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.

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 H₂ 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 H₂ 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 H₂ in an attempt to force H₂ 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 CH₄ hydrate with H₂, we observe three distinct H₂ environments. We show for the first time that these environments are not the normally observed
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
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.

References

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FIGURE 3. Seven dominant cages in sI hydrate nucleation

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

