Full Length Article

Study on speciation of $HgCl_2$ supported over activated carbon in simulated flue gases by temperature-programmed decomposition desorption mass spectrometry

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ABSTRACT

$HgCl_2$ that was homogenously dispersed over activated carbon was prepared by an HCl solution method ($HgCl_2$(HCl)/AC), in the present study. The speciation of $HgCl_2$(HCl)/AC in simulated flue gases was further investigated by a temperature-programmed decomposition desorption mass spectroscopy method, to clarify its transformation mechanism. It was found that $HgCl_2$ sublimation occurred after Hg-H_2O pretreatment, evidenced by the disappearance of the desorption peak of $HgCl_2$ at 80 °C. After Hg-H_2O pretreatment, new species of $HgCl_2$ were formed, as confirmed by similar peak intensities of $HgCl_2$ at mass numbers 270 and 272 at 335 °C. The SO_2-H_2O or H_2S-H_2O pretreatment helped stabilize the $HgCl_2$ species supported over the AC, as evidenced by the weaker desorption peak of $HgCl_2$ at around 80 °C. For the $HgCl_2$(HCl)/AC pretreated with SO_2-H_2O, four desorption peaks of mercury were found, at 280, 335, 380 and 480 °C, indicating that new mercury compounds were formed during pretreatment or the TPDD process. The mercury desorbed at 280 °C was derived from a mercury complex of $[HgCl]_2SO_4\cdots$A-C, while the mercury desorbed at 480 °C resulted from $HgSO_4$. Some HgO species might be formed and stabilized over the AC during the TPDD process, corresponding to two mercury desorption peaks at 335 and 380 °C. After the pretreatment of $HgCl_2$(HCl)/AC with H_2S-H_2O, some $HgCl_2$ were transformed to HgS and HgO species, as evidenced by the mercury desorption peaks at 280, 305 and 380 °C.

1. Introduction

The escape of mercury into the atmosphere during coal combustion and gasification remains a major environmental issue, because mercury has adverse effects on the environment and on the physiological health of humans, leading mercury to be identified as one of the 189 hazardous air pollutants [1,2]. The mercury emitted from coal-derived flue gases occurs mainly in three states: elemental (Hg^0), oxidized (Hg^{2+}), and particle-associated (Hg^p). Among these, Hg^{2+} and Hg^p can be easily removed with a wet scrubber and an electrostatic precipitator, whereas Hg^0 cannot be captured by the above devices due to its high volatility and low solubility in water [3]. In the near future, coal gasification combined with power generation will be widely used as a highly thermal-efficient and environmentally friendly technology, for clean coal conversion [4,5]. But because fuel gases generated from coal gasification contain a high quantity of elemental mercury [6], it is importance to develop a highly efficient mercury control technology.

Various technologies have already been developed for removing elemental mercury from coal-derived flue gases [7]. Activated carbon

injection (ACI) technology is one of the most widely used techniques for removing mercury from coal combustion flue gases [8–12]. However, the high cost and poor efficiency of AC has severely limited its application, and many researchers have modified AC by chemical impregnation using sulfur (S) or halogen (Cl, I and Br) to improve its mercury removal performance [13–16]. Modification of AC by non-thermal plasma treatment could further increase the content of oxygen-containing functional groups (such as the ester group and the carbonyl group) over AC, which could improve the mercury removal performance of AC [17,18]. In addition, the flue gas components also affect the mercury removal efficiency of AC [19–21]. In our previous research, we found that mercury was mainly removed in the form of mercury chloride species in the presence of HCl and the absence of SO_2 in flue gases, and that SO_4^{2-} and Cl^- -containing mercury species might be formed if the concentrations of HCl and SO_2 were higher than 100 and 500 ppm, respectively [22].

Various mercury compounds, such as HgO, HgS, $HgSO_4$ and $HgCl_2$, are generated over adsorbents during removal of mercury from flue and fuel gases [23–26,22]. Thermal stabilities of the above mercury

compounds have already been clarified by a temperature-programmed desorption technique, and these are in the increasing order of $HgCl_2 < HgS < HgO < HgSO_4$ [23,27,28]. Furthermore, the mercury compounds generated over AC will further change into other mercury species, due to the reaction of reactive substances with mercury compounds [29,30].

In our previous research, we selected HgO as the candidate mercury species produced in the first stage over AC from mercury, and investigated the reactivity of HgO with flue gas components using a temperature-programmed decomposition desorption mass spectroscopy (TPDD-mass) method [30]. We found that the presence of HCl could suppress the sulfation of HgO by SO_2 during pretreatment, and proposed possible reaction routes of HgO over AC in various flue gases. However, extensive measurements of mercury in power plant emissions show that a significant amount of gaseous mercury is oxidized to form $HgCl_2$ that could be easily captured by AC, due to the release of chlorine in coal [22,32,33]. There is a possibility that the captured $HgCl_2$ could further react with flue gas components, resulting in the conversion of $HgCl_2$ into other mercury species, although data were not available to confirm this. Therefore, we investigated the speciation of $HgCl_2$ supported over AC in simulated flue gases via the TPDD-mass method in this study, to clarify the transformation mechanism of $HgCl_2$ over AC, the results of which will be helpful for designing AC and developing a mercury recovery process.

2. Material and methods

2.1. Text sample preparation

Mercuric chloride ($HgCl_2$) and hydrochloric acid (1 mol/L) were purchased from Wako Pure Chemicals (Osaka). Commercial coconut-shell AC with a diameter of < 0.15 mm was used as a solid powder to dilute $HgCl_2$. A solid mixing method and a solution method were employed to dilute $HgCl_2$ powder; the first, as reported in our previous research [30]: the $HgCl_2$ powder was first diluted to 1/30, and then further diluted to 1/3000 with a rotary-drum-type mixture. The obtained sample was identified as $HgCl_2$/AC.

As for the solution method, 1 mL of $HgCl_2$ solution (0.16 g/L) was first mixed with 2 mL of H_2O or 1 mL of HCl (1 mol/L), and 1.0 g or 0.5 g of AC was then added into the mixed solution. Next, the AC-containing solution was evaporated by a rotary evaporator at 40 °C for 15 min to support the $HgCl_2$ over AC with a weight ratio of 1:3000. The prepared sample was identified as $HgCl_2(H_2O)$/AC or $HgCl_2$(HCl)/AC.

2.2. Temperature-programmed decomposition desorption (TPDD) experiments

The TPDD experiments were carried out in a fixed-bed reactor consisting of an Hg^0 vaporizer, an H_2O vaporizer, a gas feed system, a quartz glass U-tube reactor, an electric furnace with a temperature controller, and a quadruple mass spectrometer (Shimadzu QP2010). A detailed description of the experimental setup has been reported in our previous researches [23,30]. 20 mg of prepared sample was packed into a quartz glass U-tube reactor. The packed sample was then pretreated with a gas mixture containing SO_2 (0 or 500 ppm), H_2S (0 or 500 ppm), H_2O (0 or 3%), Hg (0 or 333 ppb) and He (balance gas) with a total flow rate of 60 cm^3 STP/min in a fixed-bed reactor at 80 °C for 90 min. After pretreatment, the TPDD experiments were carried out in the same quartz glass U-tube reactor. The pretreated sample was heated from ambient temperature to 700 °C (partially to 600 °C) at a heating rate of 10 °C/min. The reactor effluents were monitored continuously with a quadruple mass spectrometer. The mass numbers (m/z) of 202 and 200 for Hg^0, 272 and 270 for $HgCl_2$, 235 and 230 for Hg_2Cl_2, 36 for HCl, 70 and 72 for Cl_2, 64 and 48 for SO_2, 80 for SO_3, 98 for H_2SO_4, and 34 for O_2, were monitored throughout the TPDD experiment. The peaks in the TPDD spectra were separated using peak separation software (Peak Fit
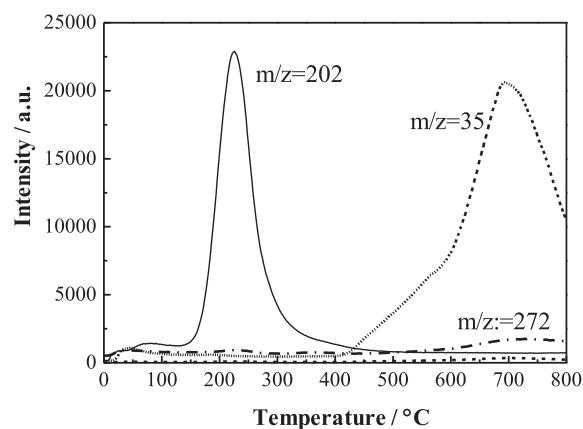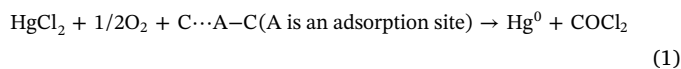

Fig. 1. TPDD-mass spectra of $HgCl_2$ over AC prepared by solid mixing method.

v4).

3. Results and discussion

3.1. Effect of preparation method on the stability of $HgCl_2$ over activated carbon

Since we had employed a solid mixing method to dilute mercury compounds (such as HgO and $HgSO_4$) in our previous researches [23,30], we first considered a solid mixing method to dilute $HgCl_2$ in the present study. As shown in Fig. 1, mercury was desorbed at the temperature range of 180–400 °C with a peak at 225 °C. HCl showed a higher desorption temperature range (400–700 °C) and the desorption peak appeared at around 700 °C. However, the peak of $HgCl_2$ that should be desorbed at 80–400 °C was not observed in the TPDD spectra, and a weak desorption peak of $HgCl_2$ appeared at around 700 °C, indicating that the $HgCl_2$ was converted to other mercury species through interactions with the AC surface during either preparation or TPDD treatment [23,31]. Although the reaction routes of mercury formation from $HgCl_2$ over AC could not be confirmed in this study, the following reactions, which are thermodynamically favorable, might have occurred [23]:

$$HgCl_2 + 1/2O_2 + C\cdots A{-}C(A\ is\ an\ adsorption\ site) \rightarrow Hg^0 + COCl_2$$

$$(1)$$

$$COCl_2 + H_2O \rightarrow CO_2 + 2HCl \tag{2}$$

The source of oxygen in Eq. 1 might be the oxygen adsorbed over AC and/or it might have appeared as an impurity in the system. The desorption of $HgCl_2$ at around 700 °C might be caused by the release of $HgCl_2$ adsorbed at the outlet of the U-tube reactor during sublimation. Additionally, the TPDD spectra of $HgCl_2$/AC also showed poor reproducibility (data not shown), because of the aggregation and heterogeneous distribution of $HgCl_2$ particles over the AC surface, caused by the hygroscopicity of $HgCl_2$. Consequently, this solid mixing method was not appropriate for diluting $HgCl_2$ in the present study.

To overcome the drawbacks of the solid mixing method, a solution method was employed to dilute $HgCl_2$, based on the solubility of $HgCl_2$. The TPDD spectra of $HgCl_2(H_2O)$/AC are shown in Fig. 2. Similar to the solid mixing method, no desorption peak of $HgCl_2$ was observed, revealing that $HgCl_2$ was also converted to other mercury species. A broad peak that corresponded to mercury appeared at the temperature range of 160–550 °C, indicating that the desorbed mercury was derived from various mercury compounds. As shown in Fig. 2b, three mercury desorption peaks presented at 250, 320 and 350 °C. The mercury desorption peak at 250 °C (peak a-), which was at a position similar to that of $HgCl_2$/AC, was probably derived from $HgCl_2$ through Eq. 1. The desorption peaks of mercury at 320 and 350 °C were in the