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# Increasing molecular $O_3$ storage capacity in a clathrate hydrate

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This paper reports an experimental study to further increase the ozone storage capacity in a clathrate hydrate and to better understand the relationship between the gas phase $O_3$ concentration and the $O_3$ storage capacity in the hydrate. We performed experiments with the $O_3 + O_2 + CO_2$ feed gas with an increased $O_3$ fraction in the gas phase exceeding that covered by a preceding study. To accurately specify the thermodynamic conditions to form the hydrate, we first measured the three-phase (gas + liquid + hydrate) equilibrium conditions for the ($O_3 + O_2 + CO_2 + H_2O$) and ($O_2 + CO_2 + H_2O$) systems. The phase equilibrium data cover the temperature range from 272 to 277 K, corresponding to pressures from 1.6 to 3.1 MPa, for each of the two different ($O_3 + O_2$)-to-$CO_2$ or $O_2$-to-$CO_2$ molar ratios in the feed gas, which are approximately 4 : 6 and 5 : 5, respectively. The $O_3$ fraction in the gas phase was ~0.025. Based on the equilibrium data, we prepared crystal samples of the $O_3 + O_2 + CO_2$ hydrates at a system pressure of 3.0 MPa and a temperature of 272 K. The highest $O_3$ storage capacity in the hydrates was measured to be 2.15 mass% which is 2.36 times higher than the highest past record of 0.91 mass%. The results also show that the dominant factor to control the $O_3$ storage capacity in the hydrates is the $O_3$ mole fraction in the gas phase in contact with the hydrates.

## Introduction

Ozone ($O_3$) is a strong oxidant which causes only slight environmental damage because of its nature of decomposing to oxygen ($O_2$). Based on these advantages, there are various applications of ozone in industry, *e.g.*, purification of water and sterilization of perishables. However, since the decomposition reaction to oxygen occurs spontaneously, ozone is difficult to preserve. Thus, in order to use ozone in industry, it has been generated by an onsite ozone generator which is a costly device. To establish ozone preservation technology, experimental and theoretical studies of $O_3$-containing clathrate hydrates have recently been reported.[1–4]

Clathrate hydrates are crystalline solids consisting of "*host*" water molecules which compose cages and "*guest*" molecules enclosed in the cages. Ozone molecules can be separated from each other by the hydrate cage walls and thus prevented from mutually interacting to cause the ozone-to-oxygen reaction. Based on this nature, the idea of storing ozone using hydrates was first proposed by McTurk and Waller[5] in 1964. This technology provides an ozone density 100 to 1000 times higher than that of modern ones such as ozonated water and ozonated ice. In the patent application document,[3] it is shown that hydrate formation from an $O_3 + O_2$ gas mixture would require a high pressure and a low temperature, *e.g.*, 13 MPa and 248 K. To decrease the hydrate-forming pressure, it is effective to use an appropriate second guest substance which is called a *help* guest. If the simple hydrate of the *help* guest is formed under milder conditions compared to the hydrate of the main-target guest substance, adding the second guest as the *help* guest in the feed gas would form a double hydrate containing the main and *help* guests under milder conditions.[6] The *help* guest needs to have sufficient chemical durability against ozone oxidation. As such *help* guests, carbon tetrachloride, xenon, 1,1-dichloro-1-fluoro-ethane and carbon dioxide were previously tested.[7–9] Due to the toxicity of carbon tetrachloride, the cost of xenon and the environmental impacts of 1,1-dichloro-1-fluoro-ethane, we selected carbon dioxide as the most promising substance in place of the other *help* guests.

For practical use of the $O_3$-containing hydrates, it is necessary to determine the thermophysical properties relevant to these hydrates. Muromachi *et al.*[10] performed three-phase (gas + liquid + hydrate) equilibrium measurements for the $O_3 + O_2 + CO_2 + H_2O$ systems. These data cover the temperature range from 272 K to 279 K, corresponding to pressures up to 4 MPa, for each of the ($O_3 + O_2$)-to-$CO_2$ or $O_2$-to-$CO_2$ molar ratios in the feed gas, which are approximately 1 : 9, 2 : 8, and 3 : 7. The concentration of ozone in

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the $O_3 + O_2$ mixture was less than 11 mol%. Nakajima *et al.*[2] performed the measurements for the $O_3$ storage capacity in the $O_3 + O_2 + CO_2$ hydrates formed from four different $O_3 + O_2$ *versus* $CO_2$ molar ratios (1 : 9, 2 : 8, 3 : 7, 4 : 6) in the feed gas. The $O_3$ storage capacity was evaluated as an ozone mass fraction in the hydrate because the mass of the storage media had an impact on the storage and transportation efficiency. Their hydrate samples were prepared at system pressures of 2.0, 2.5 and 3.0 MPa and a temperature of 272 K. The results of these tests also showed that the $O_3 + O_2 + CO_2$ hydrate stored at 248 K or lower can preserve ozone at a mass fraction of 0.4–0.6% for over 20 days. In their study, an $O_3$ storage capacity as high as 0.91 mass% was obtained, which was the highest value ever reported.

Based on the van der Waals and Platteeuw theory,[11] the gas storage capacity in a hydrate has a positive correlation with the fugacity of the gas component. Nakajima *et al.*[2] experimentally confirmed that the $O_3$ storage capacity had no systematic dependence on the pressure. The thermodynamic model developed by Muromachi *et al.*[1] showed that the $O_3$ storage capacity in hydrates can be further extended by increasing the $O_3$ fraction in the gas phase. Based on these three reasons, it is necessary to increase the $O_3$ fraction in the feed gas to increase the $O_3$ storage capacity in the hydrates.

Since ozone easily decomposes to oxygen, it is difficult to control the $O_3$ fraction in the gas phase and accurately measure the $O_3$ fraction in the gas and hydrates. The $O_3$ fraction in the gas phase might not increase by simply increasing the $O_3 + O_2$ fraction in the $O_3 + O_2 + CO_2$ mixture because the $O_3$ decomposition reaction is accelerated under high $O_3$ density conditions. To demonstrate the increase in the $O_3$ fraction in the gas phase, it is necessary to measure the time evolution of the $O_3$ concentration in the feed gas in an increased range of the nominal $O_3 + O_2$ fraction. There is no report in the literature on the relationship between the $O_3$ concentration in the gas phase during hydrate formation and the $O_3$ storage capacity in the hydrates. There is still room for the improvement in the accurate measurement of the $O_3$ concentration in the gas and hydrates.

The major objectives of this study are to further increase the $O_3$ storage capacity in hydrates by increasing the $O_3$ fraction in the $O_3 + O_2 + CO_2$ feed gas and to better understand the relationship between the $O_3$ concentration in the gas phase and the $O_3$ storage capacity in the hydrates. To accurately specify the hydrate forming conditions, we first performed the phase equilibrium measurements for the $O_3 + O_2 + CO_2 + H_2O$ system exceeding the range covered by the previous study.[10] The temperature range is from 272 K to 277 K and the pressure range is below 4 MPa for our three-phase equilibrium measurements. The molar ratios of $(O_3 + O_2)$-to-$CO_2$ or $O_2$-to-$CO_2$ in the feed gas are approximately 4 : 6 and 5 : 5, respectively. To demonstrate the increase in the $O_3$ fraction in the gas phase, the time evolution of the $O_3$ concentration in the feed gas in the range of the nominal $O_3 + O_2$ mole fraction of 0.1–0.6 were measured. Based on the equilibrium data, we prepared the crystal samples of the $O_3 + O_2 + CO_2$ hydrates formed from three different $O_3 + O_2$ *versus* $CO_2$ molar ratios (4 : 6, 5 : 5, 6 : 4) in the feed gas, monitoring the $O_3$ concentration in the gas phase in contact with the hydrates and measured the $O_3$ storage capacity. The improvements in the measurement of the $O_3$ storage capacity include sampling the formed hydrates at the low temperature of 253 K to avoid hydrate decomposition and the use of an air-tight container for mixing the hydrate sample into a potassium iodide aqueous solution to decrease the $O_3$ diffusion into the air.

## Experimental

### Materials

The fluid samples used in the experiments were deionized and distilled water: carbon dioxide of 99.995 vol% and oxygen of 99.9 vol% certified purity were provided by Japan Fine Products Corp., Kawasaki, Kanagawa Prefecture, Japan. The oxygen gas was used as received from the supplier to generate ozone with the aid of an ozone generator (ED-OG-R4DA, EcoDesign, Co., Ltd., Saitama Prefecture, Japan). For measuring the ozone concentration in each ozone-containing gas sample, we used an ultraviolet-absorptiometric ozone monitor (PG-620HA, Ebara Jitsugyo Co., Ltd., Tokyo, Japan).

### Phase equilibrium measurements

We obtained the three-phase (gas + liquid + hydrate) equilibrium pressure *versus* temperature data for the $(O_3 + O_2 + CO_2 + H_2O)$ systems. To demonstrate that ozone is clearly contained in the hydrate, we also measured the data for the $(O_2 + CO_2 + H_2O)$ system corresponding to the experimental conditions of the $O_3$-containing system and verified that the equilibrium pressure of the $O_3 + O_2 + CO_2 + H_2O$ systems is lower than that of the $O_2 + CO_2 + H_2O$ systems. This indicates that ozone can form a hydrate at a lower pressure than oxygen at a given temperature due to the preferential uptake of ozone into the hydrate compared to oxygen. The measurements were performed with the same setup as used in a previous study.[10] Hydrates were formed in a vessel, which was a cylindrical stainless-steel chamber with 35 mm diameter, 120 mm height, and total volume of 190 $cm^3$. The vessel was immersed in a temperature-controlled bath to maintain the temperature inside the vessel at a prescribed level. The pressure and temperature were measured by a strain-gauge pressure transducer (PHB-A-10MP, Kyowa Electronic Instruments Co., Ltd., Tokyo, Japan) and a platinum-wire resistance thermometer (NHRS1-0, Chino, Inc., Tokyo, Japan) connected to a resistance-measuring bridge. The expanded uncertainties in this study were estimated to be $\pm$0.05 K for the temperature, $\pm$6.0 kPa for the pressure and $\pm$0.0015 for the mole fraction of each species in the sampled gas with 95% coverage. We obtained the three-phase (gas + liquid + hydrate) equilibrium pressure *versus* temperature data for the $O_3 + O_2 + CO_2 + H_2O$ system and, for comparison, corresponding data for the $O_2 + CO_2 + H_2O$ system. Both experimental runs commenced by charging the vessel with 20 g of liquid water. For the $O_2 + CO_2 + H_2O$ system, we applied a temperature-search method.[12] The gas-mixing loop was charged with the $O_2 + CO_2$ mixture up to a prescribed level.

To induce hydrate nucleation, the vessel was immersed in the other bath in which the coolant was cooled to ~253 K. After the temperature of the vessel was decreased to ~263 K, the vessel was reconnected to the setup. Once the hydrate formation was detected during this cooling process, the temperature was increased in steps of 0.1 K. Responding to the stepwise increase in temperature, the pressure also increased stepwise. This process of the stepwise temperature rise was continued until the completion of the hydrate dissociation. The point at which the slope of the *p*–*T* data plots sharply changes was determined to be the hydrate dissociation point. This is the three-phase equilibrium point. After readjusting the system temperature to the level of the equilibrium conditions, we then performed the gas-sampling procedure.

For the $O_3 + O_2 + CO_2 + H_2O$ system, we applied a modified pressure-search method.[10] To quickly form hydrates, we performed the above-mentioned cooling before the gas charging process. The gas-mixing loop was charged with the $O_3 + O_2$ mixture to a pressure of 0.3 MPa by the ozone generator. For measurements at higher system pressures, we prepared a gas pressurizer in which the $O_3 + O_2$ gas supplied from the ozone generator could be compressed up to 2.5 MPa by a water column displaced by the oxygen gas cylinder. The mixture was pressurized by the gas pressurizer equal (on a molar basis) to that of the pure $O_2$ gas supplied to the vessel in the corresponding experiment for the $O_2 + CO_2 + H_2O$ system. The mixture was charged with $CO_2$ gas until the system pressure increased to the equilibrium pressure. The uncertainties of the molar feed ratios of $CO_2$ to $O_3 + O_2$ corresponded to that of the pressure measurements. They are estimated to be $\pm 0.016$ for the molar feed ratios of $CO_2$ to $O_3 + O_2$ with 95% coverage. It was determined in the corresponding experiment for the $O_2 + CO_2 + H_2O$ system performed at the same temperature. We measured the temperature and visually confirmed the melting of the ice phase during the hydrate-phase growth process. We defined the system conditions at the stage when a pressure increase (~3 kPa) from its minimum value was observed as the thermodynamic phase-equilibrium conditions. The gas-sampling procedure generally followed that which was used for the $O_2 + CO_2 + H_2O$ system. We separated the gas-sampling section from the test cell by closing the valves between them. We discharged the gas in the former section into the gas-sample holder to ~500 kPa. The residual gas in the gas-sampling section was immediately injected into the ozone monitor. The gas-sample holder was then heated to completely decompose the ozone to oxygen. The resultant $O_2 + CO_2$ mixture in the holder was subjected to gas-chromatographic analysis to determine the $O_2$ *versus* $CO_2$ molar ratio in the feed gas.

### $O_3$ storage capacity measurements

Fig. 1 shows a schematic of the apparatus used for the formation experiments of the $O_3 + O_2 + CO_2$ hydrates. The time evolution measurements of the $O_3$ concentration in the feed gas were performed in the gas-mixing chamber, which was immersed in a water bath temperature-controlled at 280 K. The setup was flushed at least five times with pure $O_2$ gas, then evacuated. After confirming that the $O_3$ fraction in the gas

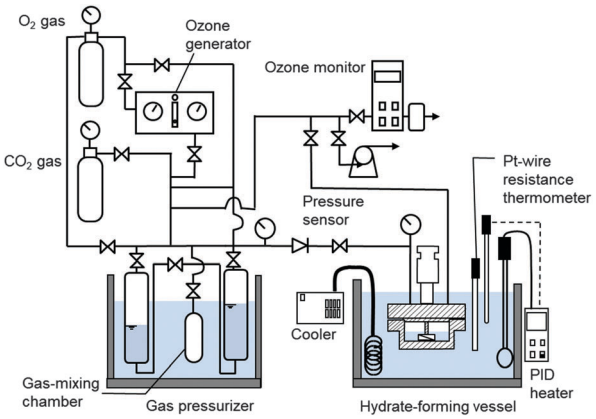


Fig. 1 Schematic of the experimental setup for determining the ozone storage capacity in hydrates.

mixture released from the $O_3$ generator was in the range 0.10–0.12, a gas-mixing chamber and a gas pressurizer were charged with the $O_3 + O_2$ mixture gas to a pressure of 0.3 MPa. The mixture was pressurized by the gas pressurizer until the pressure inside the vessel increased to the prescribed level. Subsequently, $CO_2$ gas was supplied to the gas mixing chamber until the pressure inside increased to 3.5 or 4.0 MPa.

The $O_3 + O_2 + CO_2$ hydrate samples were formed in the hydrate-forming vessel, which was charged with 30 g of water and immersed in a bath of an aqueous ethylene glycol solution temperature-controlled at 272 K. The $O_3 + O_2 + CO_2$ feed gas for forming the hydrates was mixed by the same procedure as mentioned above. The $O_3 + O_2 + CO_2$ gas mixture was supplied to the hydrate-forming vessel until the pressure inside the vessel increased to the prescribed level (2.5 or 3.0 MPa). A series of intermittent batch operations for forming the hydrates were then started by turning on the stirrer in the vessel. To prevent the system pressure from significantly decreasing from the prescribed level, additional feed gas was supplied by the gas-mixing chamber every 20 minutes.

To minimize the change in composition of the gas mixture inside the hydrate-forming vessel, the residual gas inside the vessel was discharged to a pressure of 2.5 MPa every hour and the fresh gas was charged to 3.0 MPa from the gas-mixing chamber. Also, to monitor the $O_3$ concentration in the gas phase in contact with the hydrates, the discharged gas was injected into the $O_3$ monitor to measure the $O_3$ concentration in the gas phase. These batch and gas-exchange operations were repeated several times until no decrease in the system pressure was observed during each batch operation and hence we judged that the hydrate formation had ceased. The hydrate sample was then retrieved from the vessel at a temperature below 215 K and under a dry nitrogen-gas atmosphere. Small portions of the hydrate were sampled for an iodometric measurement to determine its initial $O_3$ storage capacity. To experimentally improve the measurement of the $O_3$ storage capacity, we sampled the formed hydrates at a temperature of 253 K and used an air-tight container to mix the hydrate samples in potassium iodide to avoid ozone diffusion into the air.

An $O_3 + O_2 + CO_2$ hydrate sample was subjected to powder X-ray diffraction (PXRD) measurements to confirm its crystallographic structure and, at the same time, to examine the fraction of the condensed water phase inevitably included in the sample. The sample was finely powdered under a dry $N_2$ gas atmosphere at a temperature comparable to liquid $N_2$ ($\sim$100 K), then top-loaded on a copper (Cu) specimen holder. The PXRD measurements were done using Cu-K$\alpha$ radiation generated by an Ultima III diffraction system (Rigaku Corp., Tokyo, Japan). Analyses of the lattice constant of the hydrate and mass fractions of any unreacted solid water (ice) in the samples were performed by the Rietveld method using the RIETAN-FP program.[13]

## Results and discussion

### Phase equilibrium measurements

The phase equilibrium pressure *versus* temperature data measured for the ($O_3 + O_2 + CO_2 + H_2O$) and ($O_2 + CO_2 + H_2O$) systems in the present study are compiled in Table 1. These are not only the $p$ and $T$ values, but also the relevant values of the mole fractions, $y$, of $O_3$, $O_2$ and $CO_2$ in the gas mixture discharged from the gas-sampling cylinder. The $p$–$T$ data that we obtained may be characterized by two groups in reference to the nominal value of $y_{CO_2}$ (0.6 or 0.5). These data are plotted in Fig. 1 with the previously reported data having the nominal value of $y_{CO_2}$ (0.9, 0.8 and 0.7)[10] for comparison. As presented in Fig. 2, the equilibrium pressures corresponding to the equilibrium temperatures from 272 to 279 K ranged from 1.56 to 2.91 MPa for the $O_3 + O_2 + CO_2 + H_2O$ system. There was some scatter in the gas-phase composition in each group because the $O_3$ composition in the gas phase in contact with the formed hydrate may change from that in the feed gas due to the ozone-to-oxygen reaction. The scatter is also partially ascribed to the gas-compositional fractionation during hydrate formation. However, we found that the $p$–$T$ data points are aligned on a single smooth curve. These data have consistent tendencies with the previous study, that is, the equilibrium pressure decreases with increasing $y_{CO_2}$ at a given temperature. These data also show that even a small fraction of ozone ($y_{O_3} \approx 0.025$ to 0.03) partially replacing oxygen causes an equilibrium pressure decrease of $\sim$0.14 MPa.

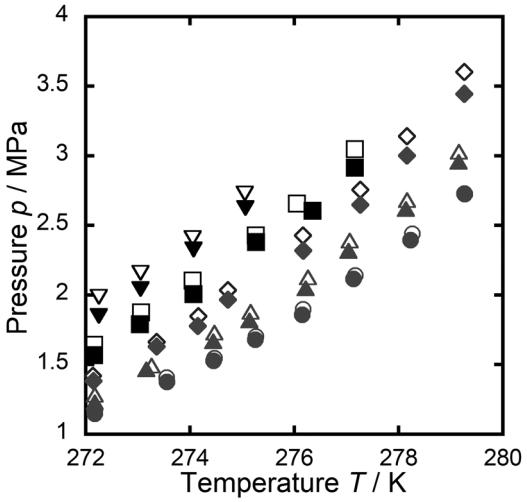


Fig. 2 Three-phase equilibrium $p$–$T$ data for the $O_3 + O_2 + CO_2 + H_2O$ system (●, ▲, ◆, ■, ▼) and the $O_2 + CO_2 + H_2O$ system (○, △, ◇, □, ▽). The details of the three gas mole fractions are specified in Table 1. The data points relevant to the five different levels of $y_{CO_2}$, the $CO_2$ mole fraction in the gas phase, are denoted by their geometries as follows: circles (●, ○) for $y_{CO_2} \approx 0.9$; triangles (▲, △) for $y_{CO_2} \approx 0.8$; rhombuses (◆, ◇) for $y_{CO_2} \approx 0.7$; and squares (■, □) for $y_{CO_2} \approx 0.6$; triangles (▼, ▽) for $y_{CO_2} \approx 0.5$. The data for $y_{CO_2} \approx 0.6$ and $y_{CO_2} \approx 0.5$ were newly obtained in this study. The other data were obtained in our previous study.[10]

Table 1 Three-phase equilibrium $p$–$T$ data for the $O_3 + O_2 + CO_2 + H_2O$ and $O_2 + CO_2 + H_2O$ systems

| Feed compositions Nominal value (mean value) of $y_{CO_2}$ | Equilibrium conditions | | | | |
|---|---|---|---|---|---|
| | | | $y$ | | |
| | $T$/K | $p$/MPa | $O_3$ | $O_2$ | $CO_2$ |
| ≈0.6 | 277.2 | 2.914 | 0.027 | 0.386 | 0.587 |
| | 276.6 | 2.605 | 0.017 | 0.332 | 0.651 |
| | 275.3 | 2.379 | 0.019 | 0.392 | 0.589 |
| | 274.1 | 2.007 | 0.031 | 0.383 | 0.587 |
| | 273.0 | 1.790 | 0.030 | 0.381 | 0.588 |
| | 272.2 | 1.567 | 0.030 | 0.382 | 0.588 |
| | 277.2 | 3.047 | — | 0.398 | 0.602 |
| | 276.1 | 2.656 | — | 0.376 | 0.624 |
| | 275.3 | 2.427 | — | 0.407 | 0.593 |
| | 274.1 | 2.104 | — | 0.415 | 0.585 |
| | 273.1 | 1.876 | — | 0.405 | 0.595 |
| | 272.2 | 1.643 | — | 0.380 | 0.620 |
| ≈0.5 | 275.1 | 2.626 | 0.022 | 0.477 | 0.501 |
| | 274.1 | 2.328 | 0.029 | 0.441 | 0.530 |
| | 273.1 | 2.045 | 0.027 | 0.471 | 0.502 |
| | 272.3 | 1.850 | 0.028 | 0.451 | 0.521 |
| | 275.1 | 2.730 | — | 0.499 | 0.501 |
| | 274.1 | 2.409 | — | 0.494 | 0.506 |
| | 273.1 | 2.162 | — | 0.494 | 0.506 |
| | 272.3 | 1.988 | — | 0.501 | 0.499 |

### $O_3$ storage capacity measurements

To better understand the relationship between the feed $O_3 + O_2$ fraction $y_{O_3+O_2,feed}$ and feed $O_3$ concentration $Y_{O_3,feed}$, we measured the time evolution of $Y_{O_3,feed}$ in the $y_{O_3+O_2,feed}$ range 0.1–0.6 as plotted in Fig. 3.

As seen in Fig. 3, $Y_{O_3,feed}$ is increased at the higher $y_{O_3+O_2,feed}$ but at the same time, the $O_3$ decomposition rate is also increased due to the increase in the partial pressure of the $O_3 + O_2$ gas. To maintain the higher $Y_{O_3,feed}$ through hydrate formation, the nominal $y_{O_3+O_2,feed}$ of 0.4–0.6 are suitable to reach a compromise between the effects of the initial $Y_{O_3,feed}$ increase and $O_3$ decomposition rate. A further increase in $Y_{O_3,feed}$ is not expected even if $y_{O_3+O_2,feed}$ is higher than 0.7.

Based on the phase equilibrium data obtained in this study, the thermodynamic conditions to form hydrate samples for the $O_3$ density measurements were specified. We performed $O_3 + O_2 + CO_2$ hydrate-forming experiments under the thermodynamically more stable conditions (*i.e.*, lower temperature/higher pressure than the equilibrium conditions).

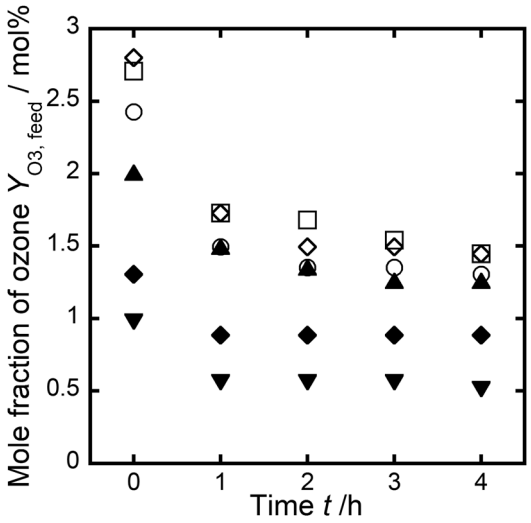


Fig. 3 The time evolution of $Y_{O_3,feed}$ in the range of $y_{O_3+O_2,feed}$ 0.1–0.6. (▼, ◆, ▲, ○, □, ◇) $y_{O_3+O_2,feed} \approx$ 0.1, 0.2, 0.3, 0.4, 0.5, 0.6.

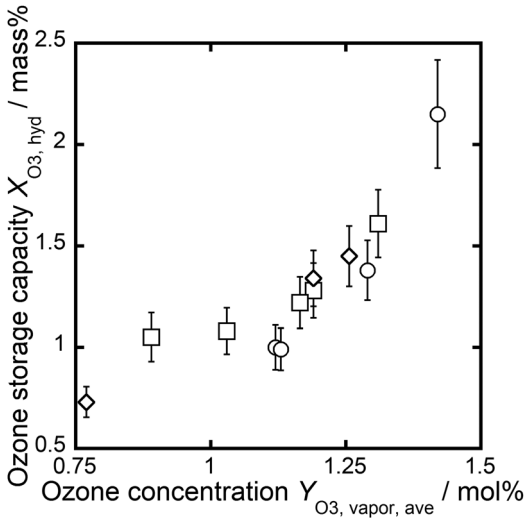


Fig. 5 $X_{O_3,hyd}$ *versus* $Y_{O_3,vapor,ave}$. These data were characterized by $y_{O_3+O_2,vapor}$. (□, ○, ◇) $y_{O_3+O_2,vapor} \approx$ 0.4, 0.5, 0.6. The error bar for each data point represents the uncertainty of the $O_3$ fraction measurement by iodometry.

The hydrates were formed from a mixture of $O_3 + O_2$ and $CO_2$ in an approximately 4 : 6, 5 : 5 and 6 : 4 molar ratio in the feed gas at a system pressure $p$ of 2.5 or 3.0 MPa and a temperature $T$ of 272 K. The hydrates formed in each experiment were then subjected to an iodometric measurement to determine their $O_3$ storage capacity $X_{O_3,hyd}$.

The system pressure dependencies on $X_{O_3,hyd}$ are shown in Fig. 4, which also includes the data measured by Nakajima *et al.*[2] Similar to their data, $X_{O_3,hyd}$ shows no dependence on the system pressure. In comparison with their data at the same $y_{O_3+O_2,feed}$ of 0.4, the data obtained in this study show a higher value of $X_{O_3,hyd}$. This increase in $X_{O_3,hyd}$ is ascribed to the improvements in the measurement of the $O_3$ storage capacity.

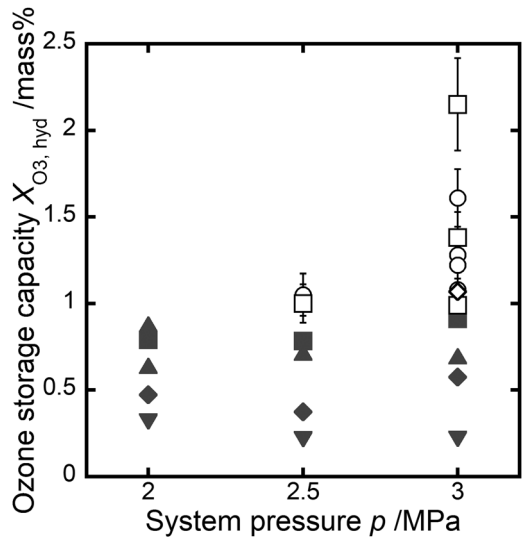


Fig. 4 $X_{O_3,hyd}$ *versus* the system pressure $p$. These data were characterized by $y_{O_3+O_2,feed}$. (▼, ◆, ▲, ■) $y_{O_3+O_2,feed} \approx$ 0.1, 0.2, 0.3, 0.4;[2] (○, □, ◇) $y_{O_3+O_2,feed} \approx$ 0.4, 0.5, 0.6 [this study]. The error bar for each data point represents the uncertainty of the $O_3$ fraction measurement by iodometry.

The highest value of $X_{O_3,hyd}$ in this study was ~2.15 mass%, which was 2.36 times higher than the highest past record of 0.91 mass%.

We then showed the relationship between the $O_3$ concentration in the gas phase $Y_{O_3,vapor}$ and the $O_3$ storage capacity in the hydrates. Since $Y_{O_3,vapor}$ decreases with time, we define $Y_{O_3,vapor,ave}$, the time average of $Y_{O_3,vapor}$, to represent "the mole concentration of ozone in the gas phase in contact with the hydrate". The relationship between $X_{O_3,hyd}$ and $Y_{O_3,vapor,ave}$ is depicted in Fig. 5. This figure shows that $X_{O_3,hyd}$ is well correlated with $Y_{O_3,vapor,ave}$. At $Y_{O_3,vapor,ave}$ = 0.77 mol%, $X_{O_3,hyd}$ is 0.73 mass%. $X_{O_3,hyd}$ increases with increasing $Y_{O_3,vapor,ave}$. The greatest value of $X_{O_3,hyd}$ is 2.15 mass% at $Y_{O_3,vapor,ave}$ = 1.42 mol%.

The highest recorded value of $X_{O_3,hyd}$, as high as 2.15 mass%, was not obtained by the hydrates formed from the mixture of $O_3 + O_2$ and $CO_2$ in an approximately 6 : 4 ratio, but from the 5 : 5 molar ratio in the feed gas. This may be appear strange because there should be a positive correlation tendency between $y_{O_3+O_2,vapor}$ and $X_{O_3,hyd}$ as observed in the previous study.[2] This apparent inconsistency is explained by carefully measuring $Y_{O_3,vapor}$.

That is, the results demonstrate the increase in $X_{O_3,hyd}$ was not controlled by the nominal value of $y_{O_3+O_2,vapor}$, but by the actual concentration of ozone in the gas phase in contact with hydrate represented by $Y_{O_3,vapor,ave}$. In comparison to the highest past $X_{O_3,hyd}$ value of 0.91 mass%, the increase to 2.15 mass% resulted from accurate measurement of $X_{O_3,hyd}$ by improving the method of the $O_3$ storage capacity measurement and increasing the mole fraction of ozone in the gas phase in contact with the hydrate during the hydrate formation by increasing the $y_{O_3+O_2,vapor}$ from 0.4 to 0.5.

Fig. 6 shows a PXRD pattern (measured at 98 K) of an $O_3 + O_2 + CO_2$ hydrate formed from a $O_3 + O_2$ and $CO_2$ mixture in an

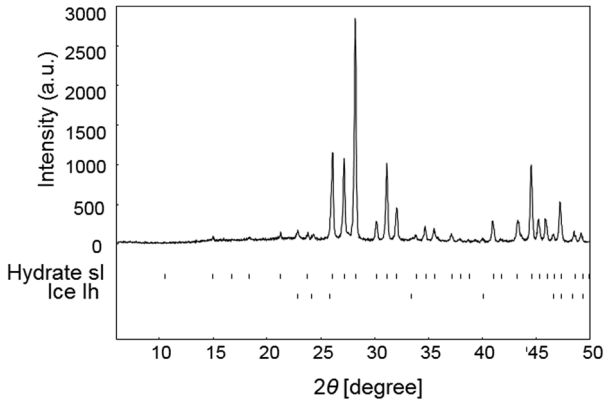


Fig. 6 PXRD pattern of an $O_3 + O_2 + CO_2$ hydrate at 98 K. Upper and lower tick patterns correspond to the structure I hydrate and hexagonal ice, respectively. The hydrate sample (accompanied by ice crystals) used in this PXRD measurement was formed from a mixture of $O_3 + O_2$ and $CO_2$ in a nearly 6 : 4 molar ratio under the conditions of $p$ = 3.0 MPa and $T$ = 272 K.

apparently 6 : 4 molar ratio at a system pressure $p$ of 3.0 MPa and a temperature $T$ of 272 K. This pattern indicates that the hydrate sample used here was a mixture of a hydrate in structure I with a lattice constant of 11.8223(4) Å and hexagonal ice, Ih with a mass fraction of 0.01. The lattice constant of the $O_3 + O_2 + CO_2$ hydrate in this study is in good agreement with that of the $O_3 + O_2 + CO_2$ hydrate with a lower $O_3$ gas capacity in the previous study.[2] The increase in the $O_3$ gas storage capacity does not affect the host structure of the gas hydrate. This result indicates the high stability of $O_3$ within the host water cages even for the higher $O_3$ capacity obtained in this study.

## Conclusions

The three-phase equilibrium $p$–$T$ data for the $O_3 + O_2 + CO_2 + H_2O$ and $O_2 + CO_2 + H_2O$ systems were measured within the temperature range from 272 K to 277 K, corresponding to pressures from 1.6 MPa to 3.1 MPa, for each of the two different $(O_3 + O_2)$-to-$CO_2$ or $O_2$-to-$CO_2$ molar ratios in the feed gas, which are approximately 4 : 6 and 5 : 5.

The $O_3$ storage capacity in the $O_3 + O_2 + CO_2$ hydrates was successfully increased by increasing the $O_3$ concentration in the gas phase and improving the experimental procedure. The highest $O_3$ storage capacity in this study was ~2.15 mass%, which was 2.36 times higher than the highest past record of 0.91 mass%.

New findings in this study are the hydrate forming conditions as well as the relationship between $Y_{O_3,vapor,ave}$ and $X_{O_3,hyd}$ and the highest $X_{O_3,hyd}$. Based on these findings, the required $Y_{O_3,vapor,ave}$ to obtain the desired $X_{O_3,hyd}$ could be predicted.

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