IV.H.9 Metastability of Clathrate Hydrates for Energy Storage

Carolyn A. Koh (Primary Contact), Amadeu K. Sum, R. Gary Grim, Matthew R. Walsh, Prasad B. Kerkar
Center for Hydrate Research
Colorado School of Mines
1600 Illinois Street
Golden, CO 80401
Phone: (303) 273-3237
Email: ckoh@mines.edu

DOE Program Officer: Bonnie Gersten
Phone: (303) 903-0002
Email: Bonnie.Gersten@science.doe.gov

Objectives

The current project aims to probe key questions surrounding the metastability of hydrates relating to synthesis, structure, and composition. The questions on metastability are crucial in all energy applications of clathrate hydrates including energy storage, energy transportation, and energy recovery. Specifically, this project addresses:

1. Self-preservation metastability – hydrates preserved outside equilibrium conditions.
2. Structure/phase metastability – coexistence/transitions of metastable phases.
3. Metastable cage composition/occupancy – variable cage occupancy and dynamics.

Abstract

Clathrate hydrates or ‘gas hydrates’ are a class of inclusion compounds that form when water and suitably sized guest gas species come into contact at favorable temperature and pressure conditions. A network of hydrogen bonds between water molecules stabilizes these polyhedral cages and depending on the size of the trapped molecule and the thermodynamic environment, different cages types/sizes or ‘structures’ may be formed. Clathrate hydrates can concentrate gases by a factor of approximately 160 times the hydrate volume at ambient conditions [1], thereby offering a potential solution for many energy-related issues including storage, transportation, and recovery.

Although thermodynamically stable clathrate hydrate structures are well known, the phenomenon known as metastability of clathrate hydrates is poorly understood. One major challenge to unraveling the complex behavior of clathrate hydrates in all energy applications is to understand guest-host interactions and metastability in terms of structure and composition. Specifically, some of the remaining challenges lie in understanding: (a) how guests can readily fill small cages, yet experience resistance in large cages, (b) how guest molecules can distort the cavities and/or form clusters, and (c) how synthesis pathways play a prominent role in guest molecule enclathration and preferential small/large cage occupancy. These synthesis-structure-stability relations of clathrate hydrates are severely under-explored, yet hold the key to successful application and control of clathrate hydrates in all energy applications.

Our most recent advances are providing new insight into synthesis and structure (objective 2) and cage dynamics (objective 3); specifically: identifying the formation mechanisms and elementary building blocks of clathrate hydrates during nucleation/growth; increasing H_2 storage capacity (3.4 wt%) with a breakthrough synthesis method of solid-solid mixing; rapid growth and novel templating of new hydrate structures. Highlights of these recent advances are described below.

Progress Report

Expanding upon the discoveries in the previous update (July 2011), we have continued to explore synthesis and structure relationships (objective 2) as well as metastable cage dynamics during hydrate nucleation (objective 3).

Synthesis Pathway for Novel Small and Large Cage Occupancy of H_2 in Structure I

In contrast to the traditional clathrate synthesis method of simply mixing water with an appropriate hydrate former and then implementing a thermodynamic driving force for nucleation by pressurizing/cooling, a new synthesis method involving the addition of preformed hydrates was studied. Using this new technique that we refer to as the “repressurization/templating method”, we prepare a preformed hydrate and then repressurize the sample to very high (>700 bar) pressures with H_2 in an attempt to force H_2 to occupy new environments. Therefore, by simply changing the initial hydrate structure (*e.g.* the structure of the preformed hydrate), we can control the final structure, and to some degree, the metastable composition of hydrogen in the system. A conceptual picture and description of this process is shown in Figure 1.

Raman spectroscopic results using the aforementioned synthesis pathway are provided in Figure 2-I. These results show that after pressurizing the sI CH_4 hydrate with H_2 we observe three distinct H_2 environments. We show for the first time that these environments are not the normally observed

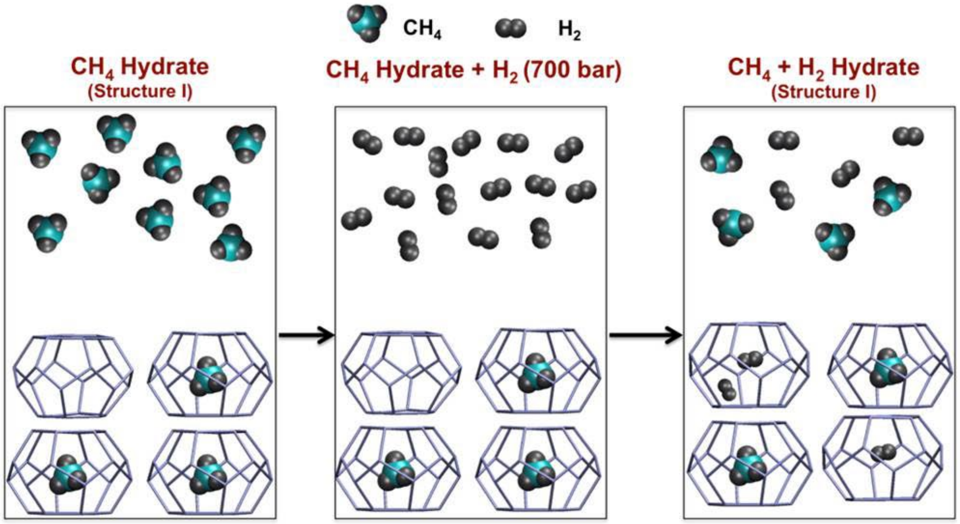

FIGURE 1. Repressurization method for clathrate hydrate synthesis. (Left) Initial sI hydrate is in equilibrium with gas phase. (Middle) The sI gas in vented and replaced with H_2 at high pressures. (Right) To establish a new equilibrium between the gas and hydrate phase, H_2 enters the preformed hydrate.

sII environments, but rather can be characterized as singly and doubly occupied sI cages. This key result shows that by altering our synthesis procedure, we were able to observe both small and large cage enclathration in sI and not the thermodynamically preferred structure for H_2 (sII). This work serves as a proof-of-concept for the synthesis technique to facilitate novel large cage filling through a potential metastable pathway.

Preservation of sVI Hydrates with H_2

Structure VI (sVI) is the only known hydrate structure which has the potential to store the amount of H_2 needed to meet the revised DOE goal of 5.5 wt%. However, previous attempts to synthesize this structure have found that upon introduction of H_2, the structure rapidly decomposes into sII. Using the same “repressurization method” as described above, we demonstrate the first experimental evidence of binary H_2 + *tert*-butylamine (tBA) sVI hydrate. This

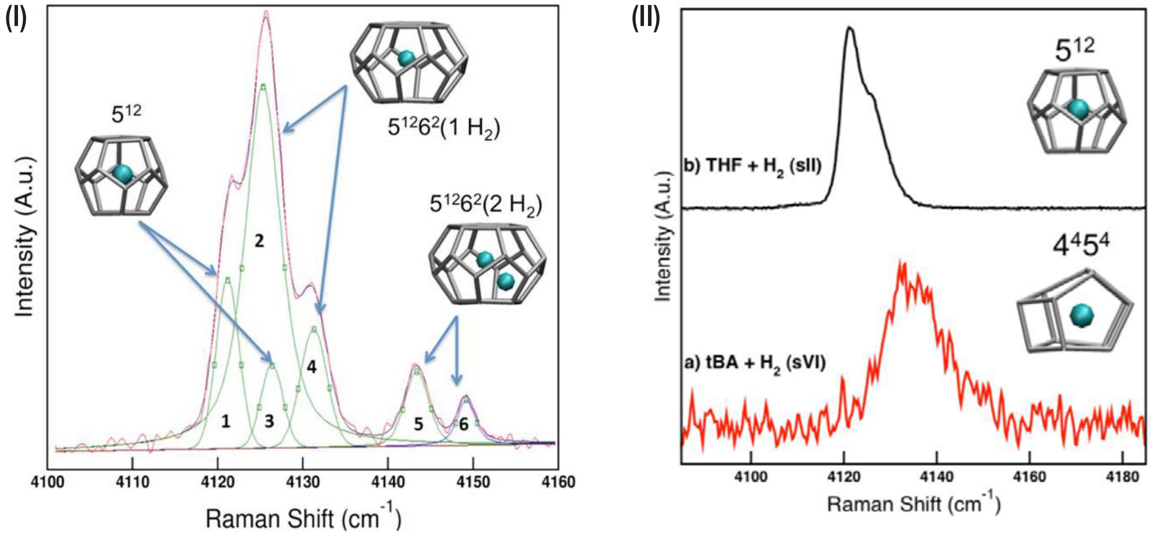

FIGURE 2. (I) Results of the repressurization method using a preformed sI hydrate showing three novel H_2 environments in sI. Peaks 1 & 3 (4,121 – 4,126 cm^{-1}) correspond to singly occupied 5^{12} cage. Peaks 2 & 4 (4,125 – 4,131 cm^{-1}) correspond to singly occupied $5^{12}6^2$ cage. Peaks 5 & 6 (4,143 – 4,149 cm^{-1}) correspond to doubly occupied $5^{12}6^2$ cage. (II) sVI H_2 peaks (a) are blue-shifted from known sII positions (b), indicating a more constrained environment.

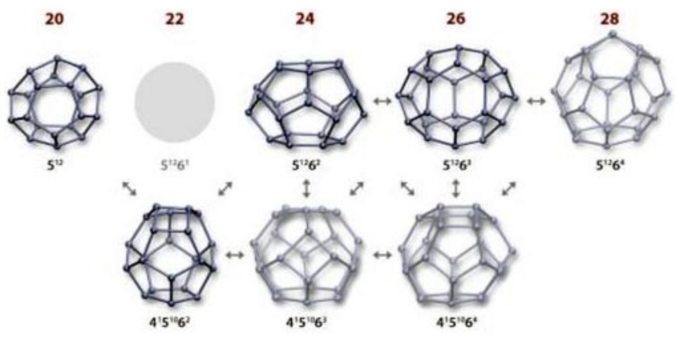

FIGURE 3. Seven dominant cages in sI hydrate nucleation

result was confirmed with both Raman and powder X-ray diffraction. Raman spectroscopic results are presented in Figure 2-II.

Discovery of Key Clathrate Hydrate Building Blocks – Metastable Pathways

Direct molecular dynamics simulations investigating nucleation and growth of sI methane hydrate identified seven common cages during hydrate nucleation (Figure 3). It was also discovered that these seven elementary cage types comprise 95% of all cages present in the nucleating trajectories. Interestingly, only two of these cages, the 5^{12} and $5^{12}6^{2}$, are present in 'normal' sI on experimental time scales.

This observation of seven cages (two stable, five metastable) leads to two important discoveries [3]: (i) the initial nucleated hydrate is a kinetic product of metastable cage clusters (Figure 4-I), (ii) after nucleation the metastable clathrate hydrate cages must undergo dynamic transitions to reach their equilibrium cage orientation. To undergo this type of solid-solid rearrangement (*cf.* solid-solid synthesis pathways), recent simulations have shown several different pathways of metastable cage insertions, deletions, or rotations as illustrated in Figure 4-II.

Future Directions

In the future stages of the project we will build upon our recent discoveries and continue to explore the synthesis-structure-stability relationships of hydrates on the molecular level. Specifically we plan to extend the new synthesis pathway described above to different, more promising, structures such as structure VI (sVI) and structure T (sT). Not only do these structures offer a potentially higher capacity for energy storage, but also present a unique opportunity to study new cage environments and dynamics.

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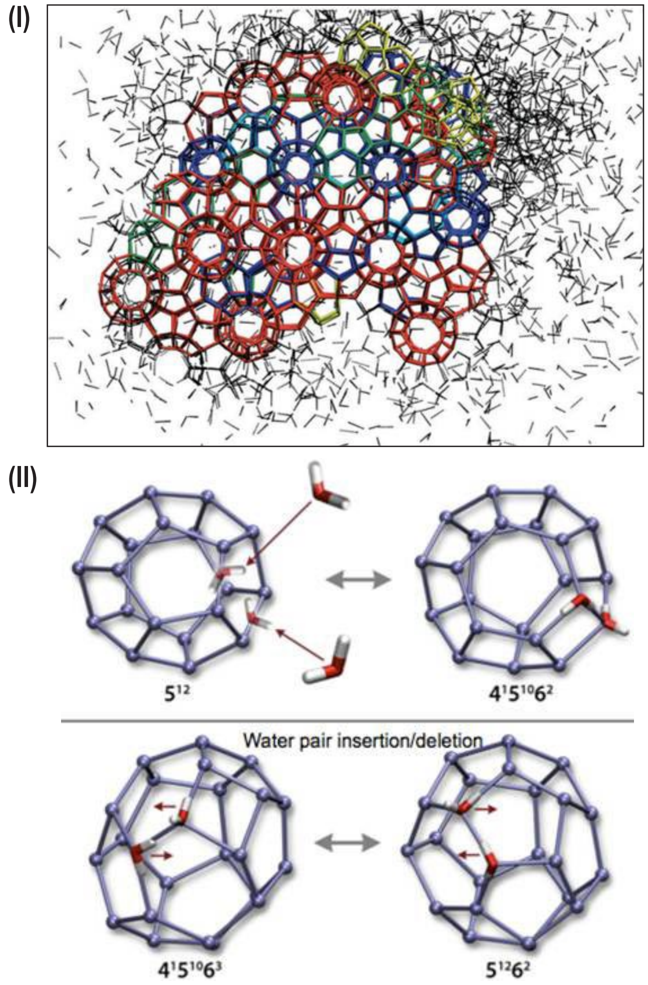

FIGURE 4. Metastable hydrate cluster after nucleation (I); insertion, deletion, and rotational cage dynamic pathways (II).

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