Investigation of Material Dependence of Clathrate Hydrate Nucleation for Energy Applications

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Background

- Clathrate hydrates are solid inclusion compounds composed of water molecules that encage hydrophobic organic molecules via hydrogen-bonding.[1]
- Given a sufficient amount of activation energy, nucleation will proceed.
- Promotion of nucleation of structure II (sII) clathrates by the addition of copper has been seen; however, structure I (sI) has now also been tested. [2]

Large Scale Hydrate Production Application

- A critical issue preventing clathrates from reaching their energy storage potential has been that they form stochastically.
- Our copper results provide means for reliably forming clathrates, which could make clathrates now an economical means for energy storage in catering to the growing demand for natural gas.

Experimental Setup

Materials Tested: Copper, Nickel, Zinc

Differential Scanning Calorimetry

Parameters: CH4(g), 1800 psi, 2°C

Microscopy

- Fig. 3 C1: HP cell, C2: Reference HP cell, TES: Pressure regulation, A1/A2: Transfer storage gas, PP1: Gas compressor [3]

Nucleation

- No nucleation occurs without copper in DI water + CH4(g) gas.
- DI Water + CH4(g) + Cu induction time = 7.52 ± 0.58 hr
- Using Gibb's Energy Minimization (CSM-GEM) statistical thermodynamics tool for the dissociation temperature (T_diss):
  T_diss (calc) = 14.83°C as compared to:
  T_diss (exp) = 15.95±1.0°C

Oxide Layer Effects on Nucleation

- Copper from RT-100°C forms Cu3O4, at ~150°C forms Cu3O2, and from 200-300°C forms CuO.

Conclusions and Future Work

- DSC and microscopy indicate that copper promotes nucleation of clathrate hydrate Type I & II, while nickel and zinc show no effect on nucleation.
- Further study is needed to determine the properties of copper responsible for promoting nucleation.
- Increasing oxide layer thickness correlates to faster induction.
- Promise has been shown for industrial application of clathrate hydrate technologies.

References


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