

Observation of the Self-preservation Effect of Methane and Ethane Hydrate

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ABSTRACT

We investigated surface changes of methane and ethane hydrates during depressurization using optical and confocal scanning microscopes. The dissociation of methane hydrate above 242 K and ethane hydrate above 267 K resulted in the formation of clear ice sheets on the hydrate surface. The ice sheets that formed at 252 K were the thickest of those from 242 to 262 K, indicating that methane hydrate stability may be greatest around 252 K. Our results reveal that the formation of ice sheets is closely related to the mechanism of the self-preservation effect of methane hydrate and ethane hydrate. Practical transportation and storage of methane hydrate and ethane hydrate should be undertaken at 250 and 270 K at atmospheric pressure. Dissociation control of methane hydrate by the self-preservation effect based on ice sheet formation may be helpful for research into methane hydrate resources, and thus our results are of value.

KEY WORDS: hydrate, self-preservation effect; sintering, in-situ observation, optical microscope, confocal scanning microscope, ice sheet thickness.

INTRODUCTION

Gas hydrates are inclusion compounds that consist of an open network of water molecules that are hydrogen-bonded in a manner similar to ice and that interstitially engage gas molecules under high pressures and low temperatures. The actual gas storage density depends on the gas occupation fraction and the particular crystallographic structure of the hydrate (Sloan, 1998; Stackelberg and Muller, 1951; Muller and Stackelberg, 1952; Ripmeester, Tse, Ratcliffe, and Powell, 1987). A volume of gas hydrate contains more than 150 times the mass of gas as that for the same volume of pure gas at the standard temperature and atmospheric pressure. The most common compound is methane hydrate. Interest in these compounds has risen in recent years due to the discovery of large deposits below the ocean floor and in permafrost regions (Sloan, 1998; Stackelberg and Muller, 1951; Muller and Stackelberg, 1952; Ripmeester, Tse, Ratcliffe, and Powell, 1987). Methane hydrate is expected to become a new energy source (Kvenvolden, 2000) and a medium for energy storage and transportation (Gudmundson and Borrehaug, 1996).

The dissociation temperature of methane hydrate under atmospheric pressure is about 193 K (Sloan, 1998). However, several reports have indicated that methane hydrate can be stored at atmospheric pressure and 267 K for two years; this phenomenon is referred to as the self-preservation effect (Yakushev and Istomin, 1992). Stern, Circone, Kirby, and Durham (2001) reported anomalous preservation of massive methane hydrates in which the storage stability of methane hydrate between 240 and 271 K was greater than that below 240 K. Therefore, the self-preservation effect makes methane hydrate meta-stable in a temperature range between 240 and 271 K. Thus, transportation and storage of methane hydrate can be undertaken at temperature conditions milder than those for liquefied methane gas at atmospheric pressure due to the self-preservation effect. Kuhs, Genov, Staykova and Hansen (2004) reported that the stacking fault of cubic ice below 240 K apparently does not present an appreciable diffusion barrier for methane gas, while annealed ordinary hexagonal ice at temperatures between 240 and 273 K hindered methane gas diffusion in *in-situ* neutron diffraction experiments for dissociation of methane hydrate. Takeya, Shimada, Kamata, Ebinuma, Uchida, Nagao and Narita (2001) measured the dissociation rates and the transition rate of methane hydrate into hexagonal ice using time-resolved, energy-dispersive X-ray diffraction at atmospheric pressure and temperatures between 148 and 253 K. They reported that the dissociation had two regimes, in which the second step was relatively slow since the methane gas had to diffuse through a thickening ice layer below 193 K. Komai, Kang, Yoon, Yamamoto, Kawamura and Ohtake (2004) estimated the diffusion coefficients of methane molecules through a hydrate surface coated with ice using Raman spectroscopy. These studies were based on the crystal structure transition and clarified that the dissociation rate is controlled by the rate of gas diffusion through ice. Shimada, Takeya, Kamata, Uchida, Nagao, Ebinuma and Narita (2005) measured surface changes of methane hydrate during its dissociation under atmospheric pressure at temperatures from 170 to 268 K using a confocal scanning microscope (CSM). They reported that the increase in storage stability of methane hydrate at 240 K is likely related to the formation of an ice sheet at the surface of the hydrate. Thus, the stability of self-preservation is considered to be related to the nature of the ice sheet that forms during hydrate dissociation.

We report here the results of observations of the surfaces of methane and ethane hydrate samples during dissociation when the atmospheric gas pressure was decreased. The surface changes of methane and ethane