



## Decomposition and Raman spectrum of dimethyl ether hydrate

Pinxian Huang<sup>a</sup>, Xiongmin Liu<sup>a,\*</sup>, Yuji Wada<sup>b</sup>, Katsumi Katoh<sup>c</sup>, Mitsuru Arai<sup>d</sup>, Masamitsu Tamura<sup>d</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

<sup>b</sup> National Institute of Advanced Industrial Science and Technology, Tsukuba 3058569, Japan

<sup>c</sup> Fukuoka University, Fukuoka 8140180, Japan

<sup>d</sup> Environmental Science Center, University of Tokyo, Tokyo 1130033, Japan

### HIGHLIGHTS

- ▶ The thermal stability and decomposition of dimethyl ether (DME) and DME hydrate were studied using a self-designed instrument.
- ▶ The thermal stability and decomposition of DME hydrate was studied.
- ▶ Raman spectroscopy analysis showed that the vibration of DME hydrate shifted toward lower wave numbers in comparison with that of DME-water and DME.
- ▶ The stoichiometric composition of DME hydrate was inferred to be DME·13H<sub>2</sub>O.

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### ABSTRACT

The thermal stability and decomposition of dimethyl ether (DME) and DME hydrate were studied using a self-designed instrument. The Raman spectra of DME, a solution mixture of DME and water (DME-water) and DME hydrate were measured. The result showed that the decomposition temperature of DME hydrate was dependent on the ambient pressure and H<sub>2</sub>O/DME molar ratio; DME hydrate tended to decompose at a higher temperature under a higher ambient pressure. The decomposition temperature of DME hydrate was  $-13.8$  °C when the molar ratio of H<sub>2</sub>O/DME was 12.0, and the stoichiometric composition of DME hydrate was inferred to be DME·13H<sub>2</sub>O. Raman spectroscopy analysis showed that the vibration of DME hydrate shifted toward lower wave numbers in comparison with that of DME-water and DME. Moreover, the spectrum of DME hydrate showed a vibration band at  $3151$  cm<sup>-1</sup>, which was not observed for DME-water or DME.

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### 1. Introduction

In recent years, increasing scientific evidences have shown that the use of fossil fuels leads to serious environmental problems, e.g., NO<sub>x</sub>, HC and CO emissions. Consequently, a considerable number of studies have been carried out to develop alternative “clean” fuel. In the last few years, dimethyl ether (DME) has attracted much attention as a substitute of diesel fuel [1–3] since it can be artificially synthesized, and exhibits good ignition properties. Furthermore, DME has low emission and less formation of soot [4–6]. DME can also be manufactured at a competitive price than natural gas-derived methanol and other natural resources. These unique features of DME could contribute greatly to the prevention of global warming as well as the construction of resource-recycling societies. The infrared and Raman spectra of DME have been obtained

from crystalline films of CH<sub>3</sub><sup>16</sup>OCH<sub>3</sub>, CD<sub>3</sub><sup>16</sup>OCD<sub>3</sub>, CD<sub>3</sub><sup>16</sup>OCH<sub>3</sub>, CD<sub>3</sub><sup>16</sup>OCD<sub>2</sub>H, and CH<sub>3</sub><sup>16</sup>OCH<sub>2</sub>D [7], but the Raman spectra of a solution mixture of DME and water (DME-water) and DME hydrate have not been reported in the literature. Moreover, DME have caused several accidents in the past. A feasibility study, including an assessment on the reactivity, ignition and explosion characteristics of DME, and its risk to both human health and the environment, needs to be carried out before introducing DME as an alternative energy source at a large-scale. The oxidation of DME and the additives effect and thermal stability of DME/LPG (dimethyl ether–liquefied petroleum gas mixture) have been studied using an accelerating rate calorimeter (ARC) [8–9]. In addition, DME hydrate might be formed when DME and water are mixed in the preparation of DME. Some accidents such as obstruction of the pipe may occur due to the formation of DME hydrate. Furthermore, the hazard of DME hydrate may be different from the hazard of DME. So far, a few studies have been done to clarify the hazard of DME hydrate. Thus, some fundamental studies are needed to evaluate

\* Corresponding author. Tel.: +86 771 3270732; fax: +86 771 3237018.

E-mail address: [xmliu1@gxu.edu.cn](mailto:xmliu1@gxu.edu.cn) (X. Liu).

the stability of DME hydrate. Gas hydrate is a type of clathrate compound in which host molecules form a cage, and a guest molecule is trapped in the cage. Many previous studies have reported the formation, structure, and property of gas hydrate [10–16]. However, only a few papers published were on DME hydrate. In the present study, we attempt to prepare DME hydrate, and its chemical structure and thermal stability were investigated.

## 2. Materials and methods

### 2.1. Materials

DME was obtained from Koike Kagaku Co., Ltd., Japan.  $N_2$  gas was obtained from Tomoe Shokai Co., Ltd., Japan.

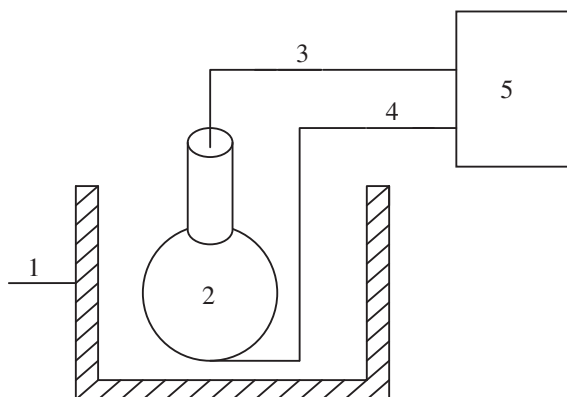
### 2.2. Thermal stability of DME hydrate

The thermal stability of DME hydrate was evaluated by measuring its pressure and temperature under heating condition using the instrument shown in Fig. 1. About 0.64 g of liquid DME and 3.0 g of  $H_2O$  were mixed in a sample vessel at room temperature (25 °C). The volume of the vessel is 9 mL. The mixture was stored at a temperature of 233 K (−40 °C) to obtain DME hydrate. The obtained DME hydrate in the vessel was covered using a heat-insulated material. The pressure and temperature were monitored when the vessel was heated gradually, and the rate of temperature rise 0.1 °C/min.

The decomposition temperature of DME hydrate under pressure-controlled condition was investigated in a  $N_2$  atmosphere. In this case, the ambient pressure was controlled at 0.84 MPa by introducing  $N_2$  gas.

### 2.3. Structure analysis by Raman spectroscopy

A vessel, which has a volume of 2 mL and can withstand a pressure up to 15 MPa, was used to prepare DME hydrate. The vessel was connected with a laser transmission window, a sampling device, and a thermo couple. The temperature of the vessel was controlled by the sampling device and the internal temperature of the vessel was monitored by a thermocouple. Liquid DME and water were mixed in the vessel at a temperature of −30 °C, and the mixture was then stored at a temperature of 233 K to obtain DME hydrate. The Raman spectra were obtained using a Raman spectrometer (RAMANOR-T-64000, HORIBA JOBIN YVON,). In the analysis, the argon ion ( $Ar^+$ ) laser (514.5 nm) was oscillated and irradiated to the sample in the vessel.



**Fig. 1.** The self-designed instrument used for evaluating the thermal stability of DME. 1 – Insulation cover. 2 – Sample vessel. 3 – Pressure sensor. 4 – Temperature sensor. 5 – Recorder and signal conditioner.

## 3. Results and discussion

### 3.1. Stability and decomposition of DME hydrate

#### 3.1.1. Decomposition temperature of DME hydrate

Fig. 2 shows the temperature-dependent pressure curves of DME hydrate (line 1) and DME (line 2). Points **A** and **B** indicate the starting and ending temperatures of the decomposition for DME hydrate, respectively. It is notable that the pressure rapidly increased from point **A** to **B** at a temperature range from −13.8 °C to −4.2 °C when the molar ratio of  $H_2O/DME$  was 12 (mol/mol). In contrast, this was not observed in the case of DME under the same temperature range. These results suggest that DME hydrate might exist stably below −13.8 °C and at a pressure lower than 0.226 MPa as indicated by point **A** and likely to decompose when the temperature is higher than −13.8 °C.

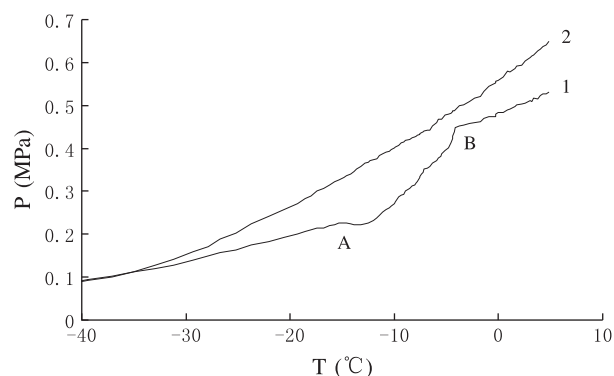
As can be seen from Fig. 2 (line 1), when the temperature was increased from −40 °C to −13.8 °C or above −4.2 °C, the pressure of the gas increased as expected. However, it is thought that the rapid increase in pressure is due to the decomposition of DME hydrate from **A** to **B**, releasing gas.

#### 3.1.2. Decomposition temperature of DME hydrate under a pressure-controlled atmosphere

Fig. 3 shows the temperature-dependent pressure curve of DME hydrate under pressure-controlled condition. The decomposition temperature of DME hydrate (point **A**) shifted to −7 °C when the ambient pressure was increased to 0.84 MPa by introducing  $N_2$  gas at a  $H_2O/DME$  molar ratio of 12. These results imply that the stability of DME hydrate is ambient pressure-dependent, and the decomposition temperature increases with increasing ambient pressure. These behaviors are similar to those of gas hydrate such as methane hydrate.

#### 3.1.3. Relationship between the decomposition temperature of DME hydrate and $H_2O/DME$ molar ratio

Fig. 4 shows the relationship between the decomposition temperature of DME hydrate and  $H_2O/DME$  molar ratio. Sign 1▲ and 2● Fig. 4 represent the temperature curves of the starting decomposition and ending decomposition for DME hydrate at different  $H_2O/DME$  molar ratios, respectively. From Fig. 4, it was found that the decomposition temperature of DME hydrate decreased with increasing  $H_2O/DME$  molar ratio. In particular, when the molar ratio was above 10.8, the decrease in decomposition temperature was more rapid. This suggests that DME might present mainly as DME hydrate at that ratio. Generally, it is known that the stoichiometric composition (the cage structure) of hydrate depends on the size of the guest molecule [12].



**Fig. 2.** Temperature-dependent pressure curves of DME hydrate (line 1) and DME (line 2).

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