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Web Proceedings

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Investigation of Cyclohexyl Amine Hydrate for Solidified Natural Gas Technology

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Abstract Natural gas, a low-carbon fossil fuel, is expected to play a crucial role in the clean energy transition for climate scenarios, but the necessity for efficient storage and transportation presents significant challenges due to harsh storage conditions. The hydrate-based solidified natural gas (SNG) storage method is energy-efficient, allowing for storage under relatively mild pressure and temperature conditions, with gas occupation property. Nonetheless, the thermodynamic conditions for SNG technology (274.2 K, 10 MPa) are still challenging to adopt. Thus, for milder condition and improved material stability of gas hydrate, various alkyl ring types of chemicals, including large guest molecules such as tetrahydrofuran (THF) and cyclopentane (CP). To achieve the maximum storage capacity of sII hydrate, which is approximately 118 mmol of CH_4/mol of H_2O, while ensuring thermodynamic stability, the water-to-hydrate conversion ratio must be maximized. To address this challenge, several strategies have been implemented, including the optimization of process conditions such as formation temperature and the use of kinetic promoters, such as porous particles, surfactants, and amino acids. Alkyl amine chemicals have been studied as potential promoter candidates in SNG technology. Despite their strong interaction with water, which may reduce water activity, polar amine groups have been adopted as thermodynamic promoters for several hydrates. Interestingly, several amine molecules form semi-clathrate hydrates with water molecules. However, when CH_4 is co-exist, it has been reported that structural transformation can occur and forming the true-hydrate, such as structure II (sII) hydrate. In this study, we focused on the cyclohexyl amine (CHA) as a thermodynamic promoter for SNG applications. First, the nature of CHA hydrate was revealed through crystallographic measurement. CHA formed tetragonal hydrate ($P2_1/n$) with water molecules due to the notable polarity of primary amine group. However, considerable molecular size, we revealed that CHA in its axial configuration can stabilize the sII-L cage with CH_4 as the gaseous guest from Rietveld refinement. Moreover, a thermodynamic promotion effect of approximately 5 K was observed compared to pure CH_4 hydrate. Additionally, through spectroscopic analysis, we revealed that CH_4 primarily occupied the sII small cage, while CHA was enclathrated in the sII large cage, thereby enhancing the stability of the CHA (5.6 mol%) + CH_4 hydrate. In subsequent kinetic experiments, the CHA (5.6 mol%) + CH_4 system achieved a methane storage capacity of approximately 100.8 mmol of CH_4 per mole of H_2O, suggesting its potential as a candidate thermodynamic promoter for SNG technology.

Keywords
Clathrate hydrate, Gas storage, Natural gas, Cyclohexyl amine, Gas uptake

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