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Project Title: First Principles Multiscale Reactive Dynamics Modeling and Simulations to Predict Decomposition and Combustion of Clathrate Hydrates

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Narrative Progress Report (2018-2019)

1. Project Summary

Our research goal is to extract the details of the kinetics, dynamics, and mechanisms describing the decomposition and combustion of complex condensed-phase clathrate hydrates under realistic conditions of pressure, temperature. In the first year of this project, the PI and his group member have focused on the quantum mechanics (QM) simulations to determine the methane decomposition and diffusion mechanism in CH₄-hydrate, as well as the effects from free electrons and holes.

2. Research Summary

Clathrate hydrates are ice-like crystalline substances, in which small molecules are trapped inside the polyhedral cavities of water molecules. They are of great interests in both scientific research and petroleum industry because of their important applications in energy technology and environmental issues.^{1,2} However, the safety issues are of serious concerns for their engineering applications because of the decomposition and combustion under external stimuli such as heat, shock, or impact. Therefore, it is essential to underlying the diffusion and decomposition mechanisms of trapped molecules in gas hydrates, which is crucial to prevent the spontaneous ignition and explosion of natural gas under extraction, storage and transportation.

Here we take methane hydrates (MH) as the prototype materials and investigate the atomistic-level diffusion and decomposition mechanism of methane (CH₄) by employed density functional theory.³ Firstly, we performed QM based molecular dynamics (QMD) simulations to investigate the cage deconstruction and methane decomposition. Then we examined the methane diffusion mechanism using the QM simulations. Finally, to improve the stability of the ice-cage, we applied extra electrons or holes and examine how these carriers affect the diffusion mechanism and barriers. Firstly, we found that the chemical reactions initiate from hydrogen transfer among water molecules at heating. The attacks from fragments of O or OH to CH₄ molecules are responsible for the destructions of the methane molecules. Then we found that the methane molecule could escape from the ice cage by diffusion through the hexagonal face with an energy barrier of 0.25 eV. To suppress the methane diffusion, we demonstrated that the diffusion barrier is significantly enhanced by adding electron or hole carriers. This is because that the extra electrons and holes increases the electrostatic repulsion between methane and water molecules at the transition state, leading to an increased diffusion barrier. Our simulation results suggest that the clathrate cage can be stabilized by adding extra electron and hole carriers.

2.1 Methane decomposition mechanism in CH₄-hydrate

To uncover the reaction mechanisms of the methane hydrate, we examined the details of the system and plot key snapshots at several temperatures during the cook-off simulation. During the initial heating-up process, from 300 to 2000 K, no chemical reactions are observed. Between 2000~3400 K, we observed the hydrogen transfer process between water molecules, leading to a large number of isolated H, HO, H₃O and O fragments. However, all CH₄ molecules remains inert. The initial reaction of CH₄ molecule, occurring at 3480 K, is a bimolecular reaction in which one O²⁻ ion attacks CH₄ molecule, leading to the formation of (OH)¹⁻ and CH₃ (Figure 1a). This mutilated CH₃ becomes chemically active and finally turns into CO₂ by a sequence of reactions shown in Figure 1. Our QMD

simulation indicated that the O plays an important role in the initial CH₄ decomposition through the continuous assaults of O or OH to the carbon atom and its affiliated hydrogen atoms. This suggests that under realistic conditions the O in the air could involve in the CH₄ decomposition, leading to more rapid reactions than our QMD simulation.

2.2 Methane diffusion mechanism in CH₄-hydrate

Methane diffusion plays an important role in the stability of MH, as well as CH₄ exploitation from MH. To uncover how the methane molecule escapes from the hydrate cage, we calculate the energy barrier of the escaping process from a 5¹²6² cage through DFT method. Two plausible diffusion paths were considered here, as shown in Figure 2: path (I) The migration via the hexagonal face, and path (II) Diffusion through pentagonal ring by breaking and reforming a hydrogen bond of that pentagonal ring.⁴ For the hexagonal path I, the diffusion barrier is only 0.25 eV, which is much lower than that of the pentagonal path II (0.58 eV), indicating that the hexagonal path I is a favorable migration way for methane.

As we impose electron or hole, the barriers are significantly increased as shown in Figure 2. The charge analysis indicates that the extra charge (or hole) are distributed in both CH₄ and H₂O, increasing the electrostatic repulsion, leading to an increased barrier. Our results suggest that the storage of the CH₄ in the clathrate can be stabilized by adding electrons or holes to the MH system.

3. References:

(1) Dickens, G.R., Paull, C.K., and Wallace, P., *Nature*, **1997**, 385, 426–428. (2) Boswell, R., *Science*, 2009, 325, 957–958. (3) Kresse, G, Hafner, J. *Phys. Rev. B.* **1993**, 47, 558–561. (4) Willow S. Y., Xantheas, S. S. *Chem. Phys. Lett.* **2011**, 525-526, 13-18.

4. The Impact of the Research

This ACS PRF project motivates the PI to work on the petroleum related research field and expand his research field. The research results provide basis for the future proposal related to petroleum research. One graduate student and one postdoc scholar are working in this project which provide the skills, knowledge and experience that will help to accomplish the tasks of the project and promote their researcher capacity for their further scientific career.

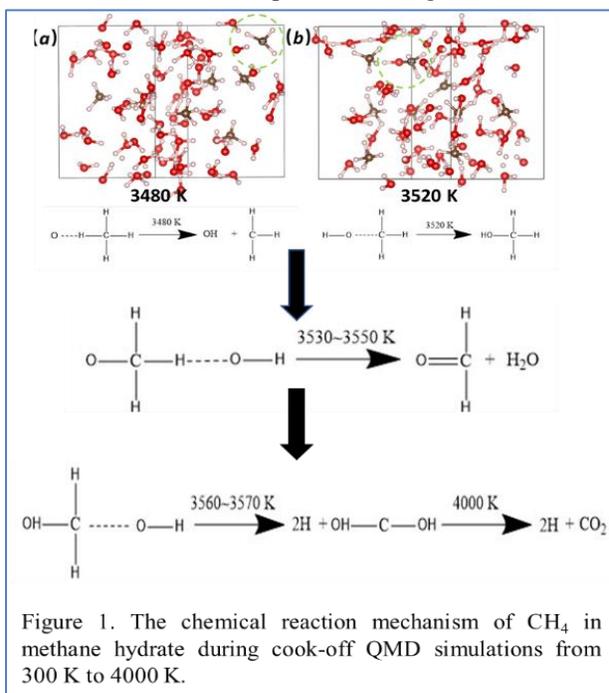


Figure 1. The chemical reaction mechanism of CH₄ in methane hydrate during cook-off QMD simulations from 300 K to 4000 K.

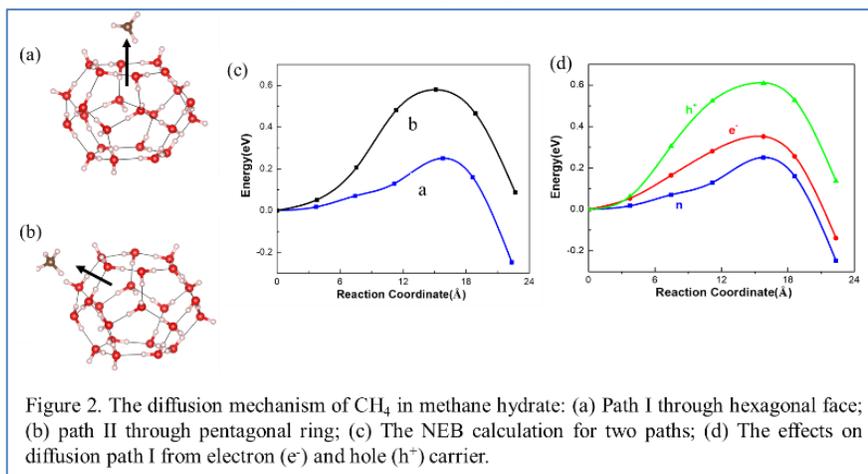


Figure 2. The diffusion mechanism of CH₄ in methane hydrate: (a) Path I through hexagonal face; (b) path II through pentagonal ring; (c) The NEB calculation for two paths; (d) The effects on diffusion path I from electron (e⁻) and hole (h⁺) carrier.