Determination of Chemical States of Mercury on Activated Carbon Using XANES

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Abstract. Although the adsorption of mercury vapor onto activated carbon is a widely used technology to prevent environmental release, the adsorption mechanism is not clearly understood. In this study, we determined the chemical states of mercury on two kinds of activated carbon using X-ray absorption near-edge spectroscopy (XANES) to elucidate the adsorption mechanism. The adsorption experiments of elemental mercury onto activated carbon were conducted under air and nitrogen atmospheres at temperatures of 20 and 160°C. Two types of activated carbon were prepared. X-ray absorption fine structure (XAFS) measurements were carried out on beamline BL01B1 at SPring-8. Hg-LIII edge XANES spectra suggested that chemical adsorption of elemental mercury on the activated carbon occurred in the 20–160°C temperature range. According to the XANES spectra, a difference occurred in the chemical states of mercury between AC#1 and AC#2. The Hg XANES spectra on AC#1 were similar to those of Hg₂Cl₂ and HgS, and the Hg XANES spectra on AC#2 were similar to that of HgO, which suggested that nitric acid treatment removed sulfur from AC#1 and functional groups that were strong oxidizers on the surface of AC#2 created HgO. According to the EXAFS oscillation, a difference occurred in the chemical states of mercury on AC#1 between 20 and 160°C. We found that impurities and oxidant functional groups on activated carbon play key roles in mercury adsorption.

Keywords: Mercury, XANES, Activated carbon.

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INTRODUCTION

Mercury is emitted into the atmosphere from both anthropogenic and natural sources, and because of its high volatility, subsequently enters oceans, lakes, and rivers directly from the atmosphere or from deposits in surrounding basins even when no specific source of mercury exists [1]. Some of the inorganic mercury in water is converted into organic mercury, which is extremely toxic and can undergo biological accumulation. Therefore, the emission of mercury is of great concern.

The U.S. Environmental Protection Agency (EPA) estimated that 87% of the mercury entering the atmosphere in 1994 and 1995 was from combustion sources, including medical waste incinerators, municipal solid waste incinerators (MSWIs), and coal-fired utilities [2]. Therefore, mercury emission due to combustion sources must be controlled. Two methods currently exist to reduce mercury emissions from combustion sources: reduce the mercury content in the combusted materials (coal, MSW, etc.) or use advanced flue gas treatment technologies to capture the mercury. The removal of mercury from flue gas is difficult because the removal efficiency by condensation or simple physical adsorption is insufficient due to the very high volatility of mercury. In recent years, researchers have studied the use of activated carbon [3-5] and confirmed its effectiveness in removing mercury in flue gas. However, the relationship between the nature of activated carbon such as impurities or functional groups and mercury adsorption has not been investigated in detail. Furthermore, limited information is available on the chemical speciation of mercury on activated carbon [6]. To develop new and effective absorbent materials for mercury removal, we need to understand the characteristics of mercury adsorption on activated carbon in detail. Consequently, we determined the chemical states of mercury adsorbed on two types of activated carbon using XAFS to elucidate the adsorption mechanism.
MATERIALS AND METHODS

Samples

A type of activated carbon made from coconut shells was used as the basis (Shirasagi Gx Takeda Pharmaceutical Co. Ltd), and was machine-milled. Following this pretreatment, the activated carbon was designated “AC#1.” Next, a portion of the AC#1 was modified by using HNO₃. Thirty grams of AC#1 was mixed and heated in 800 mL of 70% HNO₃ at 70°C for 24 h [7]. After washing with ultrapure water until the pH was neutral, the activated carbon was dried at 105°C for 24 h and then stored in a desiccator. The activated carbon treated by the above process was designated “AC#2.”

The adsorption experiments of elemental mercury onto activated carbon were conducted under air and nitrogen atmospheres at temperatures of 20 and 160°C. The experimental apparatus simulates a bag filter, which is a filtration type dust collector. The detail procedure is described elsewhere [5]. The mercury concentration ranged from 1.2 to 1.4 mg/m³, which is higher than the concentration typically observed in MSWI flue gas. The adsorption experiments were run for enough time (8.5–14 h) to detect mercury in the activated carbon. Finally, the activated carbon samples were made as shown in Table 1.

The following compounds were selected as reference materials for XAFS analysis on the basis of the likely chemical forms of mercury on activated carbon: Hg, HgO, Hg₃Cl₂, HgCl₂, and HgS (special reagent grade from Nacalai Tesque Co. Ltd.) [6].

<p>| TABLE 1. Activate Carbon Samples. |
|-------------------------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Activated carbon</th>
<th>Temperature (°C)</th>
<th>Atmosphere</th>
<th>Content (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC#1</td>
<td>20</td>
<td>Air</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>N₂</td>
<td>340</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>Air</td>
<td>380</td>
</tr>
<tr>
<td>AC#2</td>
<td>20</td>
<td>Air</td>
<td>330</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>N₂</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>Air</td>
<td>80</td>
</tr>
</tbody>
</table>

XANES Measurement

Hg-LIII edge XANES experiments were carried out on beamline BL01B1 at SPring-8 (Hyogo, Japan), which operates at a ring energy of 8 GeV and a stored current from 60 to 100 mA. The main optics consisted of the standard SPring-8 bending magnet system. The Hg-LIII edge XANES spectra were measured with a Si (111) two-crystal monochromator. Higher harmonics were reduced by reflection on the two mirrors. XANES spectra of reference materials and activated carbon samples were recorded in transmission mode using ionization chambers and in fluorescent mode using a 19-element Ge solid-state detector, respectively. Data analysis of XANES spectra was conducted using the commercial REX2000 ver. 2.3.3 software (Rigaku Co. Ltd.).

RESULTS and DISCUSSIONS

Hg-LIII edge XANES spectra for the activated carbon samples and reference materials are shown in Fig. 1; the results suggest that the chemical adsorption of elemental mercury on the activated carbon occurred in the temperature range of 20 to 160°C. According to the XANES spectra, a difference occurred in the chemical states of mercury between AC#1 (f–h) and AC#2 (i–k).

The Hg XANES spectra on AC#1 were similar to that of Hg₂Cl₂ and HgS, although only trace amounts of sulfur and chlorine were present in the activated carbon. Because Hg₂Cl₂ and HgS are relatively stable...
in this temperature range, their presence on the AC#1 was reasonable. In previous experiments employing a high concentration of mercury vapor, we confirmed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) that elemental mercury was fixed as Hg\(_2\)Cl\(_2\) or HgS on the adsorbents using mixtures with activated carbon and inorganic chloride or sulfide, respectively [5,8]. The Hg XANES spectra on AC#2 were similar to those of HgCl\(_2\) or HgO, considering a small peak at 12282–12283 eV. However, HgCl\(_2\) has a very high vapor pressure at this temperature range, and therefore cannot be present on activated carbon, particularly at 160°C. Because nitric acid treatment removed sulfur and chlorine from AC#1 and created functional groups that were strong oxidizers on the surface of activated carbon, HgO was thought to be a dominant species. It had already been confirmed that AC#2 had oxidant functional groups such as lactone and quinone [7].

EXAFS spectra for activated carbon samples and reference materials are shown in Fig. 2. The mercury concentrations in the activated carbon samples were so low that the oscillation of EXAFS was only observed by 8.2 (Å\(^{-1}\)). Therefore, Fourier transformation of the EXAFS spectra was not conducted. According to the EXAFS oscillation, a difference occurred in the chemical states of mercury on AC#1 (f,g) between 20 and 160°C. The mercury on AC#1 at 20°C was thought to be Hg\(_2\)Cl\(_2\), whereas the mercury on AC#1 at 20°C was thought to be HgS. HgS is more stable than Hg\(_2\)Cl\(_2\), so this result was in good agreement with their thermal properties. In AC#2, the effect of temperature on the chemical species was not clear because the mercury adsorbed at 160°C was so small that we were not able to obtain EXAFS spectra with a good SN ratio. AC#2 samples had only about one-fifth of the surface area and one-sixth of the pore volume owing to extensive oxidation compared with AC#1. In both AC#1 and AC#2, the Hg XAFS spectra under the different atmospheres were almost identical. Therefore, the effect of the atmosphere on the adsorption experiments was not remarkable at 20°C.

**CONCLUSIONS**

The adsorption of mercury onto activated carbon is due to a chemical reaction which is influenced by impurities such as sulfur and chlorine as well as functional groups on the surface of the activated carbon. In the future, we need to carefully investigate the relationship between the nature of the carbon and mercury adsorption using XAFS.

**ACKNOWLEDGMENTS**

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