Mercury removal from coal combustion flue gas by modified fly ash

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Abstract

Fly ash is a potential alternative to activated carbon for mercury adsorption. The effects of physicochemical properties on the mercury adsorption performance of three fly ash samples were investigated. X-ray fluorescence spectroscopy, X-ray photoelectron spectroscopy, and other methods were used to characterize the samples. Results indicate that mercury adsorption on fly ash is primarily physisorption and chemisorption. High specific surface areas and small pore diameters are beneficial to efficient mercury removal. Incompletely burned carbon is also an important factor for the improvement of mercury removal efficiency, in particular. The C–M bond, which is formed by the reaction of C and Ti, Si and other elements, may improve mercury oxidation. The samples modified with CuBr2, CuCl2 and FeCl3 showed excellent performance for Hg removal, because the chlorine in metal chlorides acts as an oxidant that promotes the conversion of elemental mercury (Hg0) into its oxidized form (Hg2+). Cu2+ and Fe3+ can also promote Hg0 oxidation as catalysts. HCl and O2 promote the adsorption of Hg by modified fly ash, whereas SO2 inhibits the Hg adsorption because of competitive adsorption for active sites. Fly ash samples modified with CuBr2, CuCl2 and FeCl3 are therefore promising materials for controlling mercury emissions.

Key words: fly ash; mercury; modified; adsorption; flue gas

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Introduction

Mercury pollution has received considerable attention from environmental researchers due to its high volatility, long persistence, and strong bioaccumulative properties. Given that coal-fired boilers account for a significant fraction of the anthropogenic emissions of mercury into the atmosphere (Pirrone et al., 2010), researchers have actively explored the speciation and control of mercury in coal combustion flue gas. Various technologies for controlling mercury emissions from coal combustion flue gas have been investigated. Such technologies include sorbent injection and catalytic oxidation combined with wet flue gas desulfurization. However, no single technology is applied broadly. Mercury in coal combustion-derived flue gas is present in three forms: elemental mercury (Hg0), oxidized mercury (Hg2+), and particulate-bound mercury (HgP). Hg2+ is water soluble and therefore can be effectively captured by wet flue gas desulfurization systems as a co-benefit. The majority of HgP can be collected by electrostatic precipitators or fabric filters. Hg0 is the most difficult to remove because of its high volatility and low solubility in water. As a representative adsorbent for Hg0, activated carbon is frequently applied using an injection chamber, but does not yield promising results due to its high price (Pavlish et al., 2003). Fly ash has attracted more and more attention because of its low price (Presto and Granite, 2006).

As indicated in numerous studies, the mercury adsorption properties of fly ash are closely related to the physical properties and chemical composition. The unburned carbon in fly ash plays an important role in adsorption (Wang and Wu, 2006), and the adsorption capacity differences between unburned carbon separated from fly ash and commercial activated carbon are negligible at low mercury concentrations (Wang and Chen, 2004). However, the structure of carbon differs, thus adsorption properties function in different ways (Wang and Chen, 2005). Because the composition and nature of fly ash is highly complex, its adsorption properties toward mercury are the result of the interaction of multiple factors. Nevertheless, the respective
effects of these factors cannot be distinguished given the numerous species of elements. Adsorption mechanisms remain incompletely understood, giving rise to the need for further studies (Li et al., 2007; Maroto-Valer et al., 2005; López-Antón et al., 2009). Ferric oxides, manganese oxides, copper oxides, and other inorganic compounds enhance Hg$^0$ adsorption by activated carbon because of their significant catalytic effect on Hg$^0$ oxidation (Bhardwaj et al., 2009; Hua et al., 2010; Shen et al., 2010; Lee et al., 2009).

Fly ash is a potential substitute for activated carbon. Inorganic compounds enhance Hg$^0$ oxidation, thereby improving mercury adsorption. To the best of our knowledge, this study is one of the few that focus on Hg adsorption by modified fly ash. We investigated mercury adsorption by fly ash collected from different plants, and by samples modified with metallic salts. Results show that the fly ash samples modified with CuBr$_2$, CuCl$_2$ and FeCl$_3$ exhibit excellent Hg$^0$ removal efficiency. On the basis of the characterization results, an adsorption mechanism is proposed.

1 Experimental

1.1 Sample preparation

The fly ash samples were collected from the electrostatic precipitators of different coal-fired plants in Hebei, Hunan, and Inner Mongolia in China, which were labeled as FA-K, FA-X and FA-Y, respectively. Modified fly ash samples were prepared by an impregnation method using the FA-K fly ash and aqueous metallic salt solutions. After impregnation at 25°C for 12 hr, the samples were dried at 110°C for 12 hr. The modified fly ash samples were marked correspondingly as metallic salt-FA, such as CuCl$_2$-FA, FeCl$_3$-FA and so on. The metallic salt loading was measured as the weight of metallic salt with respect to the support FA-K, and which was set to 14 wt.% for all the samples.

1.2 Adsorption test

The adsorption reaction was carried out in a fixed-bed quartz flow reactor at atmospheric pressure (Fig. 1). The reactor was a quartz tube (6 mm i.d.) with a thermocouple placed at the external wall of the reactor to control the temperature of the furnace. Fixed amounts of adsorbent mixed with quartz sand were used in all the experiments. The reactor was heated by a temperature-controlled furnace. Feed gases consisting of 6 vol.% O$_2$, 500 ppm SO$_2$, and 20 ppm HCl (when used) in N$_2$ were adjusted by mass flow controllers and introduced into the reactor at a total flow rate of 1 L/min. A constant quantity of 12.58 μg/m$^3$ of Hg$^0$ vapor was supplied into the gas steam, with an Hg$^0$ permeation tube immersed in a water bath maintained at 40°C. Analysis of Hg$^0$ concentrations was monitored in real time with a Lumex RA-915M Zeeman mercury analyzer (Lumex-Marketing JSC, Russia). The Hg$^0$ removal efficiency ($\eta$, %) was quantified by the following equation:

$$\eta = (1 - \frac{C}{C_0}) \times 100\%$$  \hspace{1cm} (1)

where, $C$ and $C_0$ represent Hg$^0$ concentrations at the outlet and inlet of the reactor, respectively.

1.3 Sample characterization

X-ray fluorescence spectroscopy (XRF) was used to conduct composition analysis. XRF measurement was carried out on a LABCENTER XRF-1800 scanning sequence X-ray fluorescence spectrometer (Shimadzu, Japan).

The nitrogen adsorption-desorption isotherms were obtained at −196°C over the whole range of relative pressures, using a Quantachrome NOVA4000 automatic instrument (Quanta Chrome Instrument Co., USA). Specific areas and pore sizes were calculated from these isotherms by the BET and BJH methods, respectively.

X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALab220i-XL spectrometer (Vacuum Generators, UK) using Al Kα radiation ($h\nu = 1486.6$ eV). Binding energy was corrected using adventitious carbon (284.8 eV).

2 Results and discussion

2.1 Adsorption of Hg$^0$ by fly ash samples

The Hg$^0$ removal efficiencies of the three fly ash samples were monitored as a function of time on stream at 60°C. As shown in Fig. 2, the FA-Y sample initially exhibited 12% Hg$^0$ removal efficiency. The efficiency declined to 0% after 50 min. FA-K and FA-X initially showed better activity, with 75% and 68%, respectively. Their removal efficiencies decreased to 30% and 12%, respectively, after 180 min.

The Hg$^0$ removal efficiency of FA-K under different adsorption temperatures was also studied, and the results...
are shown in Fig. 3. Temperature significantly affected the adsorption process. Hg\textsuperscript{0} removal efficiency increased as temperature increased, indicating that mercury adsorption by fly ash can be attributed not only to physisorption but also to chemisorption. Because if physisorption occurs alone, removal efficiency decreases with increasing temperature.

2.2 Characterization of the fly ash samples

A composition analysis was conducted to clarify the nature of the different performance variables of the samples. The chemical compositions of the samples are summarized in Table 1, which indicates that the fly ash mainly contains incompletely burned carbon, SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and other metallic oxides. The fly ash samples collected from different coal-fired plants also show various concentrations of the aforementioned components. The incompletely burned carbon is a core factor in mercury adsorption by fly ash and primarily captures Hg\textsuperscript{0} via physical adsorption (Zhao et al., 2010). Given the high carbon content, FA-K showed the best Hg\textsuperscript{0} removal efficiency, whereas FA-Y, which had the lowest carbon content, almost failed to remove Hg\textsuperscript{0}.

The specific surface areas and average pore diameters of the three samples are summarized in Table 2. According to Table 2, FA-K has a large specific surface area and minimal average pore diameter. Hg\textsuperscript{0} removal efficiency increased because of this large surface area. In addition, the atomic radius of mercury is 0.152 nm, which is far lower than the samples' average pore diameter. An appropriate aperture is generally favorable for adsorption (Gregg et al., 1989). An excessively large diameter decreases the effective specific surface area and increases the likelihood of desorption reactions. Therefore, FA-K exhibited good performance in mercury adsorption.

The samples were analyzed by XPS to identify the surface characteristics of the active species. The representative photoelectron peaks of C\textsubscript{1}s in relation to the three samples are depicted in Fig. 4. An essential difference in carbon properties is reflected in the behavior of the C\textsubscript{1}s lines. That is, the C\textsubscript{1}s curves of FA-K and FA-X show shoulders at high binding energies of ca. 280.9 and 281.9 eV, respectively. The FA-K and FA-X curves are assigned to the C–M bond, which is formed via the reaction of C and Si, Ti and other elements (Uhlmann et al., 1994; Seal et al., 1998; Selamat et al., 2003). The C–M bond facilitates the catalytic oxidation of Hg\textsuperscript{0} because it can grab electrons, thereby causing an oxidation reaction (Aegerter et al., 1996; Ramanathan and Oyama, 1995). On the basis of the aforementioned results, we conclude that mercury adsorption by fly ash occurs primarily through physisorption, chemisorption and the interaction between the two.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Chemical compositions of the fly ash samples</th>
</tr>
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<tbody>
<tr>
<td>Samples</td>
<td>C</td>
</tr>
<tr>
<td>FA-K (%)</td>
<td>6.85</td>
</tr>
<tr>
<td>FA-X (%)</td>
<td>4.90</td>
</tr>
<tr>
<td>FA-Y (%)</td>
<td>0.62</td>
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</tbody>
</table>

2.3 Mercury adsorption of the fly ash modified with metal chlorides

To improve Hg removal efficiency, the fly ash was modified with a series of metal chlorides and their adsorption performance is depicted in Fig. 5. The modified fly ash samples
showed better Hg removal efficiency than the unmodified samples because the chlorine in metal chlorides acts as an oxidant to promote Hg\textsuperscript{0} oxidation. Granite et al. (2000) proposed that mercury oxidation can occur via a Mars-Maessen mechanism by which adsorbed Hg\textsuperscript{0} reacts with a lattice oxidant such as O\textsuperscript{2-} or Cl\textsuperscript{-}. This idea suggests that mercury oxidation can occur via a Mars-Maessen mechanism by which adsorbed or weakly bound Hg\textsuperscript{0} reacts with Cl in chlorides. The reaction mechanism is described as follows:

\[
\text{Cl}^- + \text{Hg}^0(g) \rightarrow \text{HgCl} \tag{2}
\]

\[
\text{HgCl} + \text{Cl}^- \rightarrow \text{HgCl}_2 \tag{3}
\]

In addition, the metallic element of chlorides also influences the oxidation and adsorption of mercury. The activities of different chlorides follow the order: CuCl\textsubscript{2} > FeCl\textsubscript{3} > MnCl\textsubscript{2} > CeCl\textsubscript{3} > CoCl\textsubscript{2}. CuCl\textsubscript{2} and FeCl\textsubscript{3} show better Hg removal efficiency. Cu\textsuperscript{2+} and Fe\textsuperscript{3+} can convert Hg\textsuperscript{0} into Hg\textsuperscript{2+}, thereby facilitating the removal of Hg from the flue gas (which has strong oxidative properties). The reaction mechanism may be described as follows:

\[
\text{CuCl}_2 + \text{Hg} \rightarrow \text{HgCl}_2 + \text{Cu} \tag{4}
\]

\[
2\text{FeCl}_3 + \text{Hg} \rightarrow \text{HgCl}_2 + 2\text{FeCl}_2 \tag{5}
\]

2.4 Mercury adsorption of the fly ash modified with copper salt

The fly ash modified with CuCl\textsubscript{2} exhibited the best efficiency for mercury removal (Fig. 5). Thus the fly ash samples were modified with copper salt to investigate the effect of negative ions on mercury adsorption performance. As shown in Fig. 6, negative ions also influence the oxidation and adsorption of mercury. The fly ash modified with CuBr\textsubscript{2} showed better Hg removal efficiency than that modified with CuCl\textsubscript{2}. The activity of different types of copper salt follows the order: CuBr\textsubscript{2} > CuCl\textsubscript{2} > Cu(NO\textsubscript{3})\textsubscript{2} > CuSO\textsubscript{4}, which is in accordance with the literature (Wu et al., 2012; Sasmaz et al., 2012). Given that the weight ratios of different types of copper salt are the same, the difference in activity is caused primarily by the varying negative ions with different oxidation abilities.

2.5 Effect of reactant gas compositions on the activity of FeCl\textsubscript{3}-FA

The fly ash modified with FeCl\textsubscript{3} also exhibited good efficiency for mercury removal (Fig. 5). Fe is abundant in fly ash and FeCl\textsubscript{3} is cheaper than CuCl\textsubscript{2}. In addition, the Hg\textsuperscript{0} removal efficiency of FeCl\textsubscript{3}-FA under N\textsubscript{2} conditions enables the appropriate distinction of the effects of reactant gas on activity. Thus we chose FeCl\textsubscript{3}-FA to examine the effect of reactant gas compositions on activity. The activity of FeCl\textsubscript{3}-FA for Hg\textsuperscript{0} removal under SO\textsubscript{2} and HCl conditions was examined (Fig. 7).

O\textsubscript{2} promotes Hg oxidation and adsorption. In the initial adsorption, Hg removal efficiency reached 100%. After 180 min, Hg removal efficiency remained at 80%, which is higher than that observed under N\textsubscript{2} conditions. The promotional effect of O\textsubscript{2} is consistent with the literature.
Fig. 7 Hg removal efficiency of modified FeCl₃-FA under different reactant gas compositions. Reaction conditions: Temp. 100°C; 50 mg sorbents/1 g quartz sand; flow rate 1 L/min; O₂ = 6%; HCl 20 ppm; SO₂ 500 ppm; N₂ as balance; Hg concentration 12.58 μg/m³.

Table 3  Surface weight percentages of different C compositions on the FeCl₃ samples before and after reaction in N₂-O₂-SO₂ (as indicated by C1s XPS spectra)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C–C(H)</th>
<th>C–O</th>
<th>C=O</th>
<th>COO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before reaction</td>
<td>48.05%</td>
<td>36.29%</td>
<td>6.99%</td>
<td>8.97%</td>
</tr>
<tr>
<td>After reaction</td>
<td>78.16%</td>
<td>14.30%</td>
<td>3.38%</td>
<td>4.08%</td>
</tr>
</tbody>
</table>

In addition, SO₂ is present in coal combustion flue gas; thus, the effect of SO₂ under O₂ conditions was also investigated. Unlike O₂, SO₂ negatively affected Hg removal (Fig. 7) possibly because SO₂ competes with Hg⁰ and O₂ for adsorption active sites. To further explain the negative effect of SO₂ on Hg removal efficiency, we conducted an XPS analysis of FeCl₃-FA samples before and after reaction in N₂-O₂-SO₂. As shown in Fig. 7, the peaks at about 284.8, 286.30, 287.56, and 288.87 eV correspond to C–C(H), C–O, C=O, and COO, whose relative contents are shown in Table 3. C–O, C=O, and COO have oxidative properties, and their contents visibly decreased after reaction. Meanwhile, the content of C–C(H) increased. The peaks at about 198.5 eV correspond to the Cl bond to Fe³⁺ with a net charge of −1, while 200.0 eV corresponds to organic Cl. No significant difference was found between the Cl₂p XPS curve of the sample before and after exposure to SO₂. The peak at 169.5 eV is consistent with the (VI) oxidation state and is assigned to the sulfate species. The reactant gas compositions with SO₂, C–O, C=O, and COO convert Hg⁰ into Hg²⁺ through oxidation, and convert into C–C(H) themselves. On the other hand SO₂ is converted into SO₃ by these oxidations. Therefore, SO₂ competes with Hg⁰ on active sites, thereby negatively affecting Hg oxidation and adsorption.

3 Conclusions

Fly ash shows unique adsorption activity for mercury removal. Incompletely burned carbon is an important factor for improving mercury removal efficiency. In particular, the C–M bond, which is formed via the reaction of C and Ti, Si and other elements, may improve the oxidation of mercury. High specific surface areas and small pore diameters are beneficial for mercury removal efficiency.

Fig. 8  C1s, Cl₂p, S2p XPS spectra of FeCl₃-FA before and after reaction in SO₂-O₂.
showed excellent Hg removal efficiency. Mercury oxidation occurs via a Mars–Maessen mechanism, in which adsorbed Hg⁰ reacts with a lattice oxidant, such as O⁺ or Cl⁺, on modified fly ash. The presence of O₂ and HCl play a positive role in Hg oxidation and adsorption, whereas SO₂ inhibits Hg removal because of competitive adsorption. Modified fly ash shows promising potential for controlling mercury emissions because of its low cost and high efficiency.

Acknowledgments

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References


