Ultra-rapid uptake and highly stable storage of methane as combustible ice

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Broader Context

The emergence of natural gas as a key player in the current energy landscape tenders a rare opportunity for the development of new, robust gas storage technologies. Gas hydrate or combustible ice based Solidified Natural Gas (SNG) technology realizes compact and safe long term storage of natural gas using eco-friendly water as the major raw material (>94%). Yet, its practicality has been limited by problems in forming natural gas hydrates at a rapid rate and then ensuring prolonged stability of the same. We report on 1,3-Dioxolane (DIOX) as a dual-action chemical promoter for methane sII hydrate formation, offering elite thermodynamic and kinetic enhancement ability. A small amount (300 ppm) of kinetic promoter L-tryptophan added to the scheme further helps in achieving ultra-rapid hydrate formation rates. Mixed methane-DIOX hydrate pellet stored at atmospheric pressure and conventional freezer for 8 days remains highly stable, thereby demonstrating industrial applicability, scalability and ease of operation.

Abstract

Ever-increasing natural gas (NG) consumption trends due to its cleanest tag and abundant availability point towards an inevitable transition into an NG dominated economy. Solidified Natural Gas (SNG) storage via combustible ice or clathrate hydrates presents an economically sound prospect, promising high volume density, and long-term storage. Here we establish 1,3-dioxolane (DIOX), as a highly efficient dual-action (thermodynamic and kinetic promoter) additive for clathrate (methane sII) hydrate formation. By synergistically combining a small concentration (300 ppm) of kinetic promoter L-tryptophan with DIOX, we further demonstrate ultra-rapid hydrate formation with a methane uptake of 83.81 (±0.77) volume of gas/volume of hydrate (v/v) within 15 minutes. To the best of our knowledge, this is the fastest reaction time ever reported for sII hydrates related to SNG technology and represents a 147% increase in the hydrate formation rate compared to the standard water-DIOX system. Mixed methane-DIOX hydrates in pelletized form also exhibit incredible stability when stored at atmospheric pressure and moderate temperature of 268.15 K, thereby showcasing potential to be industrially adoptable for the development of a large-scale NG storage system.
Introduction

As economic progress and population growth drive global energy demand, fossil fuels continue to remain strategically important and natural gas (NG) will play a vital role in perpetuating the same.\(^1\) Exploration of abundant NG reserves available in unconventional form (shale, hydrates and coal-bed) coupled with NG being the cleanest burning fossil fuel compared to gasoline and coal, makes this resource—which is primarily methane,\(^2\) economically competitive and environment friendly. 2018 witnessed a 4.6% increase in NG consumption with projected 0.9% average annual increase over the next decade.\(^1\) Increased demand, however, warrants better technology for handling of gas storage by the NG importing countries including Singapore for energy security and energy resilience. While liquefied natural gas (LNG) is the best option to transport NG where pipeline is not possible, it is not considered suitable for long-term storage due to the extremely low temperature (111.2K) and associated boil-off involved. Compressed natural gas (CNG) is not suitable for a large-scale storage system due to its explosive nature and the high-pressure requirement. On the other hand, adsorbed natural gas (ANG) has gained more scientific attention in recent years with the synthesis of new materials like MOFs and graphene.\(^3\)-\(^5\)

Nature has been storing methane gas in the form of natural gas hydrates for millions of years albeit in a slow manner, presenting itself today as a huge energy resource.\(^6\)-\(^8\) Gas hydrates are crystalline inclusion compounds where under suitable conditions cages made of water molecules may host guest gas molecules within.\(^9\) Gas hydrates made of methane or natural gas are also known as combustible ice. With the appropriate tuning of formation conditions, and the identification of suitable promoters, we can accelerate the formation of gas hydrates. Thus, NG stored in hydrate form - Solidified Natural Gas (SNG), has re-emerged as an option for large volume, long term storage.\(^10\)-\(^12\) Tetrahydrofuran (THF) has been proven to be a stable thermodynamic promoter for H\(_2\) storage via clathrate hydrate formation.\(^13\),\(^14\) Recently, THF has also been demonstrated to perform as a dual-action (thermodynamic and kinetic promotion) promoter for methane storage.\(^15\) sII methane hydrate forms rapidly in presence of THF over a wide temperature range\(^15\) and has been shown to be stable at near ambient pressure of 0.15 MPa and at 271.5 K.\(^16\)

Despite the use of THF in many industrial chemical processes,\(^17\),\(^18\) its place in hydrate formation has often been questioned, given its carcinogenicity,\(^19\) high volatility\(^20\),\(^21\) and corrosive nature\(^22\) that impedes its adoption for large scale technology deployment. Thus, there is a need to identify a cleaner alternative to THF without compromising the vital dual functionality. 1,3-dioxolane (DIOX) is a heterocyclic compound closely related to THF, where the carbon atom at 3-position of THF has been replaced with an oxygen atom.\(^23\) It has similar water solubility as THF, but is less volatile and less toxic (Table S1 in the Supporting Information (SI)). DIOX by itself, stabilizes the sII hydrate.\(^24\) There is only one phase equilibrium study on methane-DIOX system, where 5.0 mol% of DIOX was found to be optimal as a thermodynamic promoter among an investigated concentration range of 0.99 mol% to 20.02 mol%.\(^25\)

Here we report rapid methane uptake for mixed methane-DIOX hydrate formation by means of a detailed kinetic study of hydrate formation, and elucidate the mechanism for this rapid enhancement by combining with crystal morphology observations. Further we report ultra-rapid mixed methane-DIOX hydrate formation at mild operating conditions with
exceptionally high gas uptake, achieved in conjunction with L-tryptophan. The hydrate formed is also analyzed using Powder X-Ray Diffraction (p-XRD) characterization technique for structure identification. Finally, this study documents the first production of sII methane-DIOX hydrate pellet along with the monitoring of its stability over an eight day period.

Results and Discussion

Phase Equilibrium Measurement for methane-DIOX/water System

Figure 1 presents thermodynamic phase equilibrium data for a methane-DIOX/water system with DIOX used in stoichiometric concentration (5.56 mol%). An isothermal pressure search method was employed at three fixed temperatures of 283.15 K, 288.15 K and 293.15 K. Lower temperatures weren’t studied as the current work focuses on enabling rapid methane hydrate formation at moderate operating conditions. The data unequivocally indicates that DIOX is an excellent thermodynamic promoter for methane hydrate formation. While the equilibrium pressure for pure methane hydrate at 283.15 K is 7.2 MPa,26 the same for a methane-DIOX system is less than 1.0 MPa. This shift augurs well for DIOX, as thermodynamic promotion ability directly co-relates to hydrate formation at milder operating conditions compared to pure methane (sI) hydrates. Average equilibrium pressures for the methane-DIOX/water system based on two individual measurements each at the three temperatures studied, can be found in Table S2 in the SI.

![Figure 1](image)

**Figure 1** Three phase (H-Lw-V) equilibrium points for methane-water27 and methane-DIOX/water systems25 along with experimental data obtained in the present study for methane-DIOX/water system containing stoichiometric concentration of DIOX (5.56 mol%).

Mixed methane-DIOX Hydrate Growth at Moderate Conditions

We present hydrate growth (gas uptake) curve for the methane-DIOX/water system operated under quiescent (unstirred) condition in Figure 2a. The experimental conditions used are 283.15 K and 7.2 MPa (initial pressure). The experimental procedure and the calculation to estimate methane uptake for hydrate formation is explained in the SI. Hydrate formation was based on the hybrid combinatorial reactor (HCR) approach. The approach is described in
detail in the literature. In HCR approach, the system is stirred (400 rpm in the present case) for a very short time until nucleation, which in the current study occurred within 2 minutes for all the experiments performed. The HCR approach offers the advantage of controlling the stochasticity of hydrate nucleation while eliminating the need for mixing during the hydrate growth phase. In Figure 2a, we can observe fast hydrate growth and high methane uptake in a simple unstirred configuration maintained during the hydrate growth phase. By 45 min, the formation process is seen to be completed, with a methane uptake of 87.03 (±0.23) v/v (volume of gas/volume of hydrate) achieved for quiescent growth. Hydrate growth reaches 90% completion (t90, referred to the time required for 90% completion of the process) in 32.45 (±3.70) minutes. Shaded regions in the figure represent remarkable reproducibility of experimental data (standard error of 3 experimental runs). Kinetic performance data for individual experiment runs represented in Figure 2a are included in Table S3 in the SI.

**Figure 2** (a) Mixed methane-DIOX hydrate growth under quiescent condition (in blue) at 283.15 K and an initial pressure of 7.2 MPa - the continuous line represents the average data of three experiments and the vertical shaded regions represent the standard deviation of three experimental data, (b) Morphology images of a typical experiment of mixed methane-DIOX hydrate formation under quiescent hydrate growth condition, and (c) p-XRD pattern of methane-DIOX mixed hydrate sample synthesized using 5.56 mol% DIOX aqueous solution at 283.15 K and an initial pressure of 7.2 MPa - the peaks corresponding to the sII hydrate have been placed inside blue boxes while the asterisks indicate the presence of ice (Ih).

Visual images captured during a typical hydrate formation experiment for the methane-DIOX/water system are presented in Figure 2b to provide insight into the physical hydrate growth patterns. We have also presented the video of the visual observation of hydrate formation in the supporting information (Video SV1). For the methane-DIOX/water system under quiescent growth condition, hydrate masses propagate from the three-phase (solid-liquid-gas) interface points on either side of the reactor (as observed through the viewing window, see visual image at t = 7 minutes), inwards towards the center, where they eventually meet and thereon, grow as bulk hydrates. It is noteworthy that at about 7 minutes in Figure 2b, there is visibly a significant amount of hydrates in the reactor but the methane uptake is only about 10.48 (±0.20) % of the total methane uptake. 89.52 (±0.20) % of the
methane uptake happens after 7 minutes of the formation experiment. This growth pattern is consistently observed for all the experiments as seen by the very small standard error in Figure 2a.

For a comparison, we also conducted experiments using the traditional stirred tank operation mode for the growth phase and the results are presented in Figure S2. As observed in Figure S2, the inclusion of stirring does not provide significant advantages to the hydrate growth characteristics, with hydrate growth rate being slightly better for the stirred system as compared to quiescent growth; \( t_{90} \) for stirred growth condition is 22.89 (±0.69) minutes whereas the same, is achieved in 32.45 (±3.70) minutes for quiescent (unstirred) growth condition. Kinetic performance data for individual experiment runs conducted in stirred tank operation mode have been included in Table S3 in the SI.

For the experimental conditions that we employed for hydrate formation (283.15 K and 7.2 MPa), from a thermodynamic standpoint, it would be practically impossible to form pure methane (sI) hydrates (refer Figure 1). Thus, only mixed methane-DIOX (sII) hydrate formation can occur. To confirm this independently, the produced hydrate was analyzed using powder x-ray diffraction (p-XRD) and the results are presented in the following section.

**Characterization of Mixed methane-DIOX Hydrates**

The rapid and repeatable kinetic data obtained stakes a fantastic claim to establish DIOX as a remarkably efficient dual-action promoter for SNG technology. It is important to understand micro-scale data such as the structure of hydrates being formed in presence of DIOX. To confirm the structure, we characterized hydrates formed from a methane-DIOX/water system using the Powder X-Ray Diffraction (p-XRD) technique. The XRD pattern obtained is shown in Figure 2c and matches perfectly to standard sII hydrate patterns from the literature,\(^{13,29}\) thus presenting strong evidence that only sII hydrates were formed in the present study. For p-XRD analysis, hydrate sample was recovered under liquid nitrogen temperature, which results in unreacted water present in the sample appearing as ice peaks in the XRD pattern.

Figure 3a compares gas uptake profiles (quiescent hydrate growth) obtained at the same initial driving force for methane-DIOX/water and methane-THF/water systems. Keeping temperature fixed, the initial experimental pressure was varied for the two systems according to their respective phase equilibrium measurements (Figure 3b) thus ensuring the initial driving force stays uniform. Gas uptake profiles for DIOX/water and THF/water systems seen in Figure 3a are mostly similar with the final gas uptake for DIOX/water system about 13.69% higher after 45 min. Kinetic performance parameters for mixed methane-THF hydrate formation experiments can be found in Table S4.
Figure 3 (a) Hydrate growth under quiescent condition for methane-THF hydrates (in pink) and methane-DIOX hydrates (in blue) at 283.15 K and an initial driving force of ~6.2 MPa - the continous lines represent the average data of three experiments and the vertical shaded regions represent the standard deviation of three experimental data, (b) Three phase (H-Lw-V) equilibrium points for methane-DIOX/water (5.56/94.44 mol%) and methane-THF/water (5.56/94.44 mol%) systems,30 (c) Comparison of relevant physical and safety aspects of DIOX31-33 and THF19,21 for their functioning as dual-action promoters for hydrate formation, (d) Molecular structure and formula of DIOX and (e) Molecular structure and formula of THF.

The kinetic gas uptake data in Figure 3 evidently indicates that the presence of DIOX results in rapid methane hydrate growth akin to that observed with THF. This observation can however feasibly be put into practice only if DIOX exhibits other clear advantages over THF, such as with regards to the operational and safety hazards of THF outlined in the introduction section. In this regard, Figure 3c compares various physical and safety aspects of DIOX and THF relevant for their application in this technology. The data presents similar water solubility for the two compounds, which is expected owing to their similar molecular structures (Figures 3d and 3e for DIOX and THF respectively), but more importantly, significant lower volatility and toxicity of DIOX as compared to THF. Moreover, DIOX is classified as non-carcinogenic33 as opposed to THF which is a confirmed animal carcinogen with unknown relevance to humans19 (refer Table S1 for details of the properties represented in Figure 3c). Lower toxicity and non-carcinogenicity of DIOX implies obvious safety benefits whereas lower volatility of the same indicates both safety and possible recyclability.
advantages due to lower promoter loss in between repeat cycles. Taking all available information into account, the DIOX/water system thus far appears to be an attractive alternative to the rather more toxic THF to be applied for SNG technology for gas storage application.

**Two-step Growth Mechanism for Mixed methane-DIOX Hydrate**

With p-XRD analysis confirming the formation of sII hydrate from the methane-water/DIOX system (Figure 2c), we postulate a hypothesis for a mechanism that would be able to describe the rapid hydrate formation kinetics observed. We propose a two-step hydrate growth mechanism for the methane-water/DIOX system (Figure 4) based on evidence from the reactor pressure profiles (or gas uptake trends) recorded for mixed methane/DIOX hydrate formation, coupled with visual observations. A schematic of a closed system containing aqueous solution of water and hydrophilic DIOX, and hydrophobic methane in the gaseous phase, is shown as Figure 4a. Figure 4b, represents Step 1 of the hydrate growth process where majority of the DIOX enclathration in the large cages of sII hydrate occurs along with some amount of methane uptake in the small cages. This can be independently corroborated in the visual images presented in Figure 2b and in Video SV1; as seen in the media, at about 7 min, there is visibly a substantial amount of hydrates in the reactor, but the methane uptake is only about 10.48 (±0.20) % of the total methane uptake (refer to Figure 2a for the gas uptake curve). Step 1 can be explained based on the hydrophobic nature of methane molecules. To avoid hydrophobic methane introduced into the system, the two polar molecules water and DIOX making up the solution would prefer interacting with each other, thus catalyzing the nucleation and fast enclathration of DIOX in the sII hydrate structure. During step 1 of the hydrate growth, the rate of methane uptake is quite slow, which persists until the ~7-minute mark (see Figure 2a).

In Step 2 of the hydrate growth process, accelerated enclathration of methane molecules in the hydrate phase (small cages of sII hydrate) takes place (Figure 4c). In Step 2, methane molecules occupy the small cages (as most of the large cages are stabilized by stoichiometric DIOX in Step 1) of the sII hydrate formed. This is represented by a steeper methane uptake rate in Figure 2a (after 7 min) and it sustains (till ~35 min) which is characteristic of large amount of methane gas entering into the hydrate structure. In Figure 2a, quantifiably 89.52 (±0.20) % of methane uptake into the hydrate occurred in Step 2 (>7 min).
Figure 4 Two-step hydrate growth mechanism for mixed methane-DIOX hydrate formation comprising a methane assisted rapid DIOX enclathration step (Step 1) and a subsequent rapid methane enclathration step (Step 2).

Ultra-rapid Mixed methane-DIOX Hydrate Growth

We further examined the DIOX/water system to form sII hydrates at ultra-rapid rates. To obtain ultra-rapid rates of hydrate formation, we explored the use of small concentrations of bio-friendly amino acids as kinetic promoters. Recently, amino acids have gained promise in the applicability to kinetically promote gas hydrate formation, owing to the peculiar morphology pattern for crystal formation. We studied the possibility of enhancing the kinetics of quiescent hydrate growth for the methane-DIOX system by introducing a hydrophobic amino acid and benign kinetic promoter, L-tryptophan into the mixture.

Figure 5 (a) Mixed methane-DIOX hydrate growth under quiescent condition without L-tryptophan (in blue) and with 300 ppm of L-tryptophan (in green) at 283.15 K and and an initial pressure of 7.2 MPa—the continuous lines represent the average of three experiments and the vertical shaded regions represent the standard deviation of three experimental data, (b) Comparison of the t90 and normalized gas uptake rate for the t90 periods (average and standard deviation of three experiments) for the methane-DIOX/water standard system and methane/DIOX/water system in presence of 300 ppm L-tryptophan, (c) Visual observations for mixed methane-DIOX hydrate formation in the presence of 300 ppm L-tryptophan under quiescent hydrate growth condition, (d) p-XRD pattern of methane-DIOX mixed hydrate sample synthesized using 5.56 mol% DIOX aqueous solution at 283.15 K and an initial
pressure of 7.2 MPa, and in the presence of 300 ppm of L-tryptophan - the peaks corresponding to the sII hydrate have been placed inside green boxes while the asterisks indicate the presence of ice (Ih). (e) Mixed methane-DIOX hydrate growth under quiescent condition for cycle 1-fresh (in solid light green) and cycle 2-repeat (in dashed dark green) runs using DIOX/water/L-tryptophan (300 ppm) solutions at 283.15K and an initial pressure of 7.2 MPa - the continuous lines (solid or dashed) represent the average of three experiments and the vertical shaded regions represent the standard deviation of three experimental data.

Figure 5a represents gas uptake (quiescent hydrate growth) obtained for a methane-DIOX/water system containing 300 ppm L-tryptophan and compares it with the gas uptake (quiescent hydrate growth) for the standard system in the present study, i.e. “the methane-DIOX/water system without any additional kinetic promoter”. As observed, the presence of L-tryptophan greatly boosts hydrate formation kinetics by inducing ultra-rapid hydrate growth even under quiescent operation. Figure 5b presents a comparison of $t_{90}$ and methane uptake rate between the standard case and the solution with 300 ppm L-tryptophan. With L-tryptophan present, mixed methane-DIOX hydrate formation reaches 90% completion ($t_{90}$) in 12.11 (±0.79) minutes after nucleation (also see Table S5 in the SI), which is faster by a factor of 2.7 times compared to the standard system without any L-tryptophan. A normalized gas uptake rate comparison for the $t_{90}$ periods between the two systems, also presented in Figure 5b, indicates a 147% increase in the hydrate formation rate for the DIOX/water/L-tryptophan mixture over the DIOX/water standard system.

With the addition of L-tryptophan, morphology observed during quiescent growth (Figure 5c), indicates a porous hydrate structure. Images of the system at 7 and 10 minutes post nucleation show hydrate structure that appear strongly consolidated near the three-phase interface points (reactor walls) and loosely stacked towards the centre of the reactor. This is indicative of a mechanism known as “capillary suction”, unique to porous hydrate character, wherein underlying water from the aqueous phase is drawn through channels present in the hydrate microstructure towards the top of the hydrate layer, thus facilitating further hydrate growth. Enhanced hydrate porosity for systems containing amino acids, has been alluded to in the literature and is plausibly a major contributing factor towards ultra-rapid methane-DIOX hydrate growth observed in presence of L-tryptophan. We have included two independent videos as supporting information (Video SV2 and Video SV3) to illustrate the ultra-rapid hydrate growth under quiescent condition. As can be seen in the videos, hydrates form extremely fast and exhibit porous and flexible nature which is a classical signature of amino acid kinetic promotion.

While the presence of 300 ppm L-tryptophan results in ultra-rapid mixed methane-DIOX hydrate formation, final gas uptake achieved sees a minute drop of about 3.7% (see Figure 5a). The slight dip observed can be attributed to mass transfer resistance to methane induced by the ultra-rapid rates of hydrate formation in presence of L-tryptophan which is also corroborated by the huge mass of hydrates observed in the morphology videos (Video SV2 and Video SV3). p-XRD characterization was also carried out for the hydrates formed for the methane-DIOX/water/L-tryptophan system with the typical sII hydrate pattern observed once again. This ascertains the fact that even in the presence of the kinetic promoter L-tryptophan, only sII mixed methane-DIOX hydrates were formed under the experimented conditions. The representative XRD pattern is shown as Figure 5d.
Recyclability of the DIOX/water/L-tryptophan solution for mixed methane hydrate formation is presented in Figure 5d. Under quiescent operation, ultra-rapid hydrate growth and predictable pattern can be observed for both fresh (cycle 1) and repeat (cycle 2) solution states. The t\textsubscript{90} for the repeat runs of the DIOX/water/L-tryptophan system is 13.44 (±0.42) minutes post nucleation, with a gas uptake at t\textsubscript{90} of 75.11 (±0.48) v/v. In comparison, for the fresh runs, the t\textsubscript{90} and gas uptake at t\textsubscript{90} are 12.11 (±0.79) minutes post nucleation and 75.43 (±0.69) v/v respectively. The final gas uptake achieved for cycles 1 and 2 using the DIOX/water/L-tryptophan solution is also similar; 83.81 (±0.77) v/v for fresh runs and 83.46 (±0.53) v/v for repeat runs. The closeness of kinetic data obtained for fresh and repeat cycles of the DIOX/water/L-tryptophan system firmly establishes its exceptional recyclability potential. This should a vital contributor towards successful scale-up of the technology under consideration currently, as recycling the solution implies considerable economic conservation.

The kinetic promotion ability of L-tryptophan should be primarily attributed to its hydrophobicity. Hydrophobic additives and surfaces are known to be effective promoters of gas hydrate formation.\textsuperscript{11,35} A recent study ascribes this to the development of local water ordering and interfacial gas enrichment in the vicinity of the hydrophobic sources.\textsuperscript{36} It is possible to postulate on similar lines that, when mixed with water, non-polar L-tryptophan creates hydrophobic pockets or zones within the solution. Water molecules in the vicinity of these pockets, so as to avoid hydrophobic L-tryptophan, strongly align with each other thus generating local water ordering. Further, hydrophobic methane molecules on introduction to the system, assemble around the L-tryptophan hydrophobic zones, driven by non-polar interactions, leading to the development of an interfacial gas enrichment. The combination of enriched gas layers with pre-existing local water ordering creates hotspots for hydrate nucleation and growth which is physically represented in the form of ultra-rapid methane hydrate formation in the presence of small concentrations of L-tryptophan. Targeted molecular level dynamic studies of hydrate growth may shed further mechanistic insights on the undeniable kinetic promotion in presence of L-tryptophan. However, such studies are computationally challenging and expensive.

Two supplemental studies were conducted to culminate the investigation on mixed methane-DIOX hydrate formation in presence of L-tryptophan. For the first, the effect of L-tryptophan concentration on mixed methane-DIOX hydrate formation kinetics was considered, with the conclusion that 300 ppm is the optimum L-tryptophan concentration needed for the current experimental investigation. The results and relevant discussion are presented in the SI (Figure S3 and Table S7). The second supplemental study involved comparing the kinetic performance parameters of mixed methane-DIOX hydrate formation and mixed methane-THF hydrate formation, each in presence of 300 ppm L-tryptophan. The overall conclusion stemming from this study is that given the initial driving force for hydrate formation is kept
constant, the methane-DIOX/water/L-tryptophan system kinetically outperforms the methane-THF/water/L-tryptophan system, with a significant edge obtained in the t_{90} period, for the system containing DIOX and L-tryptophan. The results and relevant discussion are presented in the SI (Figure S4 and Table S8).

**Highly Stable Storage Characteristics**

The stability of hydrates formed for SNG technology is an extremely important characteristic that needs to be established. SNG formed via sII hydrates can be readily stored at atmospheric pressure and at conventional freezer conditions of about 271.15 to 268.15 K. The thermodynamic stability of pure sI hydrates at atmospheric pressure is 193 K. Thus, sII mixed methane hydrates formed with DIOX or THF do not have to rely on self-preservation effect to remain stable, which happens at 253.15 K at atmospheric pressure for sI hydrates.

We investigated the stability of mixed methane-DIOX hydrate pellets, stored at atmospheric pressure and a moderate storage temperature of 268.15 K. Cylindrical mixed methane-DIOX hydrate pellets in presence of L-tryptophan were synthesized using a unique, custom designed bench-scale SNG technology prototype available in our lab. Details of the apparatus used and the procedure followed for the synthesis of such pellets have been provided in the SI. Specifically, a pellet having length 5.4 cm (Figure 6a), diameter 5.0 cm (Figure 6b), and weighing 91.57 g (Figure 6c) was produced and stored in a separate storage vessel, maintained at atmospheric pressure and 268.15 K storage temperature, and monitored to demonstrate the stability of mixed methane-DIOX hydrates. We observed a volumetric gas uptake of 82.47 (v/v) for the pellet based on gas uptake analysis at the end of hydrate formation.

A hydrate pellet, if unstable at the aforementioned storage pressure and temperature conditions would dissociate, thus releasing the trapped gas into the storage vessel which would in turn lead to increase in the pressure inside the vessel. The amount of gas in the stored hydrate pellet was 82.47 v/v which would translate to a pressure increase in the storage vessel to 973.29 kPa on complete dissociation. Conversely, no or gradual pressure increase within the storage vessel would indicate good stability of the hydrate at the experimental storage conditions. Figure 6d shows the stability of the mixed methane-DIOX hydrate pellet, monitored over a period of eight days. At the first data point (beginning of the storage period), the temperature of the storage vessel is recorded to be 255 K while the pressure inside the storage vessel is 3.25 kPa (gauge pressure). Initial low temperature in the vessel is due to the fact that the storage vessel was pre-cooled at 253.15 K before transferring the produced hydrate pellet into it and subjecting the vessel containing the pellet to the pre-determined storage conditions (vessel closed at atmospheric pressure and kept inside a freezer maintained at the storage temperature). Soon the temperature inside the storage vessel reaches the desired experimental storage temperature of 268.15 K and we also observe a slight increase in the pressure inside the storage vessel at this point (19.22 kPa; second data point in Figure 6d – 6 h into the hydrate storage period), which can be predominantly attributed to residual gas expansion due to temperature increase rather than hydrate dissociation. Hereon, both the temperature and pressure inside the storage vessel remain largely constant till the end of the 8 day hydrate storage period thus signifying that the hydrate pellet was highly stable for the period we tested. For the last five days of storage, the pressure in the storage vessel was extremely stable at 44.87 (±5.09) kPa. This basically
demonstrates the exceptional stability of the mixed methane-DIOX hydrate pellet. It is noted that the dotted pressure line at the top of Figure 6d represents the expected pressure if all the gas stored in the pellet dissociates and evolves into the storage vessel.

Thus for the first time, we demonstrate highly stable storage of mixed methane-DIOX hydrate pellets at atmospheric pressure. Through the identification of DIOX as a dual-action promoter and synergistically combining with small amounts of L-tryptophan, we thus address both the bottlenecks pertaining to SNG technology, a) ensuring ultra-rapid hydrate formation at moderate pressure and temperature conditions and b) ensuring highly stable storage of formed hydrates at moderate pressure and temperature conditions.

Figure 6 (a) Diameter of synthesized cylindrical mixed methane-DIOX hydrate pellet, (b) Length of synthesized mixed methane-DIOX hydrate pellet, (c) Weight of synthesized mixed methane-DIOX hydrate pellet and (d) Demonstration of stable storage of mixed methane-DIOX hydrate pellet at atmospheric pressure and moderate temperature of 268.15 K.

Comparison with Competing Technologies

With regards to the conventional natural gas storage methods, CNG (compressed natural gas) is a commercially adoptable technology. However, high pressure requirement and safety aspects make it economically unviable for large-scale storage. On the other hand, ANG (adsorbed natural gas) based technologies have been making constant progress, albeit on the material scale. While there are low cost adsorbent materials like activated carbon, the performance of activated carbon is not as great as promising materials like metal-organic frameworks (MOFs). In the context of on-board application, at a material scale, a recent breakthrough work by Rozyyev et al.\(^5\) reported 0.625 g/g gas uptake for their best performing material COP-150. In the same study, Rozyyev et al.\(^5\) reported a larger scale testing of methane storage using a 142 ml SS pressure vessel (similar volume to that used in the present study; refer methods) maintained at 293.15 K and filled with 30 g (88.24 ml) of COP-150 material. The authors report a gravimetric gas uptake of 0.137 g/g at the working pressure of 6.5 MPa (methane), which is the closest operating point to 7.2 MPa, the operating pressure used in the present study. Using the correlations provided by the authors, the volumetric gas uptake capacity of COP-150 is estimated to be around 64.20 v/v. The authors also reported that COP-150 outperforms other popular porous materials like HKUST-1 and polystyrene in this scale up study. In our work, we report volumetric gas storage capacity of 83.81 (±0.77) v/v for methane-DIOX/water/L-tryptophan system at a similar scale.
Akin to CNG, adsorption based large-scale gas storage ANG systems will need to be kept at high pressures. This is a great advantage for SNG; SNG formed with sII hydrates is extremely stable at atmospheric pressures and moderate temperatures. For the first time, we have demonstrated the exceptionally stable storage of mixed methane-DIOX SNG pellets at atmospheric pressure in the present work. From an economic standpoint, the cost of a storage vessel made of stainless steel for methane storage as ANG or CNG (pressure rating of 7.5 MPa) works out to be in excess of 5.5 times the cost of a vessel for SNG storage as sII mixed methane hydrate (pressure rating of 1.0 MPa), having identical volume, dimensions, orientation and material of construction. Details of the same have been included in the SI (Table S9). The practical use of large-scale high-pressure storage tanks is not advisable due to the explosive nature of the systems. Scale-out (like CNG for laboratory use) approach would mean the cost will be further heightened for both CNG and ANG for large-scale operation. On the other hand, there are industry standards for large-scale storage tanks which could be readily adopted for SNG, for example, liquefied natural gas (stored at 0.2-0.5 MPa and 111.2 K) storage tanks are designed for 1.0 MPa. Another significant advantage of SNG technology vis-à-vis ANG is that the former mainly uses water as the solvent (>94 mol%) with the addition of two small quantities of thermodynamic and kinetic promoters. Even if produced from seawater by desalination, the cost of industry grade water is less than USD$1.13 per tonne (or per m$^3$) making the economics of SNG technology highly feasible from the raw material standpoint.

Thus, in addition to ultra-rapid formation of SNG via sII methane-DIOX hydrates, the low cost for storage tank, high degree of stability at mild storage conditions and safety considerations firmly cement SNG technology as an efficient option for large-scale methane storage.

**Conclusion**

We pioneer DIOX as a clean and competent dual-action chemical promoter for SNG technology via combustible ice or clathrate hydrates, providing both thermodynamic and kinetic enhancement to the process. Rapid mixed methane-DIOX hydrate formation is achieved at experimental conditions of 7.2 MPa and 283.15 K. We highlight the existence of a synergism between DIOX and methane and propose a two-step rapid hydrate growth mechanism for the methane-DIOX hydrate system, wherein the introduction of hydrophobic methane into the system catalyzes initial formation of pure DIOX hydrate, followed by the incorporation of methane into the molecular water (host) framework. Further, by synergistically combining with small concentration (300 ppm) of kientic promoter L-tryptophan, we establish ultra-rapid rates of hydrate formation for methane-DIOX/water system, with complete hydrate formation being achieved within 15 minutes following hydrate nucleation, along with a high methane uptake of 83.81 (±0.77) volume of gas/volume of hydrate (v/v). Finally, we demonstrate extraordinary stability of a mixed methane-DIOX hydrate pellet synthesized using a bench-scale SNG technology prototype and stored at atmospheric pressure and in a conventional freezer at 268.15 K. Our current findings on mixed methane-DIOX sII hydrate formation, categorically address and overcome the two major bottlenecks of SNG technology and present exciting prospects for industry adoption. We expect our findings to prove pivotal in devising strategies for the same.

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**Author Contributions**

PL supervised the project. PL and GB conceptualized the work and designed the experiments. MNG, GB and SEKA carried out the kinetic experiments. MNG and GB analysed the data. GB and MNG performed the p-XRD characterization. GB and MNG performed the stability study. GB and MNG wrote the original manuscript draft. PL edited the manuscript and contributed to the final version. All authors read the final manuscript and consented to the submission.

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