A novel method for evaluating effects of promoters on hydrate formation

CrossMark

Jing Cai [a, b, c, 1], Chun-Gang Xu [a, b, c, 1], Fu-Hua Lin [a, c], Hai-Zhu Yu [d], Xiao-Sen Li [a, b, c, *]

[a] Key Laboratory of Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, China
[b] Guangzhou Center of Gas Hydrate Research, Chinese Academy of Science, Guangzhou, China
[c] Guangdong Key Laboratory of New and Renewable Energy, China
[d] Department of Chemistry and Center for Atomic Engineering of Advanced Materials, Anhui University, Hefei, China

ABSTRACT

Based on the SC (solute cavity) theory and the FMO (frontier molecular orbital analysis), a new method named as the SC-FMO method is established to investigate into the inherent characteristics of the hydrate formation and the effects of the hydrate promoters on the hydrate formation, and predict the hydrate structures. It is concluded from the experimental and theoretical computation results that the promoters with low frontier orbital energies, lone pairs and suitable ratios of the promoter molecular diameters to cavity diameters are favorable for moderating the hydrate formation conditions. Additionally, the water-insoluble cyclic compounds, TMS (trimethylene sulfide), CP (cyclopentane), and THT (tetrahydrothiophene) are adopted to form the binary hydrates together with methane (CH_4). The hydrate structures are characterized by using Raman spectroscopy. The analysis results from the Raman spectra indicate that TMS, CP and THT encage into the medium $5^{12}6^4$ cavities of the structure II (sII) hydrates, while CH_4 molecules not only occupy the small 5^{12} cavities, but also compete into the medium $5^{12}6^4$ cavities with CP, THT or TMS molecules. The same results are predicted from the SC-FMO method. It proves that the SC-FMO is a promising method for predicting the hydrate structures and determining an excellent hydrate promoter.

© 2016 Published by Elsevier Ltd.

1. Introduction

Clathrate hydrate is a kind of ice-like inclusion compounds. It forms when water and the guest substances with the suitable molecular sizes come into contact under the sufficiently high pressure and/or relatively low temperature conditions. Water molecules as the hosts crystallize into different cavities via the hydrogen bonds. Guest molecules are encapsulated into the hydrates via van der waal force [1]. In general, the hydrate structures depend on the sizes of guest molecules. The hydrate presents three prevalent crystal structures: cubic structure I (sI), cubic structure II (sII) and hexagonal structure H (sH). Specifically, the sI hydrate is composed of two 12-hedra (5^{12}) and six 14-hedra ($5^{12}6^2$); the sII hydrate is composed of sixteen 12-hedra (5^{12}) and eight 16-hedra ($5^{12}6^4$); and the sH hydrate is composed of three 12-hedra (5^{12}), two 12-hedra ($4^35^66^3$) and one 20-hedra ($5^{12}6^8$) [2].

Presently, a variety of promoters are developed and synthesized to moderate the hydrate formation conditions. The hydrate promoters are divided into thermodynamic promoters and kinetics promoters. The kinetics promoters, such as SDS (sodium dodecyl sulfate) and SDBS (sodium dodecyl benzene sulfonate), have positive influence on enhancing the hydrate formation rates by means of reducing the interfacial tensions of the solution, promoting gas to dissolve into solution, and further enhancing the hydrate formation driving forces [3]. The thermodynamic promoters, such as quaternary ammonium salts (e.g., tetra-n-butyl ammonium bromide) [4] and cyclic compounds (e.g., tetrahydrofuran) [5,6] take part in the hydrate formation and significantly reduce the gas hydrate formation pressures. The cyclic compounds, including the water-soluble compounds (e.g., tetrahydrofuran) [6–9] and the water-insoluble compounds (e.g., CP (cyclopentane)) [10] are verified to reduce the gas hydrate formation pressures remarkably. However, most of the thermodynamic promoters belong to the water-soluble compounds, which are difficult to be retrieved from water after the hydrate dissociation. For the sake of determining an easy recovery

* Corresponding author. Key laboratory of Gas hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China. Tel./fax: +86 20 8705 7037.
E-mail address: lixs@ms.giec.ac.cn (X.-S. Li).
[1] The first two authors contributed equally to this work.

hydrate promoter, the water-insoluble compounds are introduced in this work, and they were used in our previous thermodynamic researches [11,12]. Lv et al. [12] and Peters et al. [13] proved the water-insoluble compounds with less carbon atoms in the ring and without the branched chain have positive influence on moderating the hydrate formation conditions and enhancing the hydrate dissociation enthalpies. For example, THT (tetrahydrothiophene), as a typical cyclic water-insoluble compound, can achieve a sharp drop of the equilibrium pressure and enhance the hydrogen storage [14].

In the past several decades, many studies focused on characterizing the hydrate structures by means of XRD (X-ray diffraction), Raman spectroscopy, NMR (nuclear magnetic resonance) spectroscopy, infrared spectroscopy and neutron diffraction. For instance, Koh et al. [15] and Hirai et al. [16] proved that the hydrate structures are influenced by pressures. With the increase of the pressure, the sI hydrates can transform into sII hydrates or sH hydrates. Aside from the pressures, the compositions of gas mixtures also have the effect on the hydrate structures. Seo et al. [17] measured the structures of carbon dioxide/nitrogen (CO_2/N_2) gas mixture by XRD and NMR. It was found that the structures of the hydrate containing CO_2 and N_2 transformed between the sI and sII hydrates with the change of the CO_2 composition. Xu et al. [18,19] studied the influence of the CO_2/N_2 gas mixture and carbon dioxide/hydrogen (CO_2/H_2) gas mixture by adding hydrate promoters using XRD and Raman spectroscopy, respectively. Uchida et al. [20] investigated into the structure transformation of methane/propane (CH_4/C_3H_8) gas mixture hydrate using XRD and Raman spectroscopy. The hydrate formation was divided into two steps with the different hydrate structures. The structure transformations in the hydrate containing CH_4, ethane (C_2H_6) and C_3H_8 were observed by Schicks et al. [21] It was found that the structure transformation in the process of forming the hydrates was rather complicated because the hydrate structure was impacted by the pressures, gas compositions and hydrate promoters. Additionally, the same guest molecules can encage into both the small and large cavities and crystallize the sI or sII hydrates with the different clusters of molecules packed closely. Mao et al. [22] and Lu et al. [23] testified that both small and medium cavities of clathrate hydrates were occupied by multiple hydrogen (H_2) molecule clusters and the hydrates were presented as the sI or sII structures. Above studies focused on the changes of hydrate structure affected by exterior factors during the hydrate formation. However, few researches keep eyes on the essential relation between the structures of the hydrate promoters and intermolecular interactions, such as the host water molecule-guest molecule interactions and promoter molecule-gas molecule interactions.

In order to figure out the essential factors of moderating the hydrates formation conditions and crystallizing the hydrate structures from the point of view of intermolecular interaction, a new method, named as the SC-FMO, was established in this work, and the hydrate structures were determined in terms of it and Raman spectra of the hydrates. In the method, the solute cavity method (SC) and the FMO (frontier molecular orbital theory) are introduced to understand the intermolecular interactions between the host water molecules and guest molecules in the hydrates.

2. Experimental

2.1. Material

Chemicals, especially the water-insoluble organic compounds adopted in this work, are summarized in Table 1. The Raman spectra for cyclopentane (CP), tetrahydrothiophene (THT) and TMS (trimethylene sulfide) are shown in Fig. 2.

2.2. Procedure

As shown in Fig. 1, a special hydrate formation vessel was employed in this work [24]. The vessel was made of 316 stainless-steel with the volume of 115 ml. On the front and back side, there were two special quartz visible windows. Through the windows, the contents in the reactor can be detected by the Raman spectrometer. On the both left/right and bottom sides of the reactor, a jacket was equipped to keep the hydrates stable. The vessel was sealed by a butterfly valve, which gave a convenient way to open the vessel and had the hydrate samples obtained promptly. After water and the water-insoluble organic compound was added into the hydrate formation vessel. The jacket was then filled with water and ethylene glycol mixture and connected to a constant temperature bath with the value of 277.15 K. A pressure transducer was connected to the vessel for measuring the internal pressure. When the gas pressure reached the desired value, approximately 3.50 MPa, a magnetic stir was commenced with the speed of 500 rpm and the zero-time was recorded. The hydrates were measured by using Raman spectrometer while the hydrates were forming. Additionally, the hydrate samples obtained from this vessel can be characterized by XRD and NMR.

The Raman spectrometer (Horiba, LabRAM HR) with a single Monochromator of 1800 grooves/mm grating and a multichannel air-cooled CCD (charge coupled device) detector is employed to characterize the hydrate structures. A 532 nm incident laser beam was used. The Ar-ion laser was focused on the sample by a $1 \times$ microscope objective. The spectroscopic data were detected by a CCD detector with an energy resolution of 100 mW and recorded with a 10 s integration time over 5–30 scans. The silicon (Si) crystal standard of 520.7 cm^{-1} is employed to calibrate the subtractive spectrograph.

3. Results and discussions

3.1. SC-FMO method

Solute cavity theory has extensively applied to investigate the solvent–solute interaction in crystal nucleation, bonding energy, electrostatic potential etc. [25] Hydrate formation is similar to the solvent–solute interaction in crystal nucleation. Therefore, in this work, the SC (solute cavity theory) is introduced to calculate the molecular diameters of the guest molecules enclosing into the cavities of the hydrates. Specially, the diameters are completed by B3LYP functional [26]. In order to justify the validity and feasibility of the SC method, the molecular diameters of normal guest molecules, such as hydrogen (H_2), nitrogen (N_2), CH_4, carbon dioxide (CO_2), propane (C_3H_8), i-butane (i-C_4H_{10}) and n-butane (n-C_4H_{10}) are calculated, and the calculated results are compared with the references as shown in Table 2. In comparison with the actual diameters [1], the maximum RD (relative deviation) between the calculated diameters and the actual diameters is 7.7%, and the minimum RD is 0.92%. It is in a good agreement with the references [1]. In the next content of this section, the molecular diameters of the hydrate promoters adopted in this work, CP, THT and TMS, are calculated using the SC method.

Frontier molecular orbit analysis (FMO) [27] is firstly employed to understand the intermolecular interaction between guest and host water molecules in the hydrates. Binding energies of the guest molecules are calculated using the hybrid B3LYP functional [28], which combines exact Hartree–Fock exchange with an MP2-like correlation and long-range dispersion corrections in this work. A