



Mechanisms and roles of fly ash compositions on the adsorption and oxidation of mercury in flue gas from coal combustion



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HIGHLIGHTS

- The heterogeneous oxidation process is confirmed to be Eley–Rideal mechanism.
- The unburned carbon (UBC) is important for mercury oxidation and adsorption.
- Mercury can be adsorbed by Al₂O₃, Fe₂O₃ and TiO₂, not CaO and MgO.
- No metallic oxides catalyzed the mercury oxidation in simulated flue gas.

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ABSTRACT

Coal combustion is a predominant anthropogenic source of atmospheric mercury emissions. The oxidation and adsorption on the surface of fly ashes are crucial to mercury control. In this study, we discussed the mercury adsorption/oxidation mechanisms on the surface of fly ashes and different roles of organic and inorganic compositions based on the experimental results of a fixed-bed reactor and temperature programmed decomposition technique (TPDT). The results indicated that the fly ashes played significant roles in mercury oxidation and adsorption. The residual Cl element on the surface of fly ashes after pretreatment at 650 °C contributed to the oxidation and adsorption of mercury. The heterogeneous oxidation process in this study has been confirmed to follow an Eley–Rideal mechanism. Unburned carbon (UBC) is important for mercury oxidation and adsorption on fly ashes. O₂ promoted mercury adsorption, but not oxidation. The adsorption capacity was greatly increased in a simulated flue gas, and the oxidation rate was 60%. Al₂O₃, Fe₂O₃ and TiO₂ were capable of adsorbing mercury. Among these compounds, Al₂O₃ displayed the largest adsorption capacity. Mercury adsorption did not occur on the surface of CaO and MgO. The flue gas compositions exhibited no influences on the adsorption capacity for the above five metallic oxides. No metallic oxides catalyzed the mercury oxidation regardless of the flue gas composition.

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1. Introduction

Mercury is of great concern as a global pollutant. Extensive efforts have been made to control mercury emissions worldwide. The Minamata Convention on Mercury signed in October 2013 is the latest milestone in this progress. According to the global atmospheric mercury emission inventories, coal combustion is one of the largest anthropogenic sources of atmospheric mercury emissions [1–4]. The convention requires the reduction of future

mercury emissions resulting from coal combustion. The co-removal of mercury in air pollution control devices (APCDs) is significantly important for the control of mercury emissions from coal-fired power plants. However, the removal efficiencies of different APCDs depend on the mercury speciation in the flue gas. The mercury species in coal combustion flue gas include gaseous elemental mercury (Hg⁰), gaseous oxidized mercury (Hg²⁺) and particle-bound mercury (Hg^p). Different mercury species can be removed in APCDs with different efficiencies [5,6]. Hg^p can be efficiently captured by dust collectors, whereas Hg²⁺ is mainly removed in wet flue gas desulfurization (WFGD) because of its high water-solubility. Hg⁰ remains in the flue gas and is difficult to remove. Therefore, a comprehensive understanding of the mercury

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oxidation and adsorption mechanisms in coal combustion flue gas must be obtained.

Mercury releases from coal in its elemental form under a combustion temperature of over 1000 °C in the boiler. With the cooling of the flue gas, mercury reacts homogeneously and heterogeneously with the compositions of the flue gas and transforms into oxidized forms. Simultaneously, a certain proportion of Hg^{2+} is adsorbed onto the surface of fly ash, forming Hg^p . Although the compositions of coal combustion flue gases are complicated, HCl has been considered to be the main oxidant [7–11]. Recently, several studies have indicated that the heterogeneous oxidation occurring on the surface of the fly ashes is an important mechanism [12–16]. The heterogeneous reaction mechanisms include the Langmuir–Hinshelwood mechanism, Eley–Rideal mechanism and Mars–Maessen mechanism [15]. However, the exact mechanism remains unclear. Identification of the mercury chemical species on the fly ashes will significantly promote the understanding of the oxidation mechanism. The temperature programmed decomposition technique (TPDT) has been tested currently to identify the mercury chemical species in coal-fired fly ashes and gypsum produced in power plants [17,18]. Therefore this technique may help identify the product of mercury oxidation. Additionally, unburned carbon (UBC) and iron in fly ashes have been confirmed to be important for mercury oxidation and adsorption [19–21]. However, a systematical study on the roles of the fly ash compositions is still needed.

In this study, the fixed-bed reactor and temperature programmed decomposition technique (TPDT) were combined to identify heterogeneous mercury oxidation mechanisms on fly ashes. Pure materials were also selected to explore their roles in the mercury oxidation process by substituting the compositions of the fly ashes. Based on the experiment results, we discussed the mercury oxidation mechanisms and the roles of the organic and inorganic components of the fly ashes.

2. Experimental section

2.1. Sample pretreatment and preparation

The fly ashes used in this study were collected from an electrostatic precipitator (ESP) in a 600 MW pulverized-coal power plant. The air pollution control devices in this power plant included an ESP and WFGD. The anthracite coal burned in this plant was transported from Guizhou Province. The mercury, chlorine and sulfur contents in this coal were 0.17 ppm, 117 ppm and 1.13%, respectively. The fly ashes used in this study were pretreated before the experiments. The pretreatment was performed by heating the fly ashes to 650 °C in a muffle furnace and maintaining this temperature for 4 h. Almost all of the mercury in the fly ashes should be removed at this temperature regardless of the form of the mercury chemical [17,22,23]. However, other elements might remain on the surface of the fly ashes, such as Cl.

Reference samples with a mercury concentration of 1 ppm used in TPDT for the reference profile were prepared through successive dry dilution. In total, 0.1 g of a pure Hg compound (HgCl_2 , HgS , HgSO_4 , HgO , HgBr_2 , and Hg_2SO_4) was mixed with 10 g of pretreated fly ashes to obtain a sample with a mercury concentration of 10,000 ppm. The mixture was then diluted to 1 ppm through similar procedures with the pretreated fly ashes.

2.2. Experimental apparatus and analysis equipment

The fixed-bed apparatus was described in previous studies [24]. This apparatus consists of a quartz fixed-bed reactor, a thermocouple and a heating furnace outside the reactor to control the

reaction temperature. Mass flowmeters are used to control the flow rate of different standard gases to provide a mixed simulated flue gas. N_2 is used as the balance gas. The total flow amount of the simulated flue gas in this study is maintained at 1 L/min in all of the experiments to obtain a constant residence time, which is important for catalysis reactions. The space velocity of the experiment is $1.2 \times 10^6 \text{ h}^{-1}$, which is comparable with the typical catalysis experiments [25,26]. A mercury permeation tube is immersed in a water bath maintained at a steady temperature to supply the simulated flue gas with a constant mercury concentration. The mercury concentration is maintained at approximately $20 \mu\text{g}/\text{m}^3$. To determine the mercury species at the outlet of the fixed-bed reactor, a Mercury Freedom™ system (Thermo Fisher Scientific Inc.) is employed to monitor the concentrations of different gaseous mercury forms, including gaseous elemental mercury (Hg^0), gaseous oxidized mercury (Hg^{2+}) and gaseous total mercury (Hg^t). This system is designed based on the United States Environmental Protection Agency (US EPA) Method 30A and displays a detection limit of $0.01 \mu\text{g}/\text{m}^3$.

The TPDT system is identical to that presented in previous work [18]. This system includes a temperature-programming furnace and a high-temperature furnace. The first furnace is heated from room temperature (approximately 20 °C) to 650 °C at a constant rate of 10 °C/min. The temperature of the second furnace is maintained at 800 °C to transform all of the mercury compounds into vaporized elemental mercury. The mercury concentration is detected with a real-time Lumex Zeeman mercury analyzer (Lumex RA915+, Russia). In the TPDT experiments, a 0.5 g sample is heated under a N_2 carrier gas flow rate of 400 ml/min. The mercury compounds with different decomposition temperatures vaporize at specific temperatures in the first furnace, transform to elemental mercury in the second furnace and are detected by the analyzer at the end of the process. The mercury concentration detected exhibits distinct or partially overlapped peaks that can be used to identify the mercury compounds according to the reference profiles.

The chlorine content of fly ashes pretreated in the muffle furnace is determined referenced to ASTM D7359-08 method and the standard testing method of chlorine content in coal in China (GB/T 3558-2014) [27,28]. The fly ash is heated from room temperature (about 25 °C) to 1100 °C in the mixture atmosphere of oxygen and moisture. The chlorine in the mixture gas is absorbed by the high purity water. Then ion chromatography (IC, ICS-2000, DIONEX, Inc., USA) is used to determine the concentration of chlorine content in the solution. Therefore the chlorine content in fly ashes can be calculated based on the concentration of chlorine content in the solution, the volume of the solution and the amount of fly ashes.

A series of instruments are also used in this study to conduct a composition analysis of the fly ashes. To obtain the content of unburned carbon (UBC) in the fly ashes, a thermogravimetric analyzer (TGA/DSC 1, METTLER-TOLEDO, Inc., Switzerland) is employed in this study. The valence of the main elements on the surface of the fly ashes is determined by X-ray photoelectron spectroscopy (PHI Quantera SXMTM, ULVAC-PHI Inc., Japan). The contents of the inorganic compositions are analyzed with X-ray fluorescence spectroscopy (XRF-1800, Shimadzu Corporation, Japan).

2.3. Experimental design

To investigate the mercury oxidation mechanisms on the surface of the fly ashes and the roles of different fly ash compositions, this study is conducted in two portions. The mercury oxidation mechanisms are first explored. The mercury breakthrough curve

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