CRYSTAL STRUCTURE AND STABILITY OF BUTANE CLATHRATE HYDRATE

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ABSTRACT
In this study, powder X-ray diffraction (PXRD) studies of butane (C\textsubscript{4}H\textsubscript{10}) clathrate hydrates were performed. Crystal structure analysis of iso-C\textsubscript{4}H\textsubscript{10} hydrate and n-C\textsubscript{4}H\textsubscript{10} + CH\textsubscript{4} hydrate revealed dynamical disorder and cage occupancies of iso-C\textsubscript{4}H\textsubscript{10} and n-C\textsubscript{4}H\textsubscript{10} molecules in \(5^{12}6^4\) large cages. Kinetic stability of iso-C\textsubscript{4}H\textsubscript{10} and n-C\textsubscript{4}H\textsubscript{10} hydrate was examined by temperature ramping method by means of PXRD, and it was suggested that both of them do not show self-preservation phenomena. These results are useful for further understanding of natural gas hydrates.

Keywords: butane, methane, natural gas, hydrate, structure analysis

INTRODUCTION
Natural gas hydrate encages small amount of butane (C\textsubscript{4}H\textsubscript{10}) and pentane (C\textsubscript{5}H\textsubscript{12}) as well as methane (CH\textsubscript{4}), ethane (C\textsubscript{2}H\textsubscript{6}) and propane (C\textsubscript{3}H\textsubscript{8}). [1]. Although CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and C\textsubscript{3}H\textsubscript{8} hydrate has been investigated from both fundamental and application point of view [2-4], it is still not well known about C\textsubscript{4}H\textsubscript{10} or C\textsubscript{5}H\textsubscript{12} hydrate [5].

Herein, powder X-ray diffraction (PXRD) studies of C\textsubscript{4}H\textsubscript{10} clathrate hydrates were performed, and the effect of structural isomer, n-C\textsubscript{4}H\textsubscript{10} and iso-C\textsubscript{4}H\textsubscript{10}, was examined. Also, the effect of conformation of n-butane, anti and gauche, was examined. Ab initio crystal structure determinations of these hydrates were performed. And kinetic stability of both n-C\textsubscript{4}H\textsubscript{10} + CH\textsubscript{4} and iso-C\textsubscript{4}H\textsubscript{10} hydrate structure by temperature ramping were investigated using PXRD method.

EXPERIMENTAL METHODS
Research grade CH\textsubscript{4}, n-C\textsubscript{4}H\textsubscript{10} and iso-C\textsubscript{4}H\textsubscript{10} (purity: 99.99%, 99.8% and 99.9%, respectively, supplied by Takachiho Chemical Industry) were used for guest gases of hydrate samples. In the case of n-C\textsubscript{4}H\textsubscript{10} + CH\textsubscript{4} hydrate, finely powdered ice of about 3 g was put into a high-pressure vessel of 20 mL in volume at 255 K. The vessel was evacuated and pressurized by n-C\textsubscript{4}H\textsubscript{10} + CH\textsubscript{4} mixed-gas up to 10 MPa. The temperature was controlled at 274.2 K for more than 1.5 days to melt the ice and to form gas hydrates. After confirmation of no significant pressure decrease (less than 0.01 MPa hour\textsuperscript{-1}), the

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