

Anisotropic growth kinetics of tetrahydrofuran clathrate hydrate

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Clathrate hydrates (hereafter, clathrates) are crystalline forms of water that contain many guest molecule inclusions (hereafter, guests). Each guest in a clathrate is included in a cage formed by water molecules. Many types of gaseous molecules can be guests of clathrates. Therefore, clathrates can be used to store fuel gases, such as CH_4 and H_2 , and to separate and remove greenhouse gases, such as CO_2 , from mixtures of gas species released from factories. Thus, clathrates have attracted a great deal of attention from researchers who work in the fields of crystal growth, energy technology and environmental technology.

Clathrate guests are not restricted to gas molecules. For example, tetrahydrofuran (THF) molecules can also be guests of clathrates. THF clathrates are structure II clathrates consisting of large (hexakaidecahedra consisting of 12 pentagons and four hexagons) and small (pentagonal dodecahedra) cages. Experimental results indicate that THF molecules are included as guests in the large cages only. However, when THF clathrates are grown from a three-component system of water, THF and gas, gas molecules can also be included as guests in vacant cages of the grown THF clathrates, provided that the sizes of the gas molecules are appropriate for inclusion in the vacant cages. In such instances, gas molecules are captured in THF clathrates at much lower pressures or much higher temperatures than those required for gas molecule inclusion into pure gas clathrates. Therefore, THF clathrates have received much attention for use as materials for storage of fuel gases and for separation and removal of greenhouse gases.

It is known that the growth shape of THF clathrates is octahedral with flat $\{111\}$ planes, meaning that the $\{111\}$ planes have the slowest growth velocity of all crystallographic planes. The difference in the growth velocity of THF clathrates among crystallographic planes originates from the anisotropy in the growth kinetics of the planes. However, for all crystallographic planes of THF clathrates, the growth kinetics remain unclear because elucidation of these growth kinetics by experimental means is quite difficult.

In this study, the growth kinetics of a THF clathrate at the interface between the clathrate and an aqueous THF solution were investigated by means of a molecular dynamic simulation. The simulation was carried out for the interface of both the $\{100\}$ and $\{111\}$ planes of the THF clathrate. The simulation indicated the same anisotropic growth as that observed in real systems: the growth of the THF clathrate was much slower at the $\{111\}$ interface than at the $\{100\}$ interface. When the THF clathrate grew, THF molecules that were dissolved in the solution first were arranged at both large and small cage sites on the interface. Subsequently, the formation of cages by H_2O molecules occurred in regions surrounded or sandwiched by those arranged THF molecules. As the formation of cages progressed, the THF molecules that had once been arranged at small cage sites gradually moved away from the sites, and finally the structure of the clathrate was completely formed.

Simulation results strongly suggested that the rate-determining process for clathrate growth was the rearrangement of THF molecules at the interface from a disordered state to a state in which THF molecules were ideally arranged at large cage sites only. This rearrangement occurred much more slowly at the $\{111\}$ interface than at the $\{100\}$ interface, owing to the formation of a modified structure in which large and small cages were formed at opposite positions of the $\{111\}$ interface. The anisotropic growth kinetics of the THF clathrate, which were obtained in this study, are consistent with the fact that growth shapes of THF clathrates in real systems are octahedral with flat $\{111\}$ planes.