Effects of coexistent gases (HCl, SO$_2$, O$_2$, CO$_2$, and H$_2$O) in simulated coal combustion flue gas on mercury removal by a commercial activated carbon (coconut shell AC) were investigated in a laboratory-scale fixed-bed reactor at 80 °C. To clarify the contribution of the Deacon reaction

$$2\text{HCl} + 1/2\text{O}_2 = \text{Cl}_2 + \text{H}_2\text{O}$$ (1)
on the mercury sorption mechanisms, the experiments were also conducted in the presence of Cl$_2$ (in the absence of HCl). The characteristics (thermal stability) of the mercury species formed on the AC under the various sorption conditions were investigated by the temperature-programmed decomposition desorption (TPDD) technique. It was found that O$_2$ promoted mercury removal in the presence of SO$_2$; however, SO$_2$ suppressed mercury removal irrespective of the presence of O$_2$. The promotion of mercury removal by the presence of O$_2$ may result from the Deacon reaction. However, SO$_2$ seemed to inhibit the Deacon reaction. It is thought that mercury species formed on AC through the Deacon reaction was HgCl$_2$, which decomposed and desorbed at around 300 °C. This was supported by confirmation of the presence of HgCl$_2$ vapor in the reactor effluent gas in TPDD experiments. From the comparison of mercury removal in the gas containing 1 ppmv HCl and gas containing 0.5 ppmv Cl$_2$ system in the presence of SO$_2$, O$_2$, CO$_2$, and H$_2$O, it was suggested that Cl$_2$ enhances mercury removal more efficiently than HCl. Therefore, efficient removal of mercury with AC is possible to achieve via promoting the Deacon reaction. The high-temperature TPDD peaks were observed at around 500 °C in TPDD spectra of the spent sorbents used in mercury removal in the presence of Cl$_2$ (or high concentrations of HCl), SO$_2$, O$_2$, CO$_2$, and H$_2$O. This TPDD peak temperature range is very close to the decomposition temperature of HgSO$_4$. We suggest that the high-temperature mercury desorption peaks are related to the decomposition of mercury species similar to mercury sulfate containing chlorine (Hg$_2$SO$_4$Cl$_x$) on AC.

1. Introduction

At present, coal is one of the major energy resources worldwide. However, coal emits many hazardous pollutants when it is burnt. The emission of elemental mercury from coal combustion has been seen as a serious problem, because of the high toxicity and neurological health impact of mercury. There are three forms of mercury in the flue gas from coal-fired power plants: elemental mercury (Hg$_0$), oxidized mercury (Hg$^2+$), and particulate-bound mercury (Hg$^0$). Hg$^2+$ and Hg$^0$ can be removed by current air pollution control devices. However, Hg$^0$ is emitted in the atmosphere because of its high volatility and insolubility in water.

As a result, various mercury removal techniques from coal combustion flue gas were studied. Among them, mercury capture by activated carbon (AC) is one of the effective techniques. Generally, ACs are modified by S, I, Cl, etc. to improve its mercury sorption efficiency. However, chemical modifications increase the cost of the sorbent. Flue gas composition has significant effects on the sorption of Hg$^0$ on carbon-based sorbents. Miller et al. have conducted the mercury breakthrough test with simulated flue gas on lignite-based activated carbon (LAC) in a laboratory-scale reactor at about 100 °C. When the sorbent was exposed to SO$_2$ (in the baseline gas consisting of a mixture of O$_2$, CO$_2$, N$_2$, and H$_2$O), LAC sorbent capture improved slightly. Upon exposure of the sorbent to HCl, NO, or NO$_2$ added one at a time to the baseline gases, the mercury capture improved from 90–100%.

However, the interaction between SO_2 and NO_2 caused a rapid decrease in the mercury capture capacity of the sorbent. Recently, Presto et al. have reported that mercury capture with AC injection was suppressed in flue gases containing high concentrations of sulfur oxides (SO_x). The final mercury content of the ACs was independent of the SO_2 concentration in a simulated flue gas mixture, but the presence of SO_3 inhibited mercury capture even at the lowest concentration tested (20 ppmv). Bench-scale testing of Hg^0 sorption on selected AC sorbents was conducted by Olson et al. to develop a better understanding of the interaction among the sorbents, flue gas constituents, and Hg^0. They explained the role of acid gases in simulated flue gas on mercury capture with X-ray photoelectron spectroscopy (XPS) of the sorbents; a competition between the bound hydrogen chloride (HCl) and increasing sulfur [S VI] for a basic carbon-binding site affected the mercury removal performance of the sorbents. Huggins et al. studied the mercury-sorbed species on various carbonaceous sorbent materials. Their data from S and Cl X-ray absorption near edge structure (XANES) spectra as well as from the Hg X-ray absorption fine structure (XAFS) data strongly support the hypothesis that the interaction of acidic species (HCl, HNO_3, H_2SO_4, etc.) in the flue gas with the sorbent surface is an important mechanistic process that is responsible for the creation of active sites for mercury capture by chemisorption.

We have been studying mercury sorption mechanisms in coal combustion flue gas with various kinds of sorbents in a laboratory-scale fixed-bed reactor. Previously, we reported that a surface sulfur (S) species on the surface of AC was formed by the reaction of SO_2, H_2S was purposely added in the simulated flue gas through the Claus reaction, and then elemental mercury was removed as HgS on AC. It was also reported that SO_2 enhanced mercury removal on untreated AC in the absence of HCl in the simulated flue gas; however, SO_2 inhibited mercury removal by SO_2-pretreated and H_2SO_4-pretreated AC in the absence of HCl in the simulated flue gas. We suggested that the elemental mercury was removed as HgSO_4 in the presence of SO_2, O_2, CO_2, and H_2O in the simulated flue gas. The effects of HCl and SO_2 in the simulated coal combustion flue gas on mercury sorption mechanisms and thermal stability of the mercury species formed on the AC have also been investigated. We suggested that elemental mercury was removed as a mercury chloride species in the presence of HCl and absence of SO_2; however, mercury species containing both SO_2^- and Cl^- might be formed in the presence of HCl and SO_2 in the simulated flue gas. It was also suggested that chlorine may be formed from HCl and O_2 by the Deacon reaction on the AC surface and enhanced the mercury removal activity of AC through the following reaction:

\[ \text{Hg} + x/2\text{Cl}_2 = \text{HgCl}_x \]  

However, the contribution of the Deacon reaction to mercury sorption mechanisms was not understood clearly. To clarify it, in this study, the experiments were carried out for mercury removal on AC in the presence of HCl and Cl_2 and the effects of other coexisting gases, such as SO_2, O_2, CO_2, and H_2O, on mercury sorption mechanisms with AC were investigated by the temperature-programmed decomposition desorption (TPDD) technique.

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2. Experimental Section

2.1. Mercury Sorbent. AC produced from coconut shell was purchased from Wako Pure Chemical Co. Ltd. The granular AC particles were crushed and sieved into an average diameter of 1 mm. The surface area of the sample was measured by a conventional \( N_2 \) adsorption method (Micromeritics Gemini 2375). The coconut shell AC had a specific surface area of 970 \( \text{m}^2/\text{g} \) and a surface area per unit packed volume of 375 \( \text{m}^2/\text{cm}^3 \).

2.2. Apparatus and Procedure. The mercury vapor (Hg\(^0\)) removal performance of the AC sorbents was carried out in a fixed-bed flow-type reactor. A detailed description of the experimental setup and procedure is given elsewhere.\(^{12} \) Figure 1 shows that the test rig consisted of a mercury permeation device, a simulated coal combustion flue gas feed system, a tubular reactor (size of 6.0 mm) with an electric furnace, and a mercury analysis system. The mercury permeation device, designed to deliver a controlled amount of Hg\(^0\), is an array of liquid mercury containing \( u \)-tubes connected in series immersed in an ice-bath. A controlled amount of nitrogen gas is introduced to the reactor. All lines of feed gases after \( H_2O \) injection were heated to 100 \( \degree \text{C} \) with a tape heater. Prior to the Hg\(^0\) removal test run, about 0.125 or 0.0625 cm\(^3\) (typically 0.125 cm\(^3\)) of the AC sorbent (size of 1 mm) was packed into the quartz tube reactor. The Hg\(^0\) removal efficiency of the sorbents was evaluated at atmospheric pressure at 80 \( \degree \text{C} \) using a simulated gas mixture containing Hg\(^0\) (4.9 ppbv), HCl (0.1, and 100 ppmv), \( SO_2 \) (0 and 500 ppmmv), \( O_2 \) (0 and 5\%), \( CO_2 \) (0 and 10\%), \( H_2O \) (0 and 16\%), and \( N_2 \) (balance gas) at a gas flow rate of 500 cm\(^3\) standard temperature and pressure (STP)/min (SV = 2.4 \times 10^5 or 4.8 \times 10^5 h\(^{-1}\)) in a quartz tube reactor. When the effect of \( Cl_2 \) (0.5 pp mm) in the flue gas was investigated, HCl was not fed to the simulated flue gas. When the experiments were conducted in the absence of \( O_2, CO_2 \) was not fed to the gas stream and high-purity \( N_2 \) (purity of 99.9999\%) was used as a balance gas (basically, purity of 99.99\%) to decrease the contribution of \( O_2 \) (which was present in the experimental system at very low concentrations). It is noteworthy that \( CO_2 \) has no effect on mercury removal; therefore, the results of the effect of \( CO_2 \) will not be mentioned later. The measurement of the inlet and outlet concentrations of mercury was carried out using a cold vapor mercury analyzer (atomic absorption spectrophotometer, Shimadzu). The mercury removal efficiency of the sorbents was quantified by comparing the Hg\(^0\) contents of the gas before and after sorption. When the effect of HCl or Cl\(_2\) in the flue gas was investigated, the reactor effluent was passed through either a trap containing an aqueous solution of SnCl\(_2\) or a trap containing deionized \( H_2O \) only. SnCl\(_2\) can reduce Hg\(^{2+}\) to Hg\(^0\); therefore, when the reactor effluent passes through the aqueous solution of SnCl\(_2\), the total concentration of Hg (Hg\(^{2+}\) and Hg\(^0\)) can be measured. On the other hand, when the gas passes through the \( H_2O \) trap, only the Hg\(^0\) concentration can be measured. We measured the mercury removal efficiency at 0.5, 1, 2, and 3 h on stream by passing the reactor effluent through a trap containing an aqueous solution of SnCl\(_2\) and at 2.5 h on stream by passing through a trap containing deionized \( H_2O \) to check the presence of oxidized mercury in the reactor outlet gas after Hg removal. However, we confirmed that unsorbed oxidized mercury species were not formed downstream of the bed in this system. The error range in the percent of Hg removal measurements was from ca. \(-5\to+5\%\) absolutely.

2.3. TPDD of Mercury-Sorbed AC Sorbents. After Hg\(^0\) removal experiments, the TPDD experiments were carried out in the same fixed-bed flow-type reactor as the Hg\(^0\) removal experiments and the desorbed mercury species were monitored with an atomic absorption spectrophotometer. In the TPDD experiments, about 0.125 or 0.0625 cm\(^3\) of the mercury-sorbed AC sorbent was packed in a quartz tube reactor and \( N_2 \) was flowed in the reactor at a rate of 250 cm\(^3\) STP/min. Then, the sorbent was heated from room temperature to 550 \( \degree \text{C} \) at a heating rate of 10 \( \degree \text{C}/\text{min} \). In the TPDD experiments, the reactor effluent was monitored continuously during TPDD for Hg\(^0\) with the atomic absorption spectrophotometer after passing the reactor effluent through aqueous SnCl\(_2\) and \( H_2O_2 \) solution traps to convert the oxidized mercury (if any formed) to elemental mercury and to remove \( SO_2 \) in the effluent gas, respectively. In the TPDD experiments, the reactor effluent was also passed through an aqueous \( H_2O_2 \) solution trap and aqueous SnCl\(_2\) + \( H_2O_2 \) solution traps to examine the existence of oxidized mercury in the reactor effluent. After TPDD experiments, mercury recovery yields were calculated by the following formula:

\[
\text{mercury recovery yield (\%)} = \frac{\text{[amount of desorbed mercury]}}{\text{[amount of sorbed mercury]}} \times 100
\]

As a result of the above calculation, it was found that the mercury recovery yield was 80–110\% in most cases when the...
reactor effluent was passed through the SnCl₂ + H₂O₂ solution traps. This range might be mainly induced by the error of the percentage of Hg removal measurement. On the other hand, the noteworthy decrease of the yield was observed when the reactor effluent was passed through an aqueous H₂O₂ solution trap in a particular case.

Table 1 summarizes the completed test matrix to give a complete picture of what has been achieved in this study.

3. Results and Discussion

3.1. Mercury Removal in the HCl- and the Cl₂-Containing Gases in the Absence of SO₂. To clarify the effect of HCl and Cl₂, mercury removal experiments were carried out with 1 ppmv HCl (in a mixture of O₂, CO₂, H₂O, and N₂) and 0.5 ppmv Cl₂ (in a mixture of O₂, CO₂, H₂O, and N₂) on AC at a space velocity (SV) of 2.4 × 10⁵ h⁻¹. On the basis of the stoichiometry of the Deacon reaction, 0.5 ppmv Cl₂ was used. Figure 2 compares the mercury removal performance of AC for the gas mixture containing 0.5 ppmv Cl₂ and 1 ppmv HCl. A difference of mercury removal between those two conditions was not observed, because the mercury removal already reached near 100% under these conditions. The AC sorbents after mercury sorption were used in TPDD experiments, and the results are shown in Figure 3. A single mercury desorption peak was observed at around 300 °C in the TPDD spectra in both cases. Mercury recovery yields were 88 and 97% for the sorbent exposed to HCl- and Cl₂-containing gases, respectively. When the reactor effluent was passed through the aqueous SnCl₂ + H₂O₂ solution traps during Hg adsorption experiments and TPDD experiments, there was no difference in the mercury adsorption and desorption amount, indicating that the mercury on the AC was desorbed from the AC surface as elemental mercury vapor. A difference in mercury recovery yields of about 10% is within the range of experimental error. To demonstrate the difference in mercury removal efficiency of the AC for the above two conditions, mercury sorption experiments were conducted using half of the amount of sorbents (SV = 4.8 × 10⁵ h⁻¹). Although the mercury removal decreased in both cases because of the increase of SV, no difference in mercury removal was observed for gas containing 0.5 ppmv Cl₂ and gas containing 1 ppmv HCl, as shown in Figure 4. These results suggest that similar mercury species are formed on AC under these conditions.

Wilcox investigated the kinetic and thermodynamic parameters over a temperature range of 298.15—2000 K at atmospheric pressure on first-stage mercury oxidation reactions typical of coal combustion flue gas. It was suggested that Cl₂ and HOCl are more likely to play a major role in mercury oxidation over HCl at lower temperatures. In the present study, we can suggest that Cl₂ is formed on AC via the Deacon reaction in the presence of HCl and the
elementary mercury is transformed with HCl and/or Cl₂ to HgCl₂.

3.2. Mercury Removal in the HCl- and the Cl₂-Containing Gases in the Presence of SO₂. Figure 5 compares the mercury removal for the 1 ppmv HCl-containing gas and 0.5 ppmv Cl₂-containing gas in the presence of SO₂. The mercury removal was about 70 and 90%, respectively. These results indicate that Cl₂ enhanced mercury removal more effectively than HCl. The mercury removal for 100 ppmv HCl-containing gas was also shown in Figure 5 as a reference. Figure 6 shows the TPDD spectra of the spent sorbents used in mercury removal in the experiments of Figure 5. The peaks in the TPDD spectra of 0.5 ppmv Cl₂-containing gas were observed at higher temperatures than the 1 ppmv HCl-containing gas. These indicate that the mercury species formed on AC in the presence of 1 ppmv HCl are different from the mercury species formed in the presence of 0.5 ppmv Cl₂. The difference in the mercury species formed in the presence of low concentrations of HCl and Cl₂ may be responsible for the difference in mercury removal efficiency. However, the peaks at around 300 °C were observed in both cases, and this peak position was same as that in Figure 3. We think that the common peak (at around 300 °C) indicates the presence of HgCl₂ (most likely Hg₂Cl₂) on AC, which resulted from Cl₂ produced by the Deacon reaction. The low-temperature peaks (at around 200 °C) were observed in the carbon exposed to HCl-containing gas but not in the carbon exposed to Cl₂-containing gas. These peaks resulted from low HCl concentrations. The type of mercury species formed on AC is not understood clearly at this moment. The position (temperature) of the peaks in TPDD spectra shifted from lower temperatures for the 1 ppmv HCl-containing gas to higher temperatures for the 100 ppmv HCl-containing gas, and the peaks of the latter case corresponded to the peaks of 0.5 ppmv Cl₂-containing gas (Figure 6). In our previous study, it was apparent that the increasing HCl concentration (0–200 ppmv) resulted in the shifting of the TPDD peaks to higher temperatures. Therefore, it is certain that the shift of the TPDD peak position in Figure 6 resulted from the increase of the HCl concentration. A high concentration of HCl will result in production of a high concentration of Cl₂ via the Deacon reaction. Therefore, the reactions that occur in the 100 ppmv HCl-containing gas for mercury removal are very similar to the reactions that occur in the Cl₂-containing gas. That is the reason for the shifting of the TPDD peak position in the 100 ppmv HCl-containing gas. For the mercury removal experiments, as shown in Figure 6, the mercury recovery yields were in the range of 90–100%, confirming the reliability of the experimental results. These results again suggest that the Deacon reaction contributes to the mercury removal process. Although the direct confirmation for the occurrence of the Deacon reaction was not carried out in this study, we have checked qualitatively using a mass spectrometer in a separate experiment that Cl₂ was evolved from the HCl-adsorbed AC (HCl adsorption at 80 °C) during a temperature-programmed desorption experiment.

With regard to the decomposition characteristics of mercury compounds, Lopez-Anton et al. have reported that decomposition of HgCl₂ occurs at 70–200 °C (maximum or peak temperature at 120 °C) and decomposition of Hg₂Cl₂ occurs in two stages, i.e., with two maxima at 70 and 220 °C. The above data were taken with standard compounds (HgCl₂ or Hg₂Cl₂) diluted with silica. However, these data cannot be used to infer mercury speciation with AC directly, because there are interactions between the mercury species and AC that may affect the decomposition characteristics of the mercury compounds. Moreover, the presence of SO₂ in the flue gas system also affects the decomposition temperature of the mercury compounds. With regard to the TPDD peak at around 300 °C, we suggest the following: In the absence of SO₂, HgCl₂, (x = 1 and 2) are the Hg compounds formed on AC; moreover, if we consider the presence of Cl₂ in the system, then HgCl₂ is the most plausible species formed on the AC. However, in the presence of a strong reducing gas SO₂, it is possible that some HgCl₂ is reduced to Hg₄Cl₂, and in this case, the decomposition of the mercury species may occur at two steps: one at 200 °C and the other at 300 °C.

3.3. Effects of the Presence of SO₂ and O₂ in the Presence of HCl. To clarify the contribution of the Deacon reaction for the mercury removal process in the HCl-containing gas, the effects of O₂ in the presence and absence of SO₂ were investigated. Figure 7 shows the effects of SO₂ and O₂ on mercury removal in the presence of 1 ppmv HCl. Figure 8 shows the TPDD spectra of the spent sorbents used for mercury removal in the experiments of Figure 7, and the TPDD spectrum of the spent AC sorbent in SO₂−O₂−CO₂−H₂O-containing gas is also shown as a reference data. Several peaks in the TPDD spectra were observed in Figure 8. These spectra indicate that various kinds of mercury species containing Cl, S, and O were formed on spent ACs in each system.
In the absence of SO₂, mercury removal reached near 100%, irrespective of the presence or absence of O₂. The TPDD spectra and the mercury recovery yields were almost the same in these two conditions. To demonstrate the difference in mercury removal between those two conditions, a mercury sorption experiment was conducted using half of the amount of sorbents (SV = 4.8 \times 10^5 \text{h}^{-1}). Although the mercury removal decreased because of the increase of SV, no significant difference in mercury removal was observed in these cases (in Figure 9). Although the experiments were carried out in the absence of O₂, the presence of a trace amount of O₂ in the reaction system could not be ruled out. Therefore, we suggested that, in the absence of O₂, a trace amount of O₂ remaining in the experimental system may contribute to the mercury removal process in the same way as in the presence of O₂. Thus, HgCl₂ was formed on AC through the Deacon reaction in the both cases.

In the presence of SO₂, mercury removal was clearly enhanced because of the presence of O₂. The peak positions in the TPDD spectra and mercury recovery yields of the HCl-containing gas, CO₂-containing gas, and SO₂-containing gases were almost the same, but the peak shape was slightly different from each other. From the above results, it may be inferred that mercury compounds formed on AC in the presence of O₂ were different from those formed in the absence of O₂. The range of the peak temperatures was also consistent with that of the Hg–SO₂–O₂–CO₂–H₂O-containing gas, but the peak shape was different. It indicates that some mercury compounds formed on AC decomposed/desorbed in the similar temperature range. For the Hg–SO₂–O₂–CO₂–H₂O-containing gas, the low mercury removal is one of the reasons for a very small TPDD peak. From the Deacon reaction, the high concentration of O₂ results in the production of a high concentration of Cl₂ in the absence of O₂ (or the presence of a trace amount of O₂). Cl₂ is not produced in a sufficient quantity. As another reason for the promotion of mercury removal by the presence of O₂, we think that the reaction of elemental mercury and O₂ occurred according to reaction 3.11

\[
\text{Hg}^0 + 1/2\text{O}_2 = \text{HgO}
\] (3)

Moreover, because of the presence of SO₂, mercury removal decreased in both the absence and presence of O₂. Particularly, in the absence of O₂, mercury removal decreased drastically. The positions (temperatures) of the main peaks in TPDD spectra shifted to lower temperatures by the presence of SO₂ in both the absence and presence of O₂. The decrease of the thermal stability of mercury species formed on AC resulted from the presence of SO₂, and this is one of the reasons for suppression of mercury removal. We suggest the following mechanisms to clarify the above results.

The oxidized mercury and mercury chloride formed in the process of mercury removal are reduced to elemental mercury by SO₂ according to reactions 4 and 5.

\[
\text{HgO} + \text{SO}_2 = \text{Hg}^0 + \text{SO}_3
\] (4)

\[
\text{HgCl}_x + \text{SO}_2 = \text{Hg}^0 + \text{SO}_2\text{Cl}_x
\] (5)

The reaction of Cl₂ with SO₂ on the AC in the mercury removal process may also inhibit the mercury removal by Cl₂.

\[
\text{Cl}_2 + \text{SO}_2 = \text{SO}_2\text{Cl}_2
\] (6)

In the absence of O₂, the trace amount of O₂ remaining in the experimental system might be consumed by SO₂ and, thus, not be available for the Deacon reaction. This may also retard the mercury removal.10

\[
1/2\text{O}_2 + \text{SO}_2 = \text{SO}_3
\] (7)

In the presence of HCl and SO₂ and absence of O₂, the trace amount of O₂ is consumed by SO₂ according to reaction 7, thus hindering the Deacon reaction. As a result, the peak in the TPDD spectrum at around 300 °C was not observed in this system. In other words, when a sufficient amount of O₂ existed in the system, the Deacon reaction occurred and then HgCl₂ formed on AC in the presence of HCl and SO₂.

3.4. Effect of the Presence of O₂ in the 100 ppmv HCl-Containing Gas and 0.5 ppmv Cl₂-Containing Gas in the Presence of SO₂

In section 3.2, it was suggested that the similarity in the TPDD spectra of the spent sorbents from the 100 ppmv HCl-containing gas and 0.5 ppmv Cl₂-containing gas was due to the contribution of the Deacon reaction to the mercury removal process. Therefore, mercury removal experiments in the presence of 100 ppmv HCl and SO₂ and absence of O₂ and CO₂ were conducted. For comparison, mercury removal experiments in the presence of 0.5 ppmv Cl₂ and SO₂ and absence of O₂ and CO₂ were also conducted. The result of mercury removal is shown in Figure 10 along with the results of O₂–CO₂-containing gas. Figure 11 shows the TPDD spectra of the spent sorbents used for mercury removal in the experiments of Figure 10. The difference in mercury removal between O₂–CO₂ and O₂–CO₂-containing gases in the presence of 100 ppmv HCl was not clearly observed.
However, it is confirmed that the presence of O2 slightly enhanced mercury removal. On the other hand, the TPDD spectra were greatly changed by the presence of O2. These results supported the hypothesis that the Deacon reaction has a contribution to the mercury removal process.

In the Cl2-containing gas, the presence of O2 clearly enhanced mercury removal; moreover, the TPDD spectra were also changed, as observed in the 100 ppmv HCl-containing gas. The enhancement of mercury removal by the presence of O2 may be explained as follows. In the Cl2-containing gas, reactions 5 and 6 are the main suppression reactions for mercury removal. However, in the presence of O2, reaction 7 occurs and suppresses the mercury removal inhibition reactions 5 and 6. Thus, mercury removal was promoted by the presence of O2. The HCl-containing gas, O2 promotes mercury removal through the Deacon reaction, in addition to the above mercury removal promotion mechanisms by O2. It has been reported that SO2 inhibits the mercury adsorption with AC depending upon conditions (i.e., gas compositions). However, in our previous study on the role of SO2 for elemental mercury removal from coal combustion flue gas, we also suggested that, if SO2 reacts with H2O to form H2SO4 produced on AC, then the produced H2SO4 on AC can promote the mercury capture.

From the TPDD spectra as shown in Figure 11, it was supposed that mercury species formed on AC in the 100 ppmv HCl-containing gas were very similar to those formed in the 0.5 ppmv Cl2-containing gas in the presence of O2.

However, the lower temperature peaks in the absence of O2, which were absent in the case of 0.5 ppmv Cl2-containing gas, were observed in the 100 ppmv HCl-containing gas in the absence of O2. Therefore, it was suggested that the mercury sorption mechanisms and mercury species in the 0.5 ppmv Cl2-containing gas were not exactly the same as those in the 100 ppmv HCl-containing gas. It has been reported that the main decomposition temperature of reagent-grade HgSO4 diluted with silica powder in the stream of inert gas (He or Ar) is 500–600 °C. The peaks at around 500 °C in the TPDD spectra in the 100 ppmv HCl-containing gas and 0.5 ppmv Cl2-containing gas in the presence of O2 and H2O are similar to the decomposition temperature of pure HgSO4. In the SO2–O2–H2O-containing gas, production of sulfuric acid on AC is possible and thermally stable mercury compounds similar to mercury sulfates containing chlorine (HgSO4Clx) could be formed. In the absence of O2, a small amount of HgSO4Clx may also form. We suggest that thermally stable compounds with the composition of HgSO4Clx are the most significant species for mercury removal.

### 3.5 Effect of the Presence of SO2, O2, and H2O in the Presence of Cl2
In this section, at first, the effect of the presence of H2O and O2 was investigated in the Cl2–SO2-containing gas to confirm the formation of thermally stable mercury compounds similar to mercury sulfates containing chlorine (HgSO4Clx). The results of mercury removal experiments are shown in Figure 12. Figure 13 shows the TPDD spectra of the spent sorbents used in mercury removal in the experiments of Figure 12. The presence of H2O suppressed mercury removal. The peaks in the TPDD spectra at high temperature were not observed, and main peaks were observed at around 300 °C in the absence of H2O. From these TPDD results, it can be concluded that H2O contributed to the formation of thermally stable mercury compounds on AC. Moreover, the peaks in the TPDD spectra at high temperature were not observed in the absence of O2 and CO2 as they were in the absence of H2O. These results indicate that O2 also contributed to the formation of thermally stable mercury compounds on AC. The results shown in Figure 13 also indicate that the mercury species formed on

AC in the H₂O- and O₂-free gases were almost the same but different in the presence of both O₂ and H₂O. Therefore, mercury removal in the H₂O- and O₂-free gases differed from that in the gas containing both O₂ and H₂O. On the other hand, mercury removal in the O₂-free gas was clearly lower than that in the H₂O-free gas, despite the fact that mercury species formed on AC in O₂- and H₂O-free gases were almost the same. The above-mentioned phenomenon can be explained as follows: H₂O favors the reverse reaction of the Deacon reaction, and H₂O vapor may also occupy the active sites for mercury removal on the AC. Therefore, the mercury removal performance of the sorbent was suppressed in the presence of water.

Next, the effects of the presence of O₂ and H₂O were investigated in the presence of Cl₂ and absence of SO₂. The result of these mercury removal experiments is shown in Figure 14. Figure 15 shows the TPDD spectra of the spent sorbents used in mercury removal in the experiments of Figure 14. In the absence of SO₂, the mercury removal reached nearly 100% in all cases; therefore, the differences in mercury removal could not be evaluated. In the TPDD spectra, very similar peaks were observed; i.e., the effects of the presence of O₂ and H₂O on the formation of mercury species were not observed. However, the effects of the presence of O₂ also could not be examined because a trace amount of O₂ may remain in the O₂-free gas. HgCl₂ was mainly formed on AC though reaction 2, because it was indicated that O₂ and H₂O did not contribute to change mercury speciation in the absence of SO₂ and presence of Cl₂.

3.6. Confirmation for the Presence of HgCl₂ in the Reactor Effluent Gas. To confirm the presence of oxidized mercury in the reactor effluent during the TPDD runs, the TPDD experiments were carried out with and without passing the reactor effluent through the aqueous SnCl₂ solution trap. Figure 16 shows the effect of passing the reactor effluents through the aqueous SnCl₂ solution trap on TPDD spectra for mercury removal in the presence of Cl₂, SO₂, O₂, CO₂, and H₂O. Some differences in the peaks were observed at
around 250–300 °C. When the reactor effluent was passed through the aqueous SnCl₂ solution trap, the mercury recovery yield was 99%. On the other hand, the mercury recovery yield was 62% when it was not passed through the aqueous SnCl₂ solution trap. The difference in the mercury recovery yields during the above-mentioned TPDD experiments was due to desorption of an oxidized mercury species, which was reduced with SnCl₂ to elemental mercury. Among the mercury chlorides, HgCl₂ is highly volatile in the temperature range of the TPDD experiments; therefore, it suggested that some HgCl₂ vapor existed in the reactor effluent of the TPDD experiment. These results imply that HgCl₂ (solid) was formed from Hg⁰ and HCl (or Cl₂) on AC. However, it is worth considering that HgCl₂ (vapor) could be produced from decomposition of the other mercury species. If free HgCl₂ was produced on the AC, then HgCl₂ should be vaporized at much lower temperatures (<100 °C).¹⁴

In addition, the same investigation was conducted in the presence of 100 ppmv HCl, SO₂, O₂, CO₂, and H₂O. The results are shown in Figure 17. Slight differences in the TPDD peaks were observed at around 250–300 °C. However, the clear difference in the mercury recovery yields was not confirmed. However, the same difference in the TPDD spectra because of the change in the measurement method was observed in the range from 200 to 300 °C in both cases (100 ppmv HCl and 0.5 ppmv Cl₂). These results suggest that a small amount of oxidized mercury (HgCl₂) vaporized in this temperature range. However, the evolution of HgCl₂ vapor in the TPDD experiments was not confirmed because of the large range of the measurement error.

4. Conclusions

In this study, the effects of coexisting gases (HCl, SO₂, CO₂, O₂, and H₂O) in simulated coal combustion flue gas on mercury removal by a commercial AC (coconut shell AC) were investigated in a laboratory-scale fixed-bed reactor at 80 °C. To clarify the contribution of the Deacon reaction

$$2\text{HCl} + \frac{1}{2}\text{O}_2 = \text{Cl}_2 + \text{H}_2\text{O}$$

(1)

mercury sorption experiments were also conducted in the Cl₂-containing gas (in the absence of HCl). The characteristics (thermal stability) of the mercury species formed on the AC under the various sorption conditions were investigated by the TPDD technique.

It was confirmed that the Deacon reaction contributed to mercury sorption mechanisms in the HCl-containing gas. In the presence of SO₂, a sufficient amount of O₂ was needed for the Deacon reaction to occur. As a result of the production of Cl₂ from HCl by the Deacon reaction, HgCl₁ (including HgCl₂), which decomposed and desorbed at around 300 °C, might be formed on AC. This was supported by the confirmation of the presence of HgCl₂ vapor in the reactor effluent gas during TPDD experiments. From the comparison of mercury removal in 1 ppmv HCl-containing gas and 0.5 ppmv Cl₂-containing gas in the presence of SO₂, O₂, CO₂, and H₂O, it was indicated that Cl₂ enhanced mercury removal more efficiently than HCl. Thus, the elemental mercury can be removed efficiently on AC by promoting the Deacon reaction to produce Cl₂ from HCl. High-temperature mercury desorption peaks were observed at around 500 °C in TPDD spectra of the spent sorbents used in mercury removal in the presence of Cl₂ (or high concentrations of HCl), SO₂, O₂, CO₂, and H₂O. These high-temperature TPDD peaks indicated that thermally stable mercury species similar to mercury sulfate containing chlorine (HgSₓOᵧCl𝒛) were formed on AC, which are probably the most significant mercury species for mercury removal.

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