Following a study, international CO_2 emissions climbed by roughly 80 % between 1970 and 2004. The primary contributor to CO_2 emissions in the atmosphere is power plants which are released from the burning of fossil fuels (Dashti et al., 2015; Khan et al., 2023). Therefore, the problem motivates our researchers and the scientific community to discover further modern approaches and strategies to decrease CO_2 emissions in the environment. Among several techniques, three primary technology options exist for capturing CO_2 from fossil fuel power generation plants:

1. Post-Combustion: In this method, CO_2 is separated from the flue gas after combustion.
2. Oxy-Fuel Combustion: This approach involves using nearly pure oxygen for fuel combustion. After combustion, CO_2 is removed from the generated gases, primarily consisting of water vapor and CO_2.
3. Pre-Combustion: CO_2 is removed from the fuel before the combustion process.

However, the application of CO_2 capture technologies comes with certain drawbacks. Firstly, it can lead to a reduction in the net efficiency of a plant by up to 14 percentage points. Additionally, there's a cost implication, as the electricity cost could increase by 30–70 % (Cebrucean et al., 2014), depending on factors such as the type of fuel used, the plant type, and the specific capture technology employed. These factors underscore the challenges associated with implementing CO_2 capture technologies in power generation plants.

With an anticipated cost of 20 to 40 US dollars per tonne of CO_2 captured and an associated energy penalty of 15%, hydrate-based CO_2 separation appears to be a potentially competitive option in contrast to

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traditional (MEA) absorption methods (Nguyen et al., 2022). The latter typically involves costs ranging from 40 to 100 US dollars per tonne of CO_2 removed, coupled with a higher energy penalty of ~25%. The competitiveness of hydrate-based separation becomes more pronounced at industrial scales due to inherent advantages such as its water-based process, tolerance to impurities in the feed gas, and the possibility of energy savings through the incorporation of hydrate formation/dissociation enthalpies. However, despite these advantages, the current deployment faces challenges, notably in terms of sluggish kinetics and a limited track record in industrial applications. Table 1 summarizes the techno-economic feasibility of hydrate-based CO_2 separation when compared to some established carbon capture methods.

There are challenges presented by impurities like sulfur compounds, fine dust, and moisture in different carbon capture methods. Naturally occurring sulfur compounds in fossil fuels, for instance, can degrade materials and cause corrosion, particularly in high-temperature conditions during solvent regeneration. Fine dust from fuel processing may result in blockages in membranes and complex systems during absorption and adsorption processes, requiring additional steps for feed gas purification. Contrastingly, hydrate-based separation seems to circumvent these challenges. Sulfur compounds can form hydrates and be separated with CO_2 as mixed hydrates. Interestingly, fine dust is seen as beneficial, acting as a kinetic promoter by introducing more interfaces to the system. Consequently, this technique doesn't necessitate extra upstream units for feed gas purification, presenting a distinct advantage in tolerating impurities within the feed gas.

The precise approaches to capture CO_2 are membrane-based separation, cryogenic separation, solvent-based absorption (Dashti et al., 2015; Hashimoto et al., 2017b; Oyama et al., 2005; Zhang et al., 2013) and solid sorbent-based separation (Khan et al., 2023). Post-combustion-based CO_2 capture techniques can be employed compared to pre-combustion-based CO_2 capture techniques in power generation plants; however, the concentration limit to be dealt with by post-combustion techniques is typically 15–20 %. In addition, membrane separation, cryogenic separation, and solvent absorption-based techniques are practically challenging due to their excessive fabric cost, excessive power requirements, excessive solvent toxicity, and excessive corrosion. Compared to the methods described above, hydrate-based separation strategies are viewed as a relatively advantageous CO_2 capture method, as these techniques use only water as a separation medium and are therefore described as a simple and environmentally friendly method in addition to the cost-effectiveness of the techniques (Dashti et al., 2015; Khan et al., 2023; Yu et al., 2021). Fig. 1 depicts the methods that can be used in chemical industries and power plants to capture CO_2, including pre-combustion and post-combustion processes using a semi-clathrate hydrate reactor. CO_2 gas should be brought into contact with the hydrate formation reactor via compressor and cooling unit to capture CO_2 at atmospheric temperature and pressure utilizing semi-clathrate hydrates. Semiclathrate-based carbon dioxide separation procedure involves the passage of syn or flue gas through a hydrate formation reactor, followed by pure carbon dioxide gas recovery from the hydrate reactor unit using a separator and a dissociation reactor, resulting in the emission of flue gas devoid of carbon dioxide into the atmosphere.

Hydrates or clathrates are divided into two classes: true clathrates and semi-clathrates. The formation of CO_2 hydrates necessitates high-pressure (>4.45 MPa) and low-temperature conditions (<10 °C), which is a significant drawback of true clathrate-based CO_2 capture technologies. In contrast, semi-clathrate-based CO_2 capture is a promising technique that employs thermodynamic promoters or components (usually salt) for gas hydrate formation at moderate temperature and pressure. Additionally, the salt solution is recycled because no salts are ingested in the CO_2 binding and recovery process, and the applicable salts in the semi-clathrate hydrates formation process can be manufactured on a bulk scale in industry at a low cost. Thus, semi-clathrate hydrates can facilitate the carbon capture and sequestration process by reducing the principal cost i.e. compression cost to form gas hydrate in a CO_2 capture process.

The operating condition for capturing CO_2 using semi-clathrate hydrate would be typically 280–295 K (near ambient temperature) and below 1 MPa to 3 MPa (moderate to high pressure). These conditions can change depending on the type of semi-clathrate hydrate that would be used. To treat flue gas, which is at ambient conditions, using semi-clathrate hydrates, compressor and cooling system would be needed, which will incur some additional cost. However, even some membrane or solvent-based separation techniques need high temperature and pressure. Although Monoethanolamine (MEA) based separation operates at ambient conditions, the solvent regeneration is highly energy intensive. Around 4 MJ of thermal energy is needed for every kg of CO_2 separated during the normal regeneration of MEA solvent, which occurs at a temperature of 120 °C or higher (Li et al., 2016). The semi-clathrate hydrate-based separation uses water as the solvent, which is robust, reusable, and easily regenerable. The energy penalty associated with hydrate-based capture is 50–75 % lower than that of the traditional absorption method. One study that investigated hydrate-based CO_2 capture (HBCC) of steelmaking flue gas showed that the cost of HBCC varied from 20 to 40 (US$/ton CO_2 avoided), which is significantly lower than conventional absorption-based capture (40–100 US$/ton CO_2 avoided) (Duc et al., 2007). Considering these aspects, the Semi-clathrate hydrate-based technique is a promising alternative to absorption-based techniques. However, pre-combustion capture is more favorable to HBCC because the low concentration of CO_2 in the flue gas and incorporation of N_2/H_2 in the hydrate phase lower the efficiency of CO_2 capture. This problem can be solved using multistage HBCC or combining HBCC with other techniques like absorption. For example, combining HBCC with absorption can lead to 30 % lower energy consumption than cryogenic condensation alone (Xu et al., 2014).

There are some existing CO_2 capture technologies, such as chemical/physical absorption, adsorption, membrane separation, cryogenic separation, etc. However, the existing technologies have some significant drawbacks requiring looking for newer CO_2 capture technologies. For example, the absorption process needs a large amount of solvents and involves significant costs despite the regeneration process of the solvents. Because the regeneration process itself involves high energy consumption and loss of solvents. Apart from that, the requirement of high temperature during the regeneration of the solvent necessitates high thermal energy that eventually corrodes the facilities. The complexity of these processes make them expensive for capturing CO_2. Membrane-based CO_2 capture is also an advanced technology in this respect. However, this technology also contains significant obstacles such as poor selectivity of CO_2, low stability, aging, swelling, and sensitivity to impurities and water, and also shows poor performance at low CO_2 concentrations. Therefore, very recently, hydrate-based CO_2 capture grabbed a lot of attention due to its multifaceted advantages over other existing CO_2 capture technologies. Tables 1 and 2 below describe all the advantages and significant challenges possessed by semi-clathrate hydrates for CO_2 capture compared to other technologies.

Semi-clathrate hydrates include crystal-like compounds that can be shaped via the aggregate of water, quaternary ammonium salts (QAS)/phosphonium salts, and guest molecules of appropriate sizes. Like gas hydrates, low temperatures and higher pressures are thermodynamically favorable for the enclathration of guest CO_2 molecules in semi-clathrate hydrates. In true clathrates, the guest CO_2 molecules are no longer bonded to the water structure, while in semi-clathrate hydrates, the guest molecules may additionally be part of the water lattice and fill cages. The anions from the salts are connected to water molecules through hydrogen bonds and form a water-anion framework (host). The cavities inside this framework are then occupied via cations, also termed guests, and detached from the host molecules by a space equal to or greater than the sum of Van der Waals radii (hydrophobic attachment). Additionally, there is a distinction in dissociation pressure between usual gas hydrates and semi-clathrates; for the former, the dis-

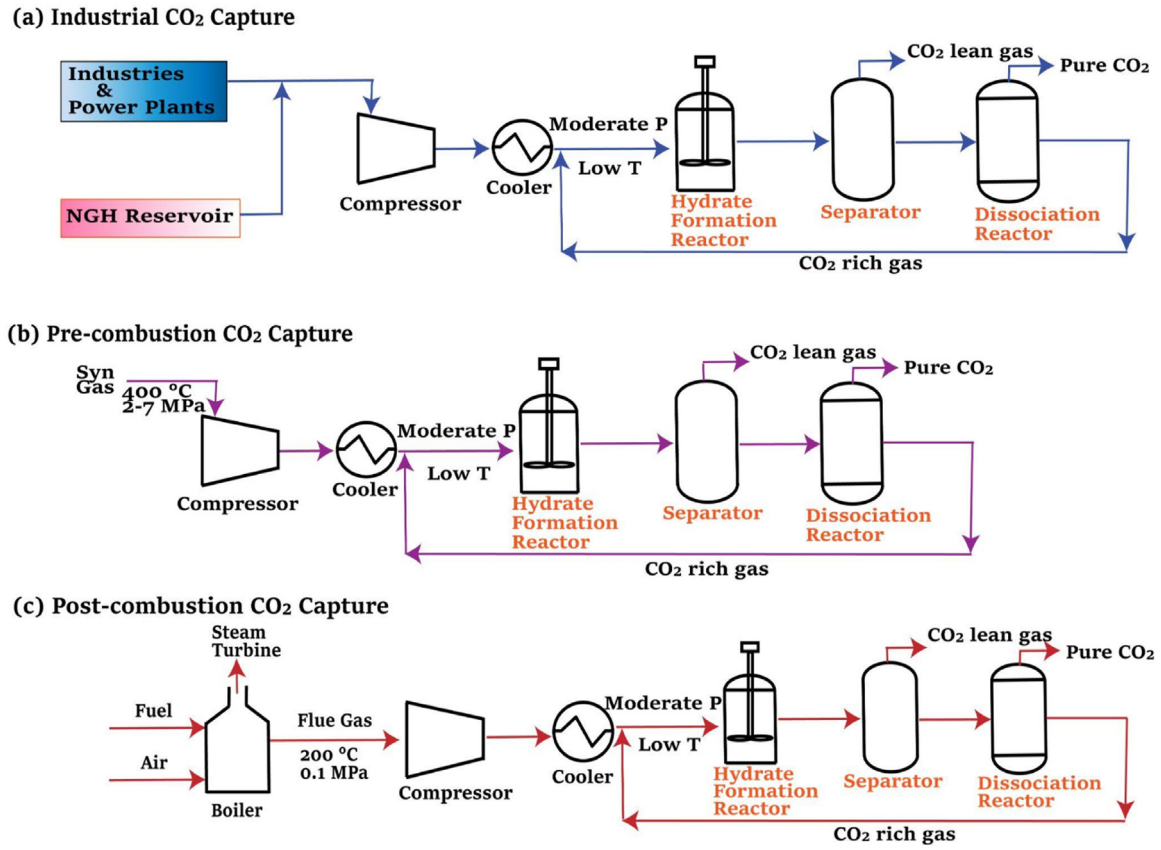

Fig. 1. Schematic diagram of industrial, pre-combustion, and post-combustion carbon capture process using semi-clathrate hydrates (Babu et al., 2015; Cannone et al., 2021).

Table 1
Techno-economic feasibility of hydrate-based CO_2 separation in comparison to other well-established carbon capture methods.

Process	CO_2 capture process	Process inlet condition	CO_2 capture (%)	Net plant efficiency (%)	Efficiency penalty (%)	Energy penalty (%)
MEA	Post combustion	313.15 K Wang et al. (2023) 2 KpaG Wang et al. (2023)	90 Bravo et al. (2021)	~32 Cebrucean et al. (2014)	10 Cebrucean et al. (2014)	~25 Cebrucean et al. (2014)
Selexol	Pre combustion	303 K Cormos (2011) 20 bar Cormos (2011)	99 Smith et al. (2023)	~35 Cebrucean et al. (2014)	~8 Cebrucean et al. (2014)	~18 Cebrucean et al. (2014)
Membrane	Post combustion	330 K Xu et al. (2019) 0.1 MPa Xu et al. (2019)	50–90 Roussanaly and Anantharaman (2017)			16–24 Nguyen et al. (2022)
Pressure swing adsorption	Post combustion	338 K Riboldi et al. (2014) 38 bar (Riboldi et al., 2014)	74–90 Riboldi and Bolland (2017)	~28.8 Riboldi et al. (2014)	~16 Riboldi et al. (2014)	
Calcium looping	Post combustion	853–973 K Sivalingam (2024) 1 bar Sivalingam (2024)	89.8 Astolfi et al. (2021)	38.6 Sivalingam (2024)	2.6–11.4 Hanak et al. (2015)	
Hydrate	Post combustion	275 K Cheng et al., 2022) 2–5 MPa Cheng et al. (2022)	13–73.8 He et al. (2017)			15 Babu et al. (2015)

Table 2
Advantages and disadvantages of Semiclathrate-based CO_2 capture process.

Advantages	(1) Semi-clathrate-based CO_2 capture technology operates under moderate temperature and pressure conditions; easy to implement and operate compared to other technologies. (i) Absorption (requiring high energy and extreme conditions as described above), the energy consumption for absorption is 4–6 MJ/Kg CO_2, whereas for hydrate base CO_2 capture techniques, the energy consumption is 1.3–4.7 MJ/Kg CO_2). (ii) Membrane separation (sometimes higher pressure is needed for efficient separation);), the energy consumption for absorption is 0.5–11 MJ/Kg CO_2). (iii) Cryogenic separation involves energy consumption equivalent to 6–10 MJ/Kg CO_2. (2) Highly selective toward specific gas molecules. (3) Present relatively high capture capacity. On the contrary, membrane-based CO_2 capture technology and cryogenic separation methods are only efficient in high CO_2 concentrations. (4) Environmental friendliness uses water and other non-volatile additives that can be recycled for hydrate transformation without involving much waste generation and toxic pollutants.
Disadvantages	(1) Still on the pilot scale at R&D facilities. (2) The slower kinetics of clathrate hydrate formation and dissociation to long process time limiting scalability. (3) Mass transfer limitation can affect the gas capture efficiency. (4) Improvement in the selectivity. (5) Industrial scaling up might pose some crucial challenges. (need for high-pressure equipment, properly recycled system for water and additives management).

sociation pressure reaches 1 atm at a temperature beneath 0 °C and is not stable at close to the melting point except under pressure (Li et al., 2019).

Tetra-n-butylammonium (TBA) and tetra-n-butylphosphonium (TBP) salts are predominantly applied for boosting semi-clathrate hydrates. When TBA hydroxide (TBAH) was concentrated to prepare a product that was as close to anhydrous as possible, it was found that in relatively diluted solutions, crystals appeared at room temperature and that the entire mass solidified at this temperature even though there was still a significant amount of water present. Fowler et al. were the first to study this phenomenon, discovering that the crystal-like substance was hydrated by TBAH and contained 31 water molecules, and melted at 30.2 °C (Hashimoto et al., 2017b), and various ranges of hydrated salts with different anions were also examined. Later, Richard McMullan and G. A. Jeffrey prolonged the investigation of n-butyl and i-amyl-based semi-clathrate hydrates with x-ray crystal analysis and concluded that certain anions are not compatible with the formation of hydrates such as tetra n-butyl ammonium iodide, dichromate, perrhenate, and periodate (Ye and Zhang, 2012). The lesser the anion varies in dimension from the water molecule in size, the more steady the hydrates are due to their more desirable capability to shape an H-bond. Such semi-clathrate hydrates were found to be stable under normal pressure and above the freezing point of ice, even at room temperature. Van der Waals and ionic interactions between the water and guest cations are possible reasons for this enhanced stability.

Semi-clathrate hydrates have latent heat in the range of 190–220 kJ/kg and a phase transition window between 0 and 27 °C, making these materials potential candidates for cold energy storage/transport applications, among which TBA bromide (TBAB) hydrates have been studied comprehensively both in prototype and pilot plant scale (Ma et al., 2010). As interest in mitigating climate change grows, so does the need to develop efficient methods of capturing CO_2 from flue gas and other gas mixtures, which can be another promising application of semi-clathrate-based separation technology. CO_2 displacement can expand the recovery of natural gas; however, it requires a high-priced CO_2/CH_4 separation. Hence, the fuel hydrate/semi-clathrate-based hydrate technological know-how has been drawing interest as a promising approach for CO_2 capture in recent years (Hashimoto et al., 2017b).

The high-pressure and low-temperature conditions required for the formation of the usual gas hydrate are not conducive to its practical use. To increase the temperature and decrease the pressure at which hydrate forms is to add chemical additives of quaternary ammonium and phosphonium salts such as TBAB and TBPB to the system (Zhang et al., 2022). Both TBAB and TBPB semi-clathrates have a superior selectivity for incorporating CO_2 gas from a mixture of CO_2 and CH_4, but there is still a lot of room for improvement in terms of gas capture before its application in industry (Li et al., 2019). Researchers studied different thermodynamic promoters extensively for the formation of semi-clathrate hydrates. However, there is still a requirement for determining the optimum operating conditions for promoters in terms of gas uptake. Therefore, the exploration for such thermodynamic promoters with enhanced performance persists. This review paper intends to highlight current research on the development of promoters and the ideal circumstances for using semi-clathrate hydrates in the CO_2 capture process. It aims to explore the principles, mechanisms, and applications of this environmentally friendly technology for mitigating CO_2 emissions. Additionally, the write-up seeks to emphasize the importance of optimizing operational conditions, including the type of promoters, in enhancing the efficiency of CO_2 capture within semi-clathrate hydrates. The current paper is organized as follows: first, the mechanism of CO_2 capture in semi-clathrate is described. Following that, comparisons between various promoters based on operational settings were highlighted to illustrate the frequently employed field-wide characterization techniques.

2. CO_2 capture mechanism by semi-clathrate

There are a couple of CO_2 capture methods, such as adsorption through sorbents, solvent-based absorption (chemical solvents are utilized to capture CO_2), membrane-based CO_2 capture (different membrane substances having CO_2 affinity are utilized to take in CO_2 from the gas mixture) or chemical looping for CO_2 separation. Among a variety of CO_2 capture techniques, clathrate hydrate-based CO_2 capture technological knowledge has acquired a lot of interest due to the system's simplicity and environmental friendliness, seeing that the separation is based totally on the water as a separation medium (Zhang et al., 2016). Also, gas hydrates have excessive gas and energy storage capacity (Darbouret et al., 2005). Generally, clathrate-based hydrates are structured via the hydrogen bonding of water molecules beneath the appropriate thermodynamic status of high-pressure and low-temperature conditions where the small guest molecules enter cage frameworks formed by the way of the water molecules. Those guest molecules essentially bond with water molecules through the Van Der Waals force. These gas hydrate types have three structures: shape I (SI), shape II (SII), and SH (Egolf et al., 2008). CO_2 and CH_4 (smaller molecules) typically shape SI and SII, whereas SH is shaped through N_2 (bigger molecules). These hydrates' distinct crystal structures contain unique water cavities.

The most common shape is the irregular dodecahedron ($4^3 5, 6 6^3$), followed by the pentagonal dodecahedron (5^{12}), the tetrakaidecahedron ($5^{1,2}6^2$), the hexakaidecahedron ($5^{1,2}6^4$), and the icosahedron ($5^{1,2}6^8$), which are all concurrently described as $5^{12}6^m$, with m = 2, 4, 8 (Muromachi et al., 2014). Here, the term "5^{12}" indicates an extremely small cavity with 12 pentagonal faces, whereas the term "$5^{12}6^m$" indi-

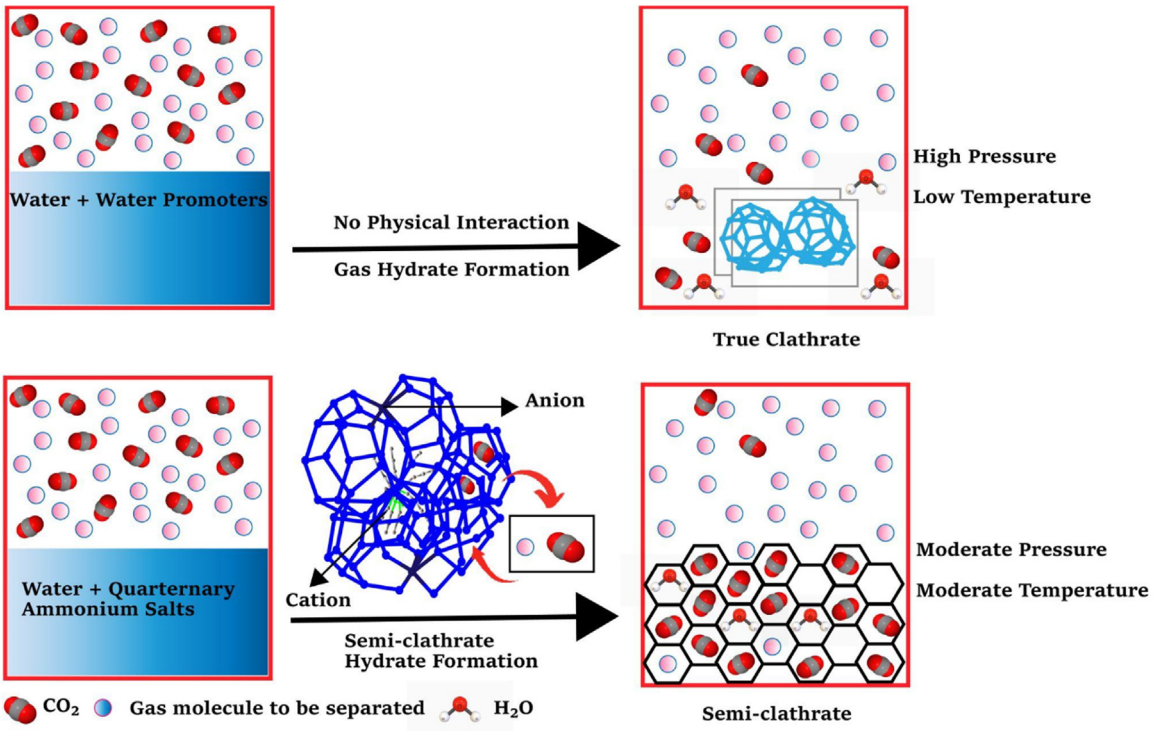

Fig. 2. A schematic diagram of comparison between clathrate and semi-clathrate-based CO_2 capture.

cates a large cavity with 12 pentagonal faces and m hexagonal faces. On the other hand, the term "$4^35,^66^3$" illustrates a medium cavity that incorporates three tetragonal, 6 pentagonal, and three hexagonal faces (Shimada et al., 2005). In true clathrate, the host and guest molecules do not interact physically (Chazallon et al., 2014), whereas there is a chemical or ionic interaction between the host and guest molecules in semi-clathrate. These ionic semi-clathrate hydrates are made up of a cationic guest and a host lattice that is balanced by anions such as OH^-, F^-, and Br^-, and in many cases, exhibit strong or mild basicity. Some cages are partially fractured in order to accommodate the large cations. Fig. 2 gives a glimpse of the comparison between the mechanism of clathrate-based and semi-clathrate-based CO_2 capture.

In TBA hydrate structures (e.g. pentagonal dodecahedral, tetrakaidekahedral, pentakaidecahedral cages), anions are responsible for altering the water lattice network to form giant cages in these hydrate structures (Uchida et al., 1995). The guest molecules stabilize the hydrate's shape at low pressures and high temperatures, allowing gas phase elements to penetrate the hydrate under more favorable conditions. In the TBA halide crystal constructions, water molecules in association with halide ions construct a polyhedral hydrogen-bonded water-anion cage structure at atmospheric pressure (Sum et al., 1997). Tetraalkylammonium ionic clathrate hydrates with a carboxylate group are blanketed in the H_2O framework along its oxygen atoms to shape a portion of a polyhedron. The cavities of the framework are occupied by the hydrophobic phase of the anion. Polyhedral cavities of water-anion host lattice are occupied by butyl groups of the cations; the nitrogen atom of cations replaces the water molecule located in the vertex that is common of 4 neighboring cavities.

CO_2 is a small nonpolar hydrocarbon that forms a hydrate with an ideal SI structure at approximately 1.2 MPa and 273 K. The system for SI hydrate is $CO_2{\cdot}nH_2O$ (n = 5.75) at some stage in contact with water molecules beneath the equilibrium temperature and above pressure (Ikeda et al., 1998). The crystalline structure can generate a total of eight cavities per forty-six water molecules. The equilibrium phase graph for CO_2 hydrate is introduced in Fig. 3. Gases such as N_2, H_2, O_2, and CH_4 form hydrates under slightly distinct equilibrium conditions and at a higher pressure than CO_2. Consequently, the hydrates formed from flue gas are typically enriched in CO_2 relative to other components if we consider the thermodynamic factor.

In industry, the hydrate-based carbon dioxide capture system consists of two sections: capturing the CO_2 and the release of CO_2. First, a strong hydrate section is shaped that is enriched with CO_2 by compressing, cooling, and mixing with water. Then, the CO_2-rich hydrate slurry is transferred to the release section. In the release section, making use of enough heat or pressure, the strong particles get dissociated. Finally, the purified CO_2 is accumulated from the dissociation reactor, and the CO_2-rich gas is recycled for similar processing. This method is problematic because it requires high pressure and low temperature, which necessitates the use of a multistage compressor. This will increase the cost of capital for the capture facility. Consequently, it is common to seek out technology that will aid in reducing the burden of the capture stage. In order to achieve this objective, forming semi-clathrates rather than true clathrates or gas hydrates is effective because they can form at atmospheric pressure and ambient temperature. Semi-clathrates have some special thermodynamic properties in contrast to gas hydrates that work beneath 1 MPa for ionic clathrate hydrates (Chen et al., 2015; Xie et al., 2021) and work at 3 MPa for structure I-type gas hydrates at 280 K for capturing CO_2 (Qing et al., 2018). This gas separation method employing semi-clathrate or ionic clathrate is still effective compared to CO_2 absorption using amine, which requires high temperatures, such as 370–410 K, to release the captured CO_2 (Wang et al., 2020a).

TBAB-based semi-clathrates are utilized to capture CO_2 supplied from the exhaust gas of the combustion heater on an industrial basis (Takeya et al., 2017). The process consists of TBAB+CO_2 hydrate formation and dissociation. At first, the exhaust gas of the combustion heater gets cooled to near ambient temperature, and the gas is compressed to approximately 1 MPa to flow into the TBA solution within a formation reactor. One of the significant steps here is the semi-clathrate (SC) nucleation. Since supercooling is important for nucleation to happen, the TBAB solutions are cooled to 280 K or lower for that purpose. After nucleation, the temperature is fixed near the equilibrium temperature for the SC growth. In the dissociation step, the temperature of the reactor

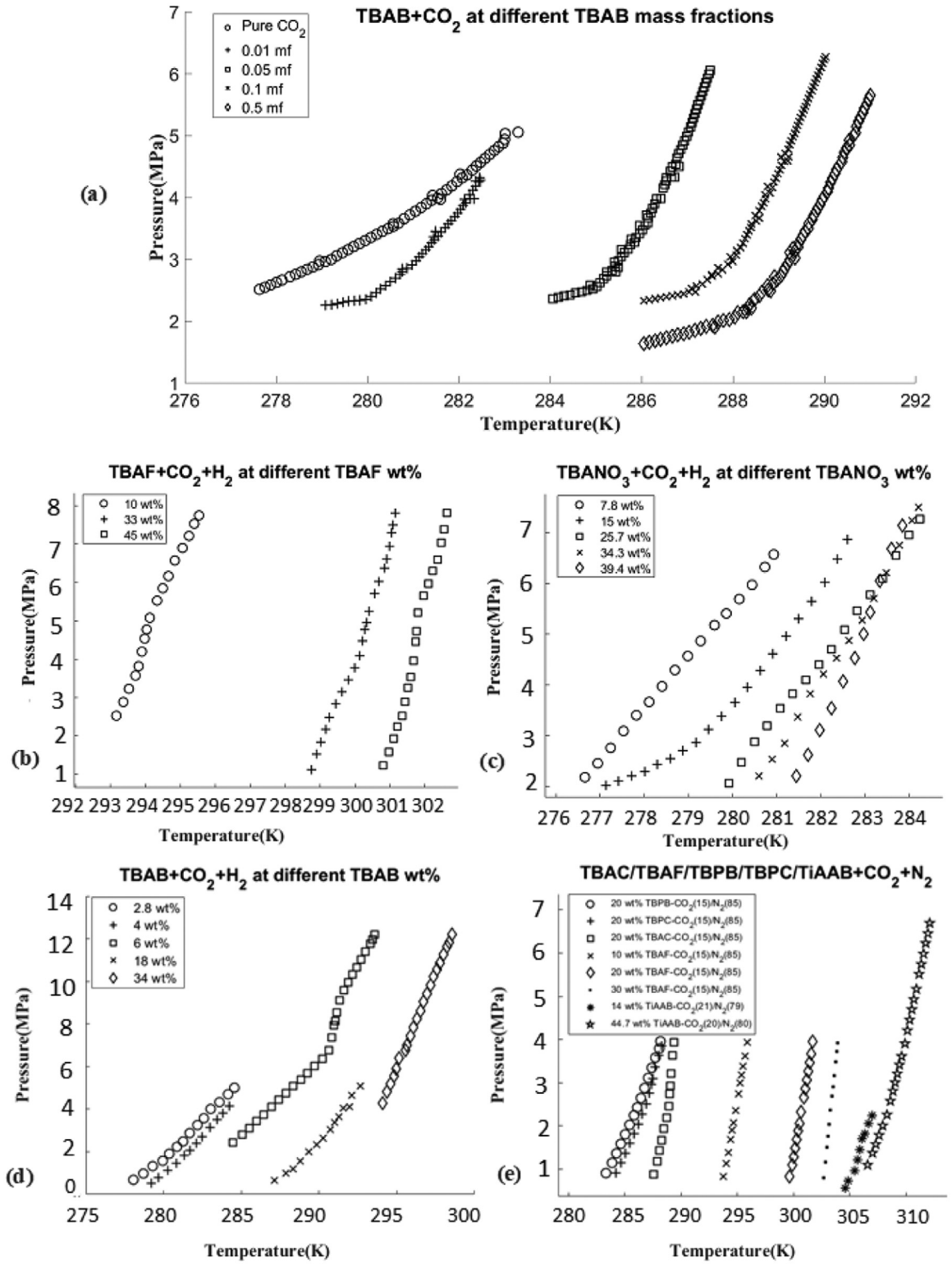

Fig. 3. (a) Model predictions of CO_2 semiclathrate hydrate phase equilibrium conditions in the presence of TBAB at various mass fractions. Phase equilibrium condition of CO_2 /H_2 mixture and quaternary salt hydrate (b) TBAF (c) $TBANO_3$ (d) TBAB (e) phase equilibrium conditions for CO_2/N_2 mixture for various salts (Avula et al., 2017; Gu and Lu, 2023).

goes above the equilibrium point of the SC hydrate, and CO_2 gas gets released into the CO_2 enrichment section. The schematic diagram of this process is shown in Fig. 4.

Crystal structures vary principally due to the type of ionic guest substance. Under different gas pressure conditions, the order of phase stability might also shift from the atmospheric pressure due to the contribution of guest gas to the stabilization of the structure. Therefore, the semi-clathrate hydrate structure can be manipulated by choosing the ionic guest substance to manipulate gas capture properties. Some issues are yet to be visited to know how they affect semi-clathrate hydrate's

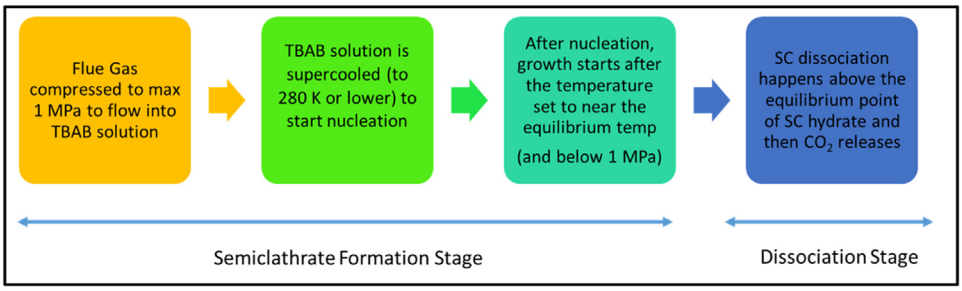

Fig. 4. A flow diagram of the semi-clathrate hydrate cycle.

CO_2 capture efficiency, such as a) cage transformation, (2) polymorphism and phase transition, and (3) gas capacity (Muromachi, 2021). In a hydrate cage, gas solubility in a solution and gas residence in a hydrate cage are characteristically proportional to the partial pressure of the gas. In contrast, captured CO_2 separation is higher at relatively low CO_2 partial pressures (0.15 MPa) and 0.42 MPa.

3. Characterization and phase behavior determination of the semi-clathrate hydrates

Comprehensive research has been performed on the fundamentals of semi-clathrate hydrates, particularly the TBAB hydrates, in terms of crystal structure and morphology (Hashimoto et al., 2017b; Li et al., 2019; Oyama et al., 2005; Ye and Zhang, 2012; Zhang et al., 2013), various thermodynamic properties including latent heat and phase diagram (Ma et al., 2010; Oyama et al., 2005), kinetics(Li et al., 2019; Zhang et al., 2022) and rheological properties (Darbouret et al., 2005; Zhang et al., 2016). The literature contains various morphological studies on the crystallization and development of semi-clathrate hydrates (Hashimoto et al., 2017b; Li et al., 2019; Oyama et al., 2005; Ye and Zhang, 2012; Zhang et al., 2013). Typically, the experimental conditions and the guest substances used have an impact on the shape of the hydrate crystals (Li et al., 2019). An extensive examination of the morphology of the semiclathrate hydrate crystals was carried out under diverse conditions (Hashimoto et al., 2017b) (Fig. 5). Notably, TBAB hydrates with a weight fraction (w) of 0.200 displayed formations in columnar shapes, with smaller crystals emerging at higher pressures due to an increase in formation rates. TBAC hydrates appeared as slender columnar crystals, while TBPB hydrates adopted hexagonal configurations that expanded and thinned under increased pressure. TBPC hydrates showed behaviors akin to TBPB, featuring clusters of columnar crystals at 1 MPa. The morphological intricacies observed were intricate and potentially correlated with a two-stage gas absorption phenomenon. At 1 MPa, TBPC hydrates demonstrated a two-stage gas absorption, capturing an amount of gas initially akin to TBAC hydrates but surpassing it subsequently. TBAB hydrates with $w = 0.320$ persistently exhibited a two-stage gas absorption across all pressure levels. The complex crystal structures and variations in growth rates contributed to the intricate observed behaviors.

There are two commonly described forms of TBAB hydrates, type A and type B, which differ in hydrate composition, crystal structures, and crystal morphology. The formation of type A or type B hydrate crystals is determined by the thermal conditions, which are illustrated in a phase diagram, as depicted in Fig. 6(a). Hydration numbers for type A and type B hydrate crystals are 26.0 and 38.0, respectively, leading to distinct shapes of the hydrate crystals (Oyama et al., 2005). The unit cell parameters of the TBAB·26H_2O (a = 23.9 (2) Å, c = 50.8 (5) Å; Z = 24 and of the TBAB·38H_2O (a = 21.060 (5) Å, b = 12.643 (4) Å, c = 12.018 (8) Å; Z = 2) indicate that type A hydrate has a tetragonal crystal structure and type B hydrate has an orthorhombic crystal structure (Rodionova et al., 2013). Kim et al. reported that the addition of pre-produced hydrate seed can accelerate the hydrate formation (Kim et al., 2022a). The morphology of type A TBAB hydrate crystals appears needle-like in the absence and presence of seed, as shown in Fig. 6 (b and c). Conversely, the inclusion of type B seed caused the immediate formation of type B TBAB hydrates without the transitional phase, indicated by irregular-shaped crystals in Fig. 6(d).

Zhang et al. (2013) numerically and experimentally investigated the morphologies and sedimentation of the two forms of TBAB semi-clathrate hydrates and estimated the solid fraction of TBAB hydrate slurry. They used a theoretical modeling approach (Egolf et al., 2008) to simulate the sedimentation of TBAB semi-clathrate hydrate crystals and introduced a method to determine the geometry of hydrate crystal particles by numerical analysis. But both the above-mentioned studies were performed without gas molecules (i.e., CO_2 or others) being involved as guests. Later a few studies have looked into the crystal structure and morphology of the growth of TBAB or TBPB semi-clathrate hydrates that form in the presence of CO_2, H_2, and other gas mixtures.

Li et al. (Li et al., 2019) investigated the morphology of the growth of TBPB and TBAB hydrates produced when CO_2 and CH_4 were present at a stoichiometric concentration of 2.57 mol%. The stoichiometric concentration was defined by the hydration number (TBPB. 38 H_2O and TBAB. 38 H_2O) provided in the literature (Muromachi et al., 2014; Shimada et al., 2005). Using a stereomicroscope equipped with a CCD camera and a double-arm LED fiber illuminator as a light source, they acquired images of the hydrate crystals as those formed. For the morphological experiment, they utilized a three-step procedure consisting of gas dissolution, chilling, and hydrate nucleation and growth (Fig. 7). *In-situ* Raman spectroscopy can also be utilized to help identify the type of semi-clathrate hydrates. Observing the peaks at different spectral ranges and shift in frequency can give valuable insights into CO_2 enclathration, bond stretching, and the possible arrangement of water molecules. When CO_2 is trapped inside the hydrate crystal cages, the locations of peaks shift somewhat lower in frequency compared to those in the gas phase, regardless of the hydrate structure (Chazallon et al., 2014; Chen et al., 2015; Ikeda et al., 1998; Sum et al., 1997; Uchida et al., 1995). Hashimoto et al.(Hashimoto et al., 2017b) performed X-ray diffraction as well as Raman spectra analyses on the gas capacity of ionic semi-clathrate hydrates (Fig. 8). The data from their examinations of the TBPB, TBAC, and TBPC semi-clathrate hydrates revealed that each type of hydrate had a consistent uniform structure. TBAC hydrates had a tetragonal structure, while TBPB and TBPC hydrates had an orthorhombic structure. The TBAB hydrates, on the other hand, may have a dual-phase, including both orthorhombic and tetragonal structural hydrates, which could explain their irregularly high selectivity of CO_2 at 1 MPa pressure.

Literature has revealed two techniques for determining phase equilibrium data, phase behavior, and hydrate formation kinetics: the stepwise method and the dynamic method (Qing et al., 2018; Wang et al., 2020a; Xie et al., 2021). The dynamic method can be utilized for investigating the phase behavior of hydrate formation and dissociation, while the sequential method can be used to measure phase equilibrium data. In the stepwise method, the sample is cooled to a specified temperature and frozen for a specific amount of time. The temperature is then increased at a rate no greater than 0.6 K below the dissociation temperature. The temperature is then increased gradually, with isothermal intervals maintained between each heating phase. The equilibrium temperature of the hydrate phase at a given pressure is determined by

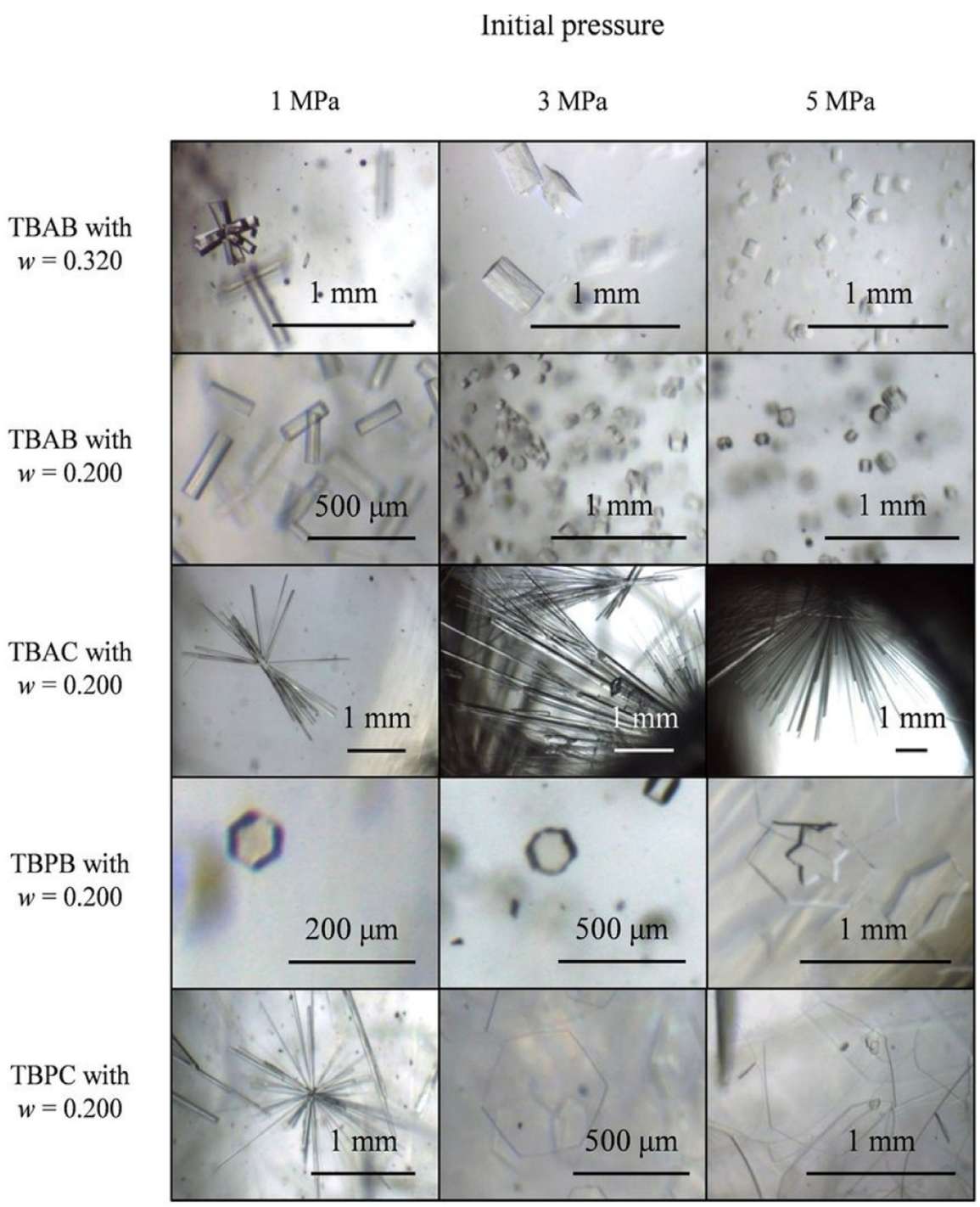

Fig. 5. Single crystals of ionic clathrate hydrates formed in 0.15 mol% CO_2 and 0.85 mol% N_2 gas separation tests (Hashimoto et al., 2017b).

the step temperature (T_{step}) after the last endothermic melting signal (Fig. 9). The illustration of the dynamic method can also be found in the literature (Qing et al., 2018; Xie et al., 2021). CSMHYD (Colorado School of Mines Hydrate), a software program that can also predict hydrate phase equilibrium conditions and other hydrate properties (Sloan Jr and Koh, 2007). The accuracy of the stepwise method can be confirmed by comparing the CSMHYD results. Another method for determining the incipient equilibrium condition for semi-clathrate hydrate formation is the isothermal pressure search procedure (Englezos and Hall, 1994; Li et al., 2017b), which involves pressurizing the equilibrium vessel to the pressure of 0.05–0.15 MPa above the estimated hydrate forming pressure, establishing the target temperature, stirring the vessel contents, and then inducing hydrate nucleation by further increasing the pressure. Once a small amount of hydrate forms, the pressure is quickly reduced, and the system is allowed to equilibrate. If there are a large number of crystals remaining, the pressure is again reduced. A final equilibrium pressure is to be determined when there is a small amount of hydrates left. Further description of this method can be found in the literature (Englezos and Hall, 1994).

The phase behavior of semi-clathrate hydrates is conducted under equilibrium conditions using phase diagram-based methodology, the calorimetric method, and the electrical resistivity or conductivity method (Godishala et al., 2013; Kim et al., 2022b; Li et al., 2019; Oyama et al., 2005). The phase behavior and kinetics of semi-clathrate

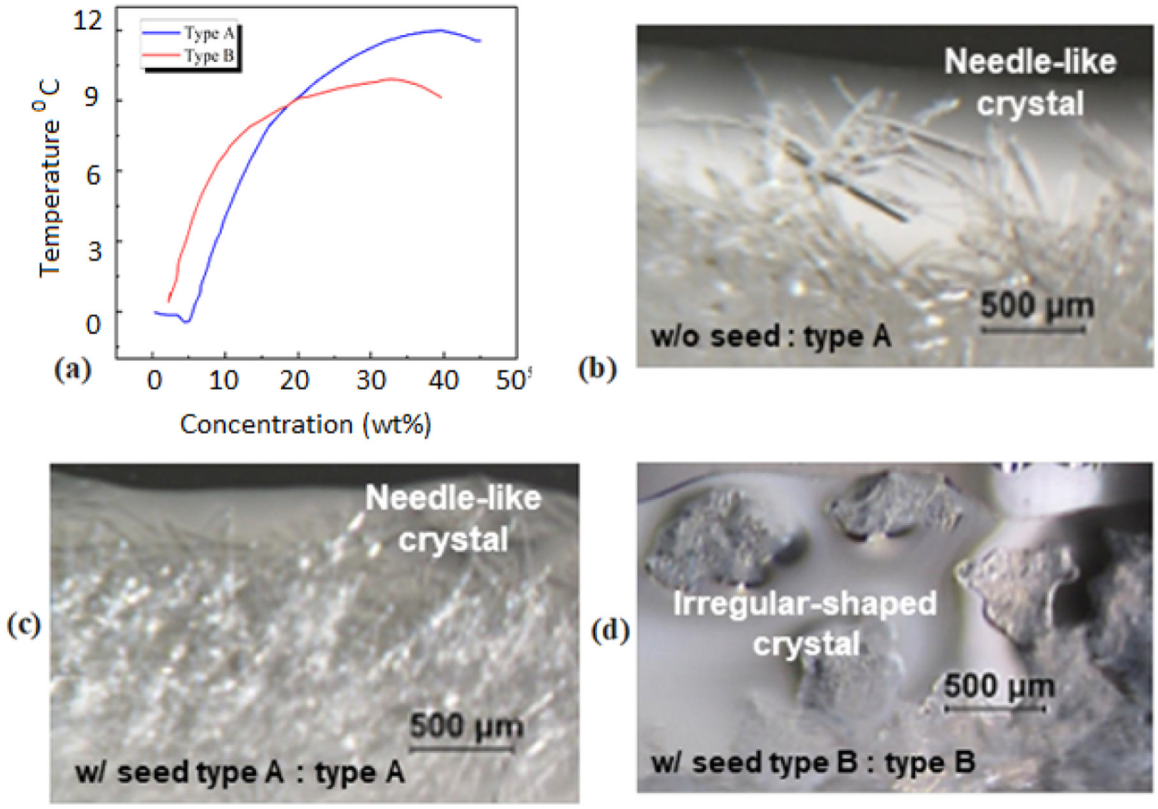

Fig. 6. Phase diagram of TBAB hydrates (Ma et al., 2010) (a); morphology images captured at 120 min to observe hydrate formation in the absence of seed (b), with type A seed (c), and with type B seed (d) (Kim et al., 2022a).

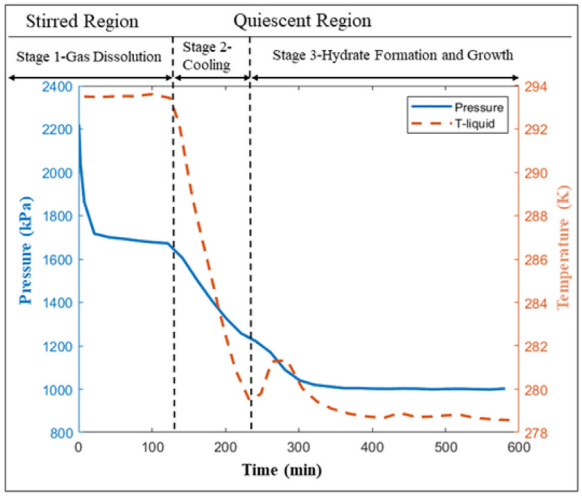

Fig. 7. Interpretation of the 3-stage procedure used for morphological study of TBAB and TBPB semi-clathrate hydrate formation (Li et al., 2019).

hydrate formation have been the subject of very few theoretical or modeling investigations (Mahmoudi et al., 2016). Mahmoudi et al. (Mahmoudi et al., 2016) employed Response Surface Methodology (Box-Behnken design) (Partoon et al., 2015) to investigate the kinetics of the formation of the TBAB-THF (Tetrahydrofuran) hydrate mixture. The sub-cooling driving force and electrical conductivity variations during hydrate formation were used to determine the kinetics of the TBAB-THF hydrate, and response surface methodology (RSM) was used to optimize the operating conditions. Their investigation concentrated on the application of semi-clathrate hydrate as a cold storage medium and did not include gas molecules as guests. Yi et al. determined the phase equilibrium data of hydrate formation using the *"T-cycle"* method in the presence of water-insoluble promoter, tetrahydrothiophene (THT) and different gas systems (Yi et al., 2022). The dissociation enthalpies of hydrate formation in these systems using the Clausius-Clapeyron equation and its modified style were also calculated based on the combined phase equilibrium data.

There have been a few studies that used a real-time measurement technique during the semi-clathrate hydrate formation process in non-equilibrium conditions. (i.e., before reaching equilibrium). Kim et al. (Kim et al., 2022b) devised a method based on electrical resistivity for measuring the kinetics of semi-clathrate hydrate formation in the absence of gas molecules as guests by a model based on Bruggeman's effective-medium approximation (Bruggeman, 1935), which can provide reliable real-time quantification of the hydrate fraction in TBAB hydrate slurry for non-equilibrium conditions. More research of this kind is needed, concentrating on CO_2 capture utilizing semi-clathrate hydrate as the guest molecule.

4. Role of promoters

The preceding section introduced the concept of CO_2 capture using semi-clathrate technology and how it facilitates the capture process. Over the last two decades, the utilization of additives to enhance the formation of hydrates has been established as a highly effective approach to advancing the implementation of hydrate technology. These additives typically encompass kinetic promoters, such as surfactants and nanofluids, as well as thermodynamic promoters like cyclopentane (Yu et al., 2020), tetrahydrofuran, and semi-clathrate promoters. Nevertheless, further research and development are required to successfully transition the hydrate technology from small-scale laboratory experiments to large-scale industrial implementation. This section will provide a comprehensive analysis of the significant role that promoters play in

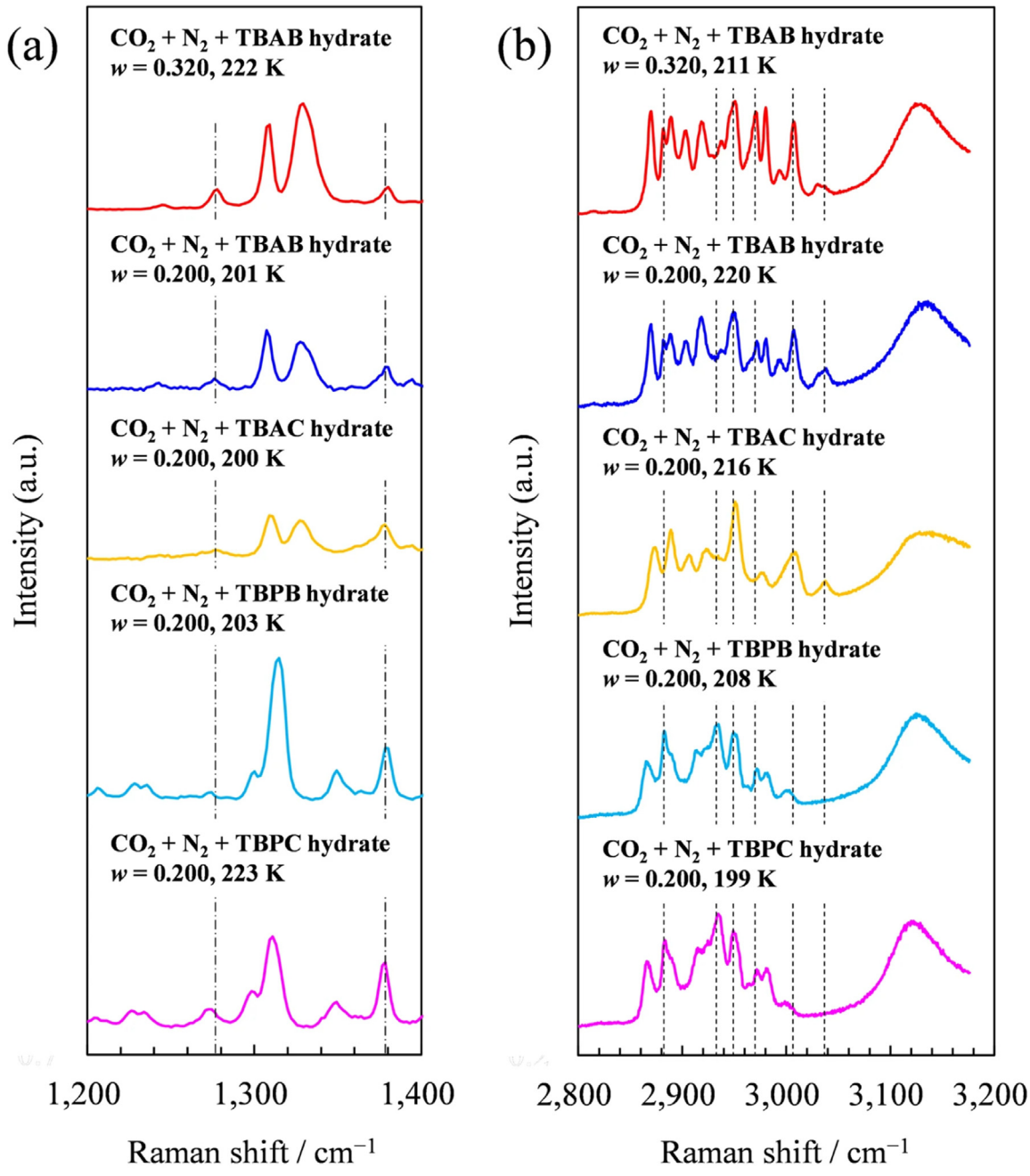

Fig. 8. Raman spectra of the semi-clathrate hydrates produced in the presence of CO_2 and N_2 gases (Hashimoto et al., 2017b).

the formation of semi-clathrates. It is known that temperature, pressure, and mechanical methods such as stirring, bubbling, and spraying can efficiently affect the hydrate formation rate (Wang et al., 2021). In addition to the aforementioned parameters, the formation and dissociation of hydrates are impacted by various chemicals, some of which act as inhibitors, while others act as promoters (Mandal and Laik, 2008). Promoters work by raising the rate of hydrate production and lowering the equilibrium condition to speed up hydrate formation (Fig. 10).

In general, there are two broad categories of hydration promoters: thermodynamic hydrate promoters and kinetic hydrate promoters (Majid et al., 2021). Thermodynamic hydrate promoters are substances that facilitate the formation of hydrates by lowering the pressure and/or temperature required for hydrate formation. These promoters facilitate hydrate formation because they increase the thermodynamic stability of the hydrate phase. Salts, alcohols, and glycols are all examples of thermodynamic hydrate promoters. On the other hand, kinetic hydrate promoters enhance the rate of hydrate formation or dissociation without affecting the thermodynamic stability of the hydrate phase. These promoters work by lowering the kinetic barrier for hydrate nucleation or dissociation, allowing for more efficient and faster hydrate formation or dissociation. Examples of kinetic hydrate promoters include surfactants, polymers, and nanoparticles. When hydrates form, they consist of water molecules forming a cage-like structure around gas molecules, such as CO_2. Subsequently, the other molecules (promoters) can enter into the empty spaces within the hydrate structure, contribute to the stabilization of the overall structure, and make it more selective towards certain gases such as CO_2. This means that when hydrates form, they can trap CO_2 more effectively than other gases, making them useful in carbon capture and storage applications. The utilization of promoters that enhance the stability and selectivity of hydrates enables the formation of

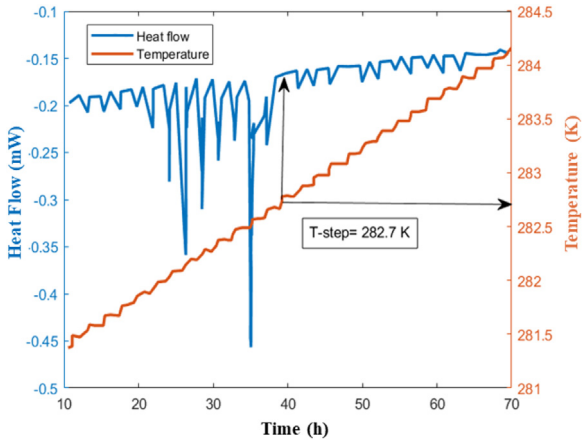

Fig. 9. Interpretation of the stepwise procedure for hydrate phase equilibrium measurement (Xie et al., 2021).

hydrates in less severe conditions, hence offering potential cost savings and improved energy efficiency.

4.1. The impact of introducing a singular promoter

To capture CO_2 from simulated flue gas [CO_2 (17 mol %)/N_2] at varied operating conditions using a one-stage hydrate separation method, Li et al. (2012) examined the effects of three quaternary salts on the development of hydrate formation and separation efficiency. The separation of carbon dioxide is found to yield more benefits when the concentration of CO_2 in the $TBANO_3$ solution is increased. $TBANO_3$ exhibits the most significant influence on the separation of CO_2, mostly attributed to the favorable kinetic properties of CO_2 inside its solution, with the highest S.F. of 15.54 compared to the other two salts. Hashimoto et al. reported that TBAB hydrates showed better CO_2 selectivity despite having a lower gas-absorption capacity than THF hydrates (Hashimoto et al., 2017a). The precise regulation of the crystal growth temperature plays a crucial role as the capture of gas by TBAB hydrates is influenced by a modest subcooling temperature. Fan et al. (2009) found that at the same temperature, TBAB and TBAF could expedite hydrate formation and lessen the associated inlet pressure. CO_2 was enhanced in the hydrate phase due to the existence of TBAB and TBAF, with the highest level of CO_2 concentration in the hydrate stage being 36.52 mol% with TBAB at 4.03 MPa and 56.55 mol% with TBAF at 3.67 MPa. Table 3 shows more of these research findings in an organized way. It provides a clear idea of the effects of individual promoters in different experiments and helps to compare the performances of different promoters.

To make a fair comparison among the promoters, a handful of parameters need to be considered. The comparison can be performed through gas uptake, induction time, CO_2 recovery, or selectivity. CO_2 can be separated from other gases (called "enclathration") when promoters are present. The process of hydrate enclathration is primarily influenced by the prevailing pressure and temperature conditions, as well as the specific quaternary salt selected and its concentration. The recovery of CO_2 means the efficiency of CO_2 removal from the initial gas stream (Li et al., 2017b). In addition, the separation factor or selectivity is determined by dividing the recovery of CO_2 by the recovery of $CH_4/N_2/H_2$, whichever gas is present (Linga et al., 2007a). This means that evaluating recovery based solely on CO_2 levels is insufficient; eradication of the other gas must also be taken into account. The more the selectivity, the better the promoter in that condition. Table 3 illustrates the operating conditions, input gas compositions, promoter concentrations, and selectivity to facilitate understanding.

4.2. The effects of co-feeding thermodynamic promoters

The hydrate phase formation equilibrium can be moved to a higher temperature and lower pressure by using the two efficient thermodynamic promoters TBAB and TBPB (Wang et al., 2020a). The addition of TBPB to the TBAB solution not only enhances the kinetics but also accelerates hydrate formation and increases CO_2 capture efficiency. This promotional impact was seen to be more pronounced at a lower subcooling ($\Delta T = 6$ K) ($\Delta T = T_{phase\ equilibrium} - T_{experimental}$), as compared to higher subcooling ($\Delta T = 9$ K and 12 K). However, the gas consumption rate and induction time decrease when the subcooling temperature rises as the size of the hydrate crystal shrinks. The results show that at a given subcooling temperature, CO_2 gas consumption using a TBAB + TBPB solution results in 49 % higher than using only TBAB (Zhou et al., 2018), and 64 % higher than using only TBPB (Wang and Dennis, 2017). The TBAB + TBPB solution also has a higher efficient hydrate conversion rate compared to TBAB alone. One reason for this is that the resistance to water mass transfer at the gas-water interface is reduced during hydrate formation. In contrast, the formation of needle-like crystals in TBAB solutions hinders the CO_2 molecules from entering the liquid for hydrate development, which slows down the formation rate of hydrates in the gas phase.

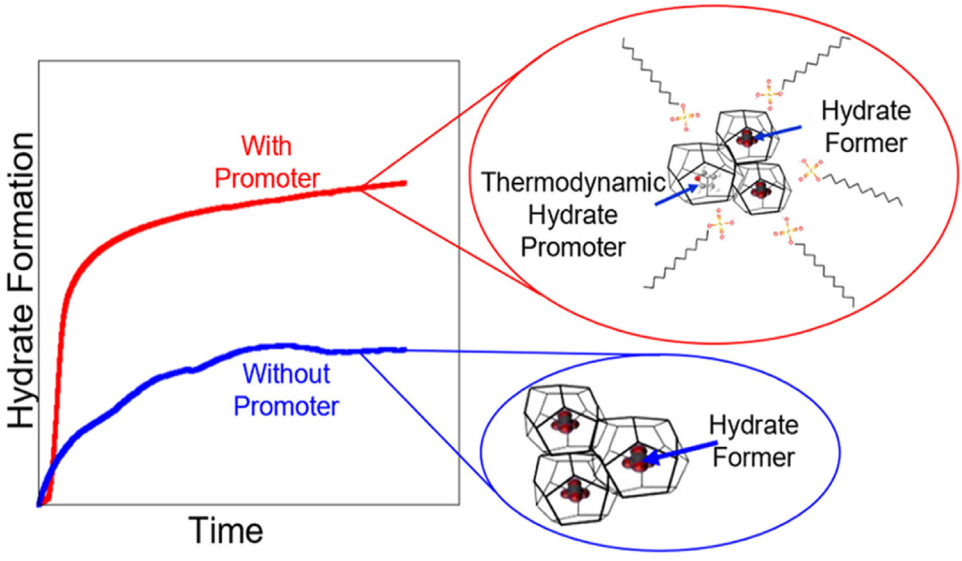

Fig. 10. Hydrate formation with or without promoters (Majid et al., 2021).

Table 3
Comparison among promoters based on their recovery of CO_2 and selection factor.

Promoter	Feed	Weight/mole%	T (K)	P (MPa)	CO_2 recovery (%)	Selection factor	Refs.
TBPB	40% CO_2 + 60% CH_4	2.57 mol%	278	2.8	29.1	29.8	Li et al. (2019)
	17% CO_2 + 83% N_2	1 mol%	275.15	3.3	62	14.06	Li et al. (2012)
				2.5	63	12.5	
	40% CO_2 + 60% CH_4	33.2 wt%	278.1–284.2	2.8	41.7	31.7 ± 3.3	Li et al. (2017b)
	17% CO_2 + 83% N_2	0.28 mol%	277.5	3.5		13.25	Ye and Zhang (2014)
	40% CO_2 + 60% CH_4	5 wt%	278.1	0.30	46.3	14.3	Li et al. (2017a)
		10 wt%	283.4		50.2	8	
		20 wt%	283.4		42.1	29.3	
	39.7% CO_2 +60.3% H_2	2.23 mol%	284.1	3.032	45	26	Muromachi, 2021)
TBAB	15.2% CO_2 +84.8% N_2	20 wt%	282.2	1.017		21.9	Hashimoto et al. (2017a)
		32 wt%		2.012		12.7	
	17% CO_2 + 83% N_2	5 wt%	277.5	4.3	42	7.5	Li et al. (2009)
				5.02	45	6	
				6	43	5.6	
				7.3	40	5.2	
	17% CO_2 + 83% N_2	0.28 mol%	277.5	3.5		12.81	Ye and Zhang (2014)
	20% CO_2 +80% N_2	5 wt%	274	0.748	77	3.3	Komatsu et al. (2019)
				0.864	68	5.3	
				0.912	64	4.8	
				1.216	64	5.8	
			277	1.008	68	5.2	
				1.31	65	7.2	
				1.99	54	9.8	
	40% CO_2 + 60% CH_4	2.57 mol%			34.4 ± 0.7	67.5 ± 21.4	Li et al. (2019)
	40% CO_2 + 60% H_2	0.29 mol%	277.15	3.5	87.6		Yu et al. (2018)
TBAF	16.60% CO_2 + 83.4% N_2	0.293 mol%	277.65	2.46	50	36.98	Fan et al. (2009)
	12% CO_2 + 88% N_2	0.76 mol%	ΔT=3	5		15	Hashimoto et al. (2020)
		1.69 mol%				7.7	
		2.87 mol%				2.8	
	61.3% CO_2 + 38.7% H_2	3.4 mol%	253	3	14.1 ± 2.7	5.8 ± 1.1	Kida et al. (2023)
			293		11.9 ± 1.9	2.3 ± 0.4	
			253	9	33.7 ± 2.3	8.1 ± 1.2	
			293		18.1 ± 1.5	2.2 ± 0.3	
$TBANO_3$	40% CO_2 + 60% H_2	1 mol%	278.2	6		32.65	Babu et al. (2014b)
	40% CO_2 + 60% H_2	0.5 mol%	274.2	6		32.21	Babu et al. (2014c)
	17% CO_2 + 83% N_2	1 mol%	275.15	2.5	65	14.5	Li et al. (2012)
				3.3	66	15	
				4	68	15.7	
TBAC	17% CO_2 + 83% N_2	0.34 mol%	277.5	3		11.23	Ye and Zhang, 2014)
	39.7% CO_2 +60.3% H_2	2.73 mol%	288.2	3.02	29	61	Muromachi, 2021)
TBPC	17% CO_2 + 83% N_2	1.06 mol%	277.5	3		11.60	Ye and Zhang, 2014)
	20% CO_2 + 80% N_2	5 mol%	277.65	4.3		7.3	Li et al. (2009)
	16.60% CO_2+84.4% N_2	5 mol%	277.65	4.0		9.82	Fan et al. (2009)

4.3. The effect of subcooling temperature

As the temperature of subcooling increases, there is a significant reduction in the induction time (Wang et al., 2020b). Induction time (IT) typically provides information regarding the likelihood of hydrate nucleation. As the subcooling temperature increases and induction time decreases, the process of hydrate nucleation accelerates. Once the agitation was initiated, the TBAB semi-clathrate hydrate instantly underwent nucleation at the largest subcooling of 12 K (Wang et al., 2020b). As a result, the liquid phase immediately changed into the bulk hydrate and impeded gas transfer, resulting in nearly negligible CO_2 consumption. Adding TBPB to the TBAB solution leads to a reduction in the induction time at ΔT = 6 K, with the TBAB + TBPB mixed solution having an induction time of 95 min, less than that of the TBAB (190 min) and TBPB (107 min) solutions (Wang et al., 2020a). As induction time decreases, subcooling time increases, and the CO_2 consumption rate drops. Gas consumption was observed to be the highest for all solutions at ΔT = 6 K, while the lowest was observed at ΔT = 12 K. This is because the higher temperature and prolonged induction time at low subcooling cause more CO_2 gas to dissolve in the liquid phase. However, as the subcooling increases, the operating temperature decreases, and the induction time decreases, resulting in a smaller quantity of CO_2 dissolved in the liquid, which results in a greater driving force for hydrate formation (Wang et al., 2020b).

4.4. The effect of combining thermodynamic and kinetic promoters

The hydrate formation kinetics can be improved by the addition of kinetic promoters with thermodynamic promoters. Kinetic promoters are frequently used to increase the rate of hydrate formation by altering the gas-liquid contact but not the equilibrium conditions. Surfactants are the primary type of kinetic promoters, which enhance the rate of hydrate formation without actively participating in the formation process. The surfactants frequently employed in hydrate-forming systems are sodium dodecyl sulfate (SDS), Tween-80 (T-80), and dodecyltrimethyl-ammonium chloride (DTAC). Among several surfactants studied so far, SDS has been demonstrated to be an excellent kinetic promoter (Kumar et al., 2013; Okutani et al., 2008). The effects of SDS on the production of gas hydrates were investigated by Zhong and Rogers and revealed that the rate of hydrate formation can be significantly enhanced by multiple orders of magnitude when an SDS solution or a surfactant solution with similar properties is present (Zhong and Rogers, 2000). Tajima et al., Rossi et al., and Torre et al. conducted additional investigations to confirm that the surface-active properties of SDS at the critical micelle concentration (CMC) have the most significant impact on improving the pace of hydrate formation (Rossi et al., 2012; Tajima et al., 2010; Torré et al., 2011). Nevertheless, the utilization of thermodynamic additives or kinetic additives alone does not offer a comprehensive solution to address all the challenges associated with

hydrate-based CO_2 capture and separation from gas mixtures, including harsh conditions, low gas consumption, low hydrate formation, and low CO_2 recovery. As a result, researchers have directed their attention toward investigating the synergistic effect of thermodynamic promoters and kinetics promoters.

4.4.1. TBAF and kinetic promoters

Zeng et al. studied the kinetic performance of CO_2/H_2/TBAF semi-clathrate formation at 6.0 MPa with a temperature driving force of 4.1 K at varied TBAF concentrations in a stirred tank reactor for pre-combustion CO_2 capture from fuel gas (Zheng et al., 2018). The TBAF concentration was varied from 0.80 to 3.38 mol%. For the gas uptake at various TBAF concentrations, 3.38 mol% solution yielded the highest gas uptake when normalized by the amount of water used, whereas 0.8 and 1.5 mol% solution achieved the highest total gas uptake (normalized by the solution volume), hydrate formation rate, and CO_2 composition in the captured gas. The highest hydrate production rate and the maximum recorded value of CO_2 composition was 98.2 mol%, which was achieved by 0.8 mol% TBAF solution. The addition of three kinetic additives, including SDS, leucine, and tryptophan reduced the induction time compared to the system with TBAF alone. The presence of a surfactant enhances the kinetics due to the capillarity-driven transport of water into the porous hydrate phase, gas dissolution, and lower interfacial tension between gas and water (Okutani et al., 2008; Zheng et al., 2018; Zhong and Rogers, 2000). A concentration of 300 ppm SDS and 3000 ppm leucine resulted in a reduction of 96 % and 16.5 % in induction time respectively compared to the standard TBAF solution. However, the inclusion of kinetic additives limits the dissolving phase and reduces the gas uptake rate, except for 500 ppm SDS and no noticeable impact on the composition of CO_2 was observed.

4.4.2. TBPB and SDS

Xie et al. reported the phase behavior of TBPB semi-clathrate hydrate produced in the presence of CO_2 at a stoichiometric concentration (Xie et al., 2021). The results showed that the phase equilibrium conditions for CO_2 hydrate formed in pure water and TBPB + CO_2 semi-clathrate hydrate formed at 0.5 mol% TBPB were more significant than those for TBPB + CO_2 semi-clathrate hydrate formed at 2.57 mol% TBPB. However, the CO_2 hydrate dissipated and additional TBPB + CO_2 semi-clathrate hydrate was generated when 500 ppm SDS was added to the 2.57 mol% TBPB solution. The rate of CO_2 consumption was slowed during TBPB + CO_2 semi-clathrate hydrate production at the same temperature and pressure when SDS was added to the TBPB solution. The possible reason might be the formation parameters for ice and CO_2 hydrate are more severe than those for TBPB semi-clathrate hydrate, the presence of SDS caused water molecules to preferentially convert to TBPB + CO_2 semi-clathrate hydrate rather than ice and CO_2 hydrate. Another possible cause could be the presence of kinetic promoters, which decreased the surface/interfacial tension of the liquid and increased CO_2 solubility (Wu et al., 2022). Hydrate formation rate increases after adding SDS, but CO_2 separation efficiency gets reduced, which explains that using kinetic promoter with thermodynamic promoter may only increase hydrate nucleation kinetics. The introduction of low-concentration SDS (100 ppm) results in a reduction in gas consumption rate. However, when the concentration of SDS increases, the rate of CO_2 gas consumption also increases (Wang et al., 2020b).

4.4.3. TBAB and tween-80

Zhang et al. (2022) looked into Tween-80 as a kinetic promoter to examine the impact of non-ionic surfactant on CO_2 hydrate production in a thermostatic reactor using CO_2-rich gas mixtures with varying concentrations of Tween-80. The addition of Tween-80 with TBAB can have a significant effect on the separation efficiency and CO_2 recovery.

From Fig. 11, it can be demonstrated that the highest split fraction and separation factor for semi-clathrate hydrates at t = 126 min and

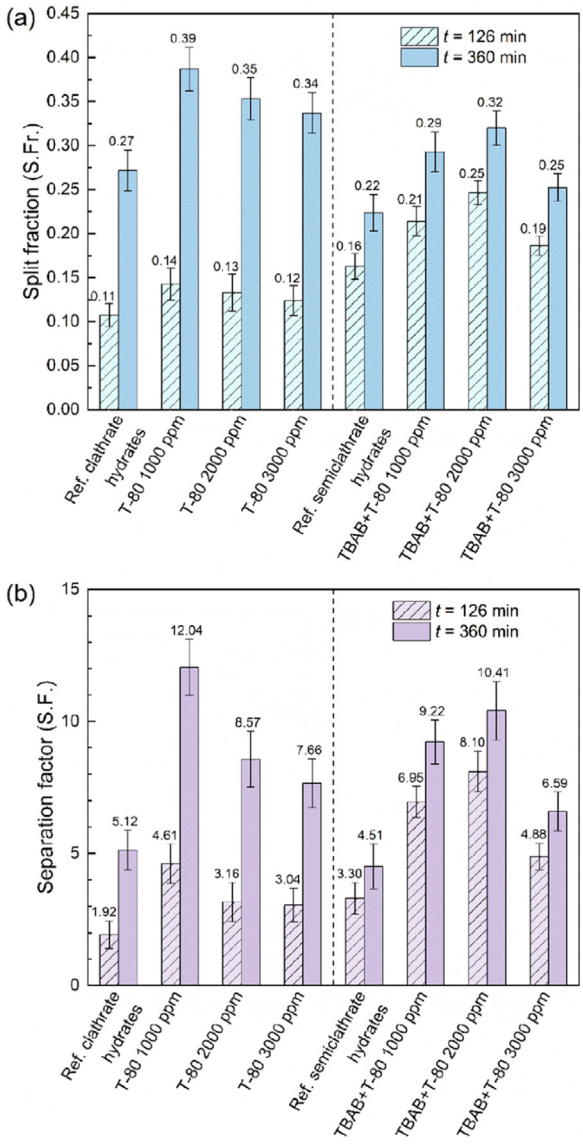

Fig. 11. Variation of (a) CO_2 split fraction and (b) separation factor with different concentrations of T-80 (Pexp=3.8 MPa) (Zhang et al., 2022).

t = 360 min was achieved at TBAB+*T*-80 2000 ppm. Therefore, the separation factor and split fraction will both rise when TBAB+*T*-80 concentrations rise. Though TBAB+*T*-80 shows a different result because of the inhibition effect on the total gas uptake, it is still greater than the values of the gas uptake of "Ref. semi-clathrate hydrates". But in the case of clathrate hydrate, with the increase in T-80 concentration, the CO_2 split fraction drops.

Fig. 12 shows that the CO_2 gas intake of the three systems, including T-80 is greater than the gas uptake of the "Ref. semi-clathrate hydrates" reference case. T-80 at 2000 ppm shows the maximum gas uptake of any concentration at the end of the experiments (t = 360 min). It is important to highlight that while the gas uptake continues to rise steadily at approximately 360 min, the rates of increase in gas uptake exhibit a decelerating trend after 200 min.

4.5. The effect on separation efficiency

Indicators of separation efficacy include the separation factor and CO_2 recovery. The concentration of the promoter, experimental conditions, and motivating factors all play a role. When TBAB or $TBANO_3$ is added to the mixture, the separation factor drops dramatically. At a

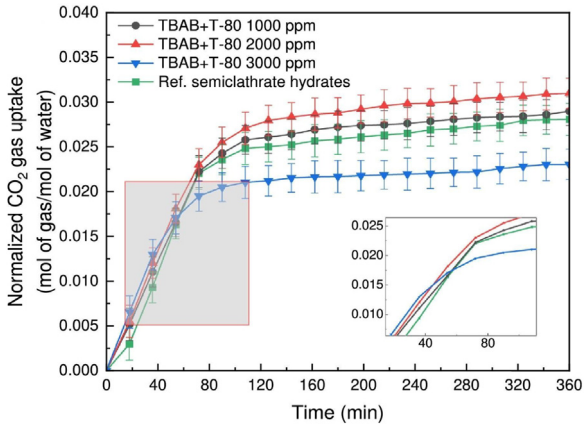

Fig. 12. Normalized CO_2 uptake in semi-clathrate hydrates at P_{exp}= 3.8 Mpa (Zhang et al., 2022).

driving force of 2.5 MPa, the separation factors for 0.29 and 0.5 mol% TBAB were 105.2 and 106.7, respectively. It indicates that the semi-clathrate hydrate cages incorporate negligible amounts of H_2. In addition, the maximum CO_2 recovery was obtained with 0.29 mol% TBAB and without a promoter, respectively, indicating that the presence of a promoter increases the split fraction (Linga et al., 2007b; Xu et al., 2012). In the case of TBPB, the highest separation factor (31.1 ± 3.3) was achieved at the highest concentration of TBPB (33.2 mol%) and the highest CO_2 recovery was found at a lower concentration (10 mol%)(Li et al., 2017b) but at this concentration, the separation factor was the lowest (8.0 ± 0.7). In another study with 0.1 mol%, 0.293 mol% and 0.9 mol% TBAB, among them, 0.293 mol% TBAB showed the best separation result with CO_2 separation factor (42.17), and CH_4 separation and recovery factor (1.430) (Fan et al., 2016). In the illustration of semi-clathrate hydrates, we observed that, up until the point where the effect of inhibition set in, the separation efficiency increased along with the concentration of a kinetic promoter (Tween-80) (Zhang et al., 2022). However, when SDS is included, the CO_2 separation is weakened (Wang et al., 2020b).

4.6. The effect on gas uptake

Both the gas uptake and gas capacity are greatly dependent on the structure of the QAS semi-clathrates. TBAF has a cubic structure in which 79.5 % of the small cages are filled with water (Komarov et al., 2007), which is why only a few vacant small cages are left to capture CO_2. Both TBAB and TBAC have tetragonal structures, resulting in a greater number of vacant small cages. Consequently, they have demonstrated higher gas uptake capacities as compared to TBAF. Furthermore, TBAB has a higher extent of filling cages with TBA cations, which means that TBAB has less CO_2 storage capacity than TBAC (Kim and Seo, 2015).

The gas uptake process is influenced by the concentration of the promoter. Ma et al. found out that for 0.9 mol% TBAB solution, gas uptake was lower than in 0.293 mol% TBAB solution at 3 Mpa (Hashimoto et al., 2017b). In a separate study utilizing TBAF as the semi-clathrate promoter, the highest normalized gas uptake (10.90 ± 0.70 mmol of gas/mol of water) was obtained with a 3.38 mol% TBAF solution, while the lowest uptake was observed with a 2.00 mol% TBAF solution (8.47 ± 0.78 mmol of gas/mol of water). The amount of water consumed served as a benchmark for this measurement of petrol consumption. Results at various concentrations were achieved, however, when gas absorption was normalized by the amount of solution. The largest gas uptakes were seen in solutions containing 0.8 and 1.5 mol% TBAF, with 440.3 ± 9.7 and 440.2 ± 1.7 mmol of gas/L of the solution, respectively. By increasing the concentration to 2.0 mol% and beyond, gas absorption was seen to decrease drastically. The underlying cause of this behavior may be attributed to the fact that solutions with lower concentrations contain more water, allowing for greater gas dissolution during the dissolution phase and resulting in higher gas uptake (Zheng et al., 2018).

4.7. Inhibition effect on semi-clathrate

Based on the prior research, it has been observed that the inhibition effect on promoter can bring significant change in separation factor, split fraction, semi-clathrate formation, etc., i.e., by combining TBAB with Tween-80 (a kinetic promoter), both the separation factor and split fraction can be increased with the increase in the concentration of TBAB+ *T*-80. However, reaching a certain concentration (TBAB + *T*-80 2000 ppm), any increase causes a decrease in separation factor and split fraction. The observed phenomenon can be due to the inhibition effect on the total gas uptake. However, when the concentration exceeds 0.35 wt%, an inhibition effect occurs and causes a different result (Lee et al., 2010).

There are two primary categories of gas hydrate inhibitors: thermodynamic inhibitors and low-dose hydrate inhibitors (Koh et al., 2002). The impact of concentrated brine, NaCl, a well-known thermodynamic inhibitor on gas hydrate formation has been extensively studied. Because of their impact on water activity, these inhibitors are often referred to as "inert inhibitors", or inhibitors that do not enter the gas hydrate phase but still affect the thermodynamic equilibrium. By implementing this approach, they shift the pressure and temperature ends of the hydrate formation equilibrium curve up and down, respectively. The hydrate formation temperature drops as the salt concentration increases (Holzammer et al., 2016).

The salt ions form bonds with the water molecules through the coulomb force. Therefore, the involved water molecules cannot develop hydrogen bonds with the non-involved water molecules anymore. Thus, the inhibition impact on the hydrate formation by the solvation of salts is obtained, and this impact increases with the increase in the concentration of the salt (Holzammer et al., 2016). Gas hydrates are basically like ice crystalline solids formed with water molecules and guest gas. The water molecules form a lattice structure with several interstitial cavities through hydrogen bonding, and the cavities are filled with molecules of the guest gas. The crystalline structure reaches stability when a certain number of cavities are filled (Qi et al., 2012). Hence, because of the inhibition impact, fewer water molecules can form lattice structures with each other, and fewer lattice cavities will be available for CO_2 to occupy.

Muromachi et al. stated a noteworthy finding from the experimental data (Muromachi, 2021). Gas hydrate stability conditions in the electrolyte solution are predominantly dominated by anion but to a lesser extent by cation. Cation and anion were found to play diverse roles in restricting hydrate formation in electrolyte solutions. This difference is qualitatively related to the impact of electrolyte solutions on ambient water networks and the fact that cations and anions have different hydration characteristics.

In conclusion, the equilibrium pressure is higher than pure hydrates when a pair of Na^+ and Cl^- is incorporated in a unit cell of hydrates. In addition, since 4 Na^+ ions are already present in the unit cell of the hydrates, the Na^+ ions have a far smaller effect on the equilibrium pressure and crystal structure deformation than the Cl^- ions (Qi et al., 2012).

5. Semi-clathrate hydrate based CO_2 capture process advantages and disadvantages

Most of the studies performed on ionic semi-clathrate hydrate-based CO_2 separation have used either batch or semi-batch type separation techniques. Kim et al. (2022b) used semi-batch type separation methods and found that the phase equilibrium pressure decreased from 5.4 MPa to 0.6 MPa using an aqueous solution of TBAB (mass fraction of 0.08) for an operating temperature of 280 K and a feed gas composition of H_2: CO_2 = 0.6: 0.4. Wang et al. (2020b) investigated the kinetics of TBAB

Table 4
Summary of the previous studies for batch, semi-batch and continuous operation.

Feed gas Composition (by mole fraction)	Method of Operation	Experimental condition			Result	Refs.
		Temperature (K)	Pressure (MPa)	TBAB mass fraction	Mole fraction of CO_2 in the ionic hydrate phase	
H_2/CO_2 = 0.6/0.4	Semi-batch	280.15	3.0	0.15	0.89	Kim et al. (2011)
	Semi-batch	278.15	3.0	0.05	0.97	Li et al. (2011)
	Batch	279.2	6.0	0.05	0.95	Babu et al. (2014a)
	Semi-batch	273.9	3.8	0.10	0.86	Gholinezhad et al. (2011)
	Semi-batch	ΔT_{sub}[a] = 4.0 K	8.0	0.10	0.95	Park et al. (2013)
	Continuous	277.4	5.0	0.05	0.82	Horii and Ohmura (2018)
		281.3		0.10	0.79	

[a] Temperature difference between experimental and equilibrium temperature.

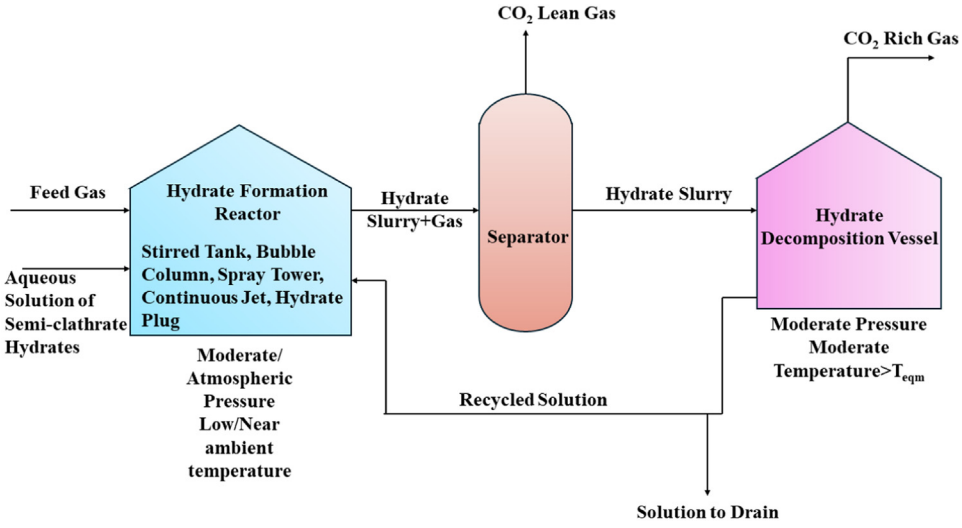

Fig. 13. Flow diagram for the semi-clathrate hydrate-based continuous CO_2 capture process.

hydrate formation, the efficiency of CO_2 separation, and the synergetic effect of SDS and TBAB on CO_2 separation using a batch-type stirred tank reactor. The kinetics of TBAB hydrate nucleation and growth were found to be accelerated in the presence of SDS in TBAB solution, but CO_2 separation efficiency was found to be decreased. Muromachi (2021) studied the effect of TBAB, TBAC, TBPB, and TBPC on CO_2 capture using batch-type apparatus and found TBPB to be most suitable for gas capture among the four salts due to their efficient gas capture and simple phase behaviors. Some other studies on CO_2 capture in semi-clathrate hydrate using batch or semi-batch type methods are summarized in Table 4.

Methods of batch or semi-batch separation have inherent drawbacks. For continuous production of purified gas, multiple sets of reactors are needed to work in parallel, which is expensive and cumbersome (Horii and Ohmura, 2018). However, for commercial operation, a continuous separation process is desirable because it allows the treatment of a large amount of gaseous stream continuously. The continuous gas separation process involves the formation, transportation, and decomposition of hydrates (Tomita et al., 2015). A simplified flow diagram for semi-clathrate hydrate-based continuous separation is shown in Fig. 13. It is critical to understand the time evolutions of composition in each phase inside the hydrate-forming vessel during continuous operation because compositions in the gas, liquid, and hydrate phases change continuously until a steady state is reached. Very few studies have been found that have focused on semi-clathrate hydrate-based CO_2 separation continuously. Horii and Ohmura (2018) performed continuous separation of CO_2 from fuel gas (H_2+CO_2) by semi-clathrate hydrate (H_2+CO_2+TBAB+H_2O) using various mass fractions of TBAB and compared the performance with hydrate (H_2+CO_2+H_2O) based separation. They found the most suitable mass fraction of TBAB to be 0.05 or 0.10 for successful continuous separation. The stoichiometric concentration of TBAB of 0.32 was not suitable because of the loss of fluidity in the hydrate phase and transportation problems. However, in terms of CO_2 uptake, the structure I hydrate showed better performance than the TBAB semi-clathrate hydrate. Ionic semi-clathrate hydrates have the strongest influence on phase equilibrium conditions as they allow separation using milder operating conditions. A multistage continuous process can be used to capture high concentrations of CO_2 (Gholinezhad et al., 2011). Table 4 presents the summary of studies for a fuel gas and various mass fractions of TBAB that were used for CO_2 separation. As mentioned earlier, studies on continuous separation using ionic semi-clathrate hydrate are very few. Results in the table indicate that CO_2 separation efficiency might be lower for continuous operation than for batch or semi-batch operation. This conclusion, however, cannot be derived in the absence of sufficient evidence, as continuous operation has several advantages over batch or semi-batch operation. Also, using multiple stages in continuous operation can increase separation efficiency. More studies are required to support these hypotheses.

Some studies have found that conditions for hydrate formations become difficult as the concentration of CO_2 in the gas decreases (Li et al., 2018; Yang et al., 2017, 2014). In addition, because of the incomplete capture of CO_2 by semi-clathrate hydrate, some studies have proposed semi-clathrate hydrate-based separation coupled with other technology like chemical absorption for complete removal (more than 99 %) of CO_2 (Xu et al., 2012; Xu et al., 2019).

Some process improvements can be made to make the separation more efficient. Using a spraying device in a hydrate formation reactor can induce rapid hydrate formation by increasing the contact between the aqueous solution and gas (Xu et al., 2019). The hydrate transportation problem is a technical issue that hinders the operability of continuous operation. One of the most important issues to run continuously is

maintaining the fluidity of the hydrate slurry (Horii and Ohmura, 2018). CO_2 semi-clathrate hydrate transport is a vital area for future research. Hydrate dissociation caused by local pressure drop during continuous operation also inhibits operational efficiency, which also needs attention for further research.

Continuous operation of hydrate-based carbon capture is still a gray area among investigators based on what we see in the literature. Most of the studies have been performed on lab-scale. Few studies exist that tried to investigate in pilot-scale or even larger scale. There are a number of limitations and complications around implementing a continuous hydrate-based capture process, which are discussed in the manuscript. These limitations need to be addressed before we can successfully implement a continuous process. Since the operating conditions and information on specific units for a continuous process are scarce or in the development stage, Fig. 13 might give us a general idea on how the continuous capture by semi-clathrate hydrates would work.

6. Challenges and future work

Although hydrate and semi-clathrate hydrate-based CO_2 capture (HBC and SCHBC) has emerged as a potential replacement for conventional CO_2 capture and storage techniques, still many uncertainties remain. As of right now, structural data for SCH, CO_2 hydrate, and quaternary salts under various circumstances are lacking (Rodionova et al., 2022). Hydrate formation is a form of crystallization, and crystallization needs time, sufficient contact area, and the right supersaturation conditions (Rehman and Lal, 2022). If the conditions for hydrate formation are not controlled properly, SCH with undesired structure and morphology can lead to inefficient capture, which is one of the limitations of its industrial application. The conditions for good hydrate formation and consequent good storage capacity would depend upon the gas mixture and type of ionic guest compound involved, which complicates the process. Moreover, the hydrate formation process can be unhindered as well since hydrate formation itself is an exothermic process. The degree of supercooling greatly affects the kinetics of hydrate formation with quaternary salts. A low degree of supercooling and low induction time are generally desirable from an economic point of view. The maximum degree of supercooling that is permitted for TBAB hydrate can reach 17.7 K (Sugahara and Machida, 2017). Nucleating agents and the memory effect, a phenomenon where recrystallization happens at a lower degree of supercooling, have been proposed as ways to restrain the degree of supercooling (Machida et al., 2020, 2018; Stoporev et al., 2020). The remaining hydrogen-bond structures in the aqueous solution after hydrate breakdown provide a potential explanation for the memory effect (Lederhos et al., 1996). When halloysite clay nanotubes were used as TBAB hydrate nucleating agents, the onset temperature of hydrate crystallization was raised by 2 °C with just 1 wt% of halloysite added (Machida et al., 2020). However, nucleating agents have the possibility to affect also the structure of the hydrates.

Most of the studies that exist in the literature are laboratory-scale experiments or low-capacity processes. Moreover, most of the studies have used combinations of CO_2, N_2, and H_2 as the gas mixture. Studies on CH_4/CO_2 or other mixtures involving CH_4 are very few. Utilizing ionic semi-clathrate hydrates for CH_4/CO_2 system can potentially open doors to exploit SCH system for pre-combustion carbon capture, natural gas reservoirs, and biogas. CO_2 is more favorable towards stable hydrate formation than H_2 and N_2, whereas CO_2 and CH_4 have similar properties when it comes to hydrate formation, which is challenging. That is why extensive research is needed to find suitable promoters or additives that can favor preferential capture from CH_4/CO_2 system either thermodynamically or kinetically. Molecular dynamic (MD) simulations of CH_4 and carbon dioxide (CO_2) hydrates have been the focus of recent breakthroughs (Rehman and Lal, 2022). As mentioned before, the concentration of CO_2 in the supply gas and the efficient uptake by hydrates counteract with each other. Although CO_2 capture from post-combustion flue gas may seem promising, pre-combustion capture is generally more efficient than the other because of the more concentrated CO_2 gas. Besides, the incorporation of N_2/H_2 in the hydrate phase from the flue gas lowers the efficiency of CO_2 capture. This problem can be solved using multistage capture or combining SCH-based techniques with other techniques like absorption, which can improve the energy efficiency of the process compared to conventional techniques. For example, compared to cryogenic condensation alone, hydrate-based capture and absorption could result in a 30 % reduction in energy usage (Xu et al., 2014).

There are issues with hydrate formation reactors that need to be addressed with more extensive research. This is one of the major barriers for implementing a continuous industrial-scale semi-clathrate hydrate-based separation process. Stirred-tank reactor is the most studied batch reactor for the acquisition of hydrate-based gas capture data. Mixing of gas and liquid phases during hydrate formation leads to long induction time in stirred-tank reactors due to the prevention of hydrate accumulation (Khan et al., 2019). The study of the relationship between temperature and viscosity of the hydrate solution can give insights into the fluidity inside the reactor, which in turn, can determine the suitable mixing needed during hydrate formation. The other types of reactors that are also common include bubble column and spray reactors. Without a stirrer mechanism, bubble columns are unable to offer enough contact area for the continuous synthesis of gas hydrate (Yasuhiko and Mori, 2003). Spray reactors use simple design and eliminate the drawbacks associated with mixing, but are associated with weak temperature control, which is essential for proper hydrate formation (Rehman and Lal, 2022). So, there is a need for improved reactor performance to achieve good control of the hydrate formation. Finally, as mentioned before, transportation of the hydrate phase is another aspect that needs attention for continuous implementation of the hydrate-based technique.

7. Conclusions

Semi-clathrate hydrates have been shown interest for applications like H_2 storage, CO_2 consumption from flue gas, secondary refrigeration, and cold storage because of their hydrate formation under milder experimental conditions than gas hydrates, which allow small gas molecules like CH_4, H_2, and CO_2 to reside the small cages. The addition of promoters reduces the hydrate phase equilibrium considerably. CO_2 capture and storage are crucial for tackling some of the most serious societal and environmental issues. The employment of CCS technologies like adsorption, absorption, membrane, cryogenic distillation, etc. necessitates large capital costs and significant operating complexity, thereby shifting the emphasis to the development of more viable alternatives. Compared to absorption, hydrate-based CO_2 capture can reduce energy costs by 50–75%, making it a cost-effective technology. The hydrate-based gas separation cycle is more practical in the precombustion stage than from a flue gas compound due to the low CO_2 concentration, which necessitates high-pressure costs and/or a massive reactor. In addition, hydrate additives such as THF, SDS, and TBAB can be used to enhance the hydrate rate and improve the separation performance.

However, most of the research is in the developmental stage and involves low-capacity batch processes that use stirred pots, bubble columns, or spray towers as crystallizers. This resulted in a paucity of knowledge on the influence of hydrodynamic parameters on continuous or semi-batch hydrate processes. More intensive multistage reactor design considerations should be made to shift towards a continuous hydrate production stage equipped with a high rate of viscous slurry removal. In addition, hydrate formation is an exothermic process; as the rate of hydrate formation increases, so does the system's temperature, potentially altering the conditions for hydrate formation. In addition, the need for a large contact area, supersaturated conditions, and a longer nucleation time limit the industrial applications of this system. One of the directions ahead for the semi-clathrate hydrate-based pre-combustion CO_2 capture process is a comprehensive investigation or development of new QASs that provide improved gas uptake, kinetics, and thermodynamic stability in a more reasonable environment to

avoid energy penalties. Simulation studies can supplement experimental research and aid in predicting the optimum parameter conditions and QAS combinations for achieving high CO_2 storage capacity.

Declaration of competing interest

None.

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