HYDROGEN ABSORPTION BEHAVIOR OF ORGANIC-COMPOUND CLATHRATE HYDRATES

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ABSTRACT
The hydrogen absorption behavior of organic-compound clathrate hydrate was investigated using five kinds of organic compounds as well as tetrahydrofuran (THF). These hydrates were pressurized by hydrogen, and Raman analysis, the determination of the amount of hydrogen and calorimetric measurement were carried out. The Raman results show that the samples investigated in this work formed binary clathrate hydrate of hydrogen and each organic compound. The organic-compound clathrate hydrate presented similar performances to that of THF clathrate hydrate regarding hydrogen absorption and heat of dissociation. These results suggested that the organic compounds investigated in this work may become alternatives to THF.

Keywords: clathrate hydrate, hydrogen, storage, organic compounds

INTRODUCTION
Recently, many kinds of new hydrogen storage media have been investigated in anticipation of the upcoming future where hydrogen is expected to be a major fuel. It is widely known that hydrogen can be contained in sII-type clathrate hydrate [1,2], and it is expected to become one of the possible storage media of hydrogen. Recent researches are revealing its physical properties i.e. phase diagram, cage occupancy and so on [3-6]. The trials to reduce the storage pressure or increase the hydrogen storage capacity using a kind promoter, structure H or semi-clathrate hydrate are also active [7-23]. The promoter effect of tetrahydrofuran (THF) is widely known, and 1,4-dioxane has been investigated as a promoter in recently study [20]. This study is intended to search for alternative chemical compounds to THF. In this study, the hydrogen absorption behavior of organic-compound clathrate hydrates was investigated. For a start, clathrate hydrate structure was constructed using five kinds of organic compounds, as well as THF. These hydrates were pressurized by hydrogen and Raman spectroscopic analysis was carried out. Also, the amount of absorbed hydrogen was determined and the heats of dissociation were obtained to prospects for industrial use.

EXPERIMENTAL
Sample preparation
Clathrate hydrates were synthesized using five kinds of organic compounds. The organic compounds used in this work were acetone, propylene oxide, 1,3-dioxolane, 2,5-dihydrofuran and 1,4-dioxane. Each compound was mixed with pure water in a molar ratio of 1/17. Each mixture was solidified at the temperature of 253K over 2-4 days.

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**Raman spectroscopic analysis**

Each obtained sample was crushed into a fine powder, with grain diameters smaller than 250μm at temperatures below 173K. Each powder was pressurized by hydrogen under the T-P conditions of 253K and 12MPa for 24hours. The samples obtained were subjected to Raman spectroscopic analysis at temperatures below 173K to prevent hydrogen release and other reactions. The laser Raman microprobe spectrometer used in this work was the Jobin Yvon Ramanor T6400 with a single monochromator and CCD detector. The wavelength of the Ar+ laser was set at 514.5nm with a beam spot size of 10μm.

**Absorption measurement**

Each sample was crushed into a fine powder by the same procedure as described above. The powder obtained was set into a high-pressure cell, the temperature and pressure of which can be controlled and measured. The powder sample was pressurized by hydrogen under the T-P condition of 233K and 10MPa. After a sufficient of time (more than 3hours), hydrogen in the void space of the cell was rapidly released from the release valve to atmospheric pressure, and the valve was shut quickly. The inner pressure of the cell was slightly recovered because of hydrogen released from the powder sample. The amount of increase of pressure can be considered as the amount of absorbed hydrogen at 233K and 10MPa within a margin of error. The amount of hydrogen was estimated from factors such as the pressure increase, void space and the amount of initial sample using an equation of state.

**Calorimetric investigation**

The enthalpy change of dissociation of each sample (without hydrogen) was determined using a differential scanning calorimeter (DCS). The DSC used in this work was NETZCH DSC 204HP / 1 / G Phoenix. The T-P condition was from 223K to 313K at atmospheric pressure, and the heating rate was 1K / min. Measurements were carried out more than three times for each sample and the average was obtained.

**RESULTS AND DISCUSSION**

**Raman spectroscopic analysis**

Figure 1 shows Raman spectra from each sample. A broad peak spectrum was observed at 4131cm$^{-1}$ for all samples except for 1,4-dioxane. This peak can be identified as the H-H vibron peak originating from hydrogen in a small cage of sII clathrate hydrate [2,8,11,16,18,20,22], since it can be assumed that most of the large cages are occupied by the organic compound. In the case of 1,4-dioxane, the H-H vibron peak could not be detected in this work, but it might be detected by improving the measuring conditions [20]. In any case, it can be confirmed that the samples investigated in this work formed binary clathrate hydrate of hydrogen and each organic compound.

![Figure 1 Raman spectra at H-H vibron region for each organic compound hydrate (after pressurization with hydrogen).](image)

**Absorption measurement**

Figure 2 shows the amount of absorbed hydrogen for each organic-compound clathrate hydrate at 233K and 10MPa. Table 1 shows the average of the each case. The result for THF clathrate hydrate is also listed for comparison. The amount of hydrogen was represented as mol of hydrogen per mol of water in clathrate hydrate, since the specific gravities differ for each hydrate because of the difference in the molecular weight of the guest compound. As shown in Table 1, the amounts of absorbed hydrogen were approximately 0.027-0.029mol/mol for acetone, propylene oxide, 1,3-dioxolane and 2,5-dihydrofuran. They are clearly similar to the amount in THF clathrate hydrate (0.027mol/mol). In the case of 1,4-dioxane clathrate hydrate, the quantities fluctuated widely and were smaller values, 0.008-0.019mol/mol, than for other organic-compound clathrate hydrates. This result does not conflict with the Raman results, in which the H-H vibron peak was nominal in the case of 1,4-dioxane.
Calorimetric investigation
The heat of dissociation of each organic-compound clathrate hydrate (without hydrogen) was measured to investigate how much energy is required to obtain the initial material (organic-compound clathrate hydrate) to investigate the feasibility of industrial use. Figure 3 shows the results of the DSC measurement of propylene oxide clathrate hydrate as an example. Generally, it can be assumed that the initial material consisted of mainly clathrate hydrate and a very small amount of ice. In the case of THF clathrate hydrate, the ice peak can be separated from the hydrate peak, since the dissociation temperature of THF clathrate hydrate is 277K. For the organic-compound clathrate hydrates investigated in this work, since the dissociation temperatures were around 273K, as shown in Figure 3, the two peaks were minimally separated. Accordingly, the heats of dissociation were corrected under the assumption that the proportion of ice in the initial material was 1 wt%. The heats of dissociation per unit weight of clathrate hydrate are listed in Table 2. It is clear that they are very close to that of THF clathrate hydrate [24]. Note that these results might include a significant amount of uncertainty. Thus, they are not reliable indicator of the physical properties, but it is clear that the heats of dissociation of organic-compound hydrates are not so different from each other. These results suggest that the organic compounds investigated in this work may become alternatives to THF.

Table 1 Amount of absorbed hydrogen at 233K and 10MPa.

<table>
<thead>
<tr>
<th>Guest</th>
<th>Absorbed hydrogen [mol/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0.027</td>
</tr>
<tr>
<td>Propylene oxide</td>
<td>0.029</td>
</tr>
<tr>
<td>1,3-Dioxolane</td>
<td>0.028</td>
</tr>
<tr>
<td>2,5-Dihydrofuran</td>
<td>0.029</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>0.014</td>
</tr>
<tr>
<td>Ice</td>
<td>0.00065</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>0.027</td>
</tr>
</tbody>
</table>

Table 2 Heat of dissociation of each clathrate hydrate (without hydrogen). * Literature [24]

<table>
<thead>
<tr>
<th>Guest</th>
<th>$\Delta H_d$ [J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>261.2</td>
</tr>
<tr>
<td>Propylene oxide</td>
<td>286.8</td>
</tr>
<tr>
<td>1,3-Dioxolane</td>
<td>268.2</td>
</tr>
<tr>
<td>2,5-Dihydrofuran</td>
<td>227.2</td>
</tr>
<tr>
<td>Tetrahydrofuran*</td>
<td>262.9</td>
</tr>
</tbody>
</table>

CONCLUSION
The hydrogen absorption behaviors of five kinds of organic-compound clathrate hydrates were investigated. The Raman results show that the samples investigated in this work formed binary clathrate hydrate of hydrogen and each organic compound. Regarding the hydrogen absorption ability, the organic-compound clathrate hydrates, except for 1,4-dioxane, showed much the same quantities of absorbed hydrogen compared with
THF clathrate hydrate. Also, the heats of dissociation were clearly similar to that of THF clathrate hydrate. These results suggested that the organic compounds investigated in this work may become alternatives to THF.

ACKNOWLEDGMENT
The authors would like to thank Prof. J-H Yoon, Dr. S. Takeya, Prof. H. Hirai, Prof. T. Tsuji and Dr. K. Ogasawara for guidance and advice.

REFERENCES