



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

Table 1
Compositions of the flue gas atmosphere.

	Original concentration	Flow (ml/min)	Actual concentration
NO	1%	30	300 ppm
HCl	1000 ppm	40	40 ppm
SO ₂	2%	50	1000 ppm
O ₂	99.99%	60	6%
CO ₂	99.99%	120	12%
N ₂	99.99%	700	Balance

of the pretreated fly ashes in N₂ atmosphere is determined in a fixed-bed reactor, and the formed mercury compounds on the fly ashes are subsequently identified using TPDT. To further confirm the mercury oxidation mechanisms, mercury and HCl are alternately introduced into the fixed reactor in the following sequence: HCl (4 h) + N₂ (2 h) + Hg (4 h) + N₂ (2 h) + HCl (4 h). Monitoring the mercury concentration and speciation at the outlet of the reactor can elucidate the mercury oxidation pathways. Mercury oxidation by fly ashes is then confirmed in the simulated flue gas atmosphere. Table 1 gives the compositions of the flue gas atmosphere.

The roles of different fly ash compositions are then studied. The composition analyses are first conducted to obtain the contents of the organic and inorganic compositions. Substitutes are then selected to simulate the UBC and five metallic oxides in the fly ashes according to the composition analyses. The mercury oxidation and adsorption are evaluated in three different atmospheres: N₂, N₂ + O₂ and the simulated flue gas for each composition substitute.

3. Results and discussion

3.1. Breakthrough curves of mercury

The Hg⁰ and Hg^t concentrations at the outlet of the fixed-bed reactor are presented in Fig. 1 when nitrogen and the simulated flue gas atmosphere were used. To clearly present the mercury concentrations, a normalized mercury concentration (the proportion of the real concentration to 20 μg/m³) is used in this study. The normalized Hg^t concentration gradually rose from 0.4 to 1 during a period of more than 4 h. As discussed in a previous study, fly ashes can be regarded as a type of sorbent, and the adsorption can be described by a Langmuir adsorption isotherm formula. The statistical data for the field measurements confirmed this point [5]. Theoretically, when the Langmuir adsorption occurs on the surface of sorbents in a fixed-bed reactor, the mercury concentration at the outlet of the reactor follows a logarithmic curve with time. In this study, the adsorption curve of total mercury in Fig. 1(a) was similar to a typical logarithmic curve. In another study, Xu et al. obtained removal efficiency curves that varied with time for three different fly ashes using a fixed-bed reactor. In this study, the removal efficiency was defined as one minus the normalized mercury concentration. The shape of the adsorption curves for the two types of fly ashes after converting the removal efficiency curves were similar to that in Fig. 1 of this study [24]. However, the adsorption capacity was apparently different. The differences of the UBC content and the surface area were considered to be the main reasons for this difference. Generally speaking, the mercury adsorption capacity is also affected by the compositions of carrier gas besides the characteristics of adsorbents itself. The adsorption capacity may change significantly when other gas is added.

As exhibited in Fig. 1(a), the mercury oxidation rate declines rapidly from more than 40% to almost zero in a period of approximately 1 h when N₂ is used. Generally speaking, N₂ is an inactive gas. Thereby, the mercury oxidation in a N₂ atmosphere should be attributed to the fly ashes. This will be further discussed in the next

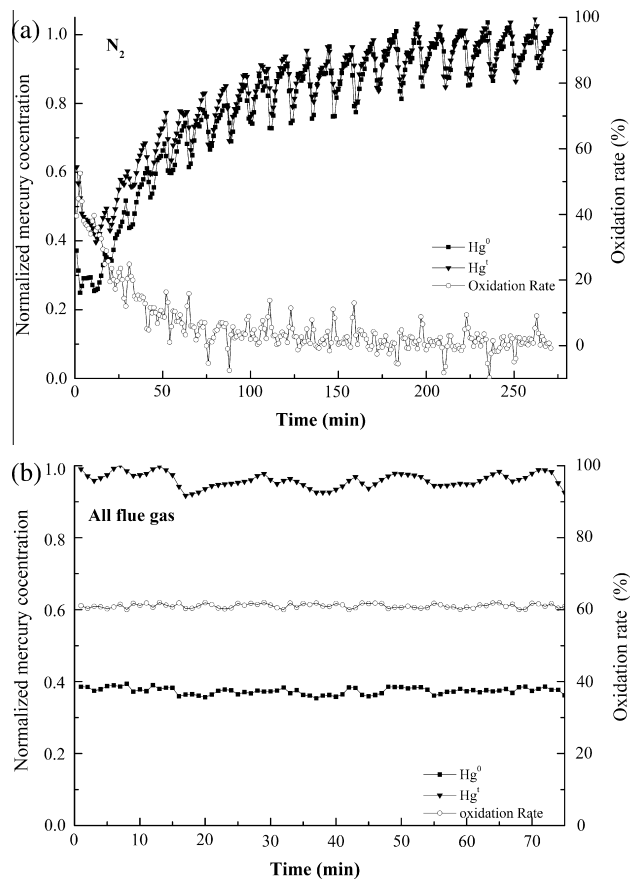


Fig. 1. Mercury oxidation and retention by the fly ashes: (a) N₂ atmosphere; (b) simulated flue gas.

section. It can also be seen that the mercury adsorption occurred simultaneously with the mercury oxidation in the N₂ atmosphere. Since both of the mercury oxidation and adsorption occur on the active sites of the fly ashes, there may be two kinds of active sites on the surface of the fly ashes. Some active sites can be took off after reacting with the mercury and other active sites cannot under the experiment conditions in this study. The mercury oxidation in the simulated flue gas is shown in Fig. 1(b). The fly ash reached its adsorption capacity before initiating the study of mercury oxidation. The oxidation rate was stable at 60% throughout the experimental period. Previous studies have demonstrated that the mercury in coal flue gas is oxidized homogeneously and heterogeneously. The homogeneous mechanism displays a lower oxidation rate when considering the 40 ppm HCl concentration in this study [29–31]. The mercury oxidation rate only reached 13% when similar simulated flue gas were used in a study, especially considering that NO (the confirmed main oxidant in flue gas) in this study was much lower [31]. Recent studies have confirmed that mercury oxidation predominantly occurs through a heterogeneous reaction on the surface of fly ashes [15,32]. To understand the adsorption and heterogeneous oxidation mechanisms on the fly ashes, the role of different fly ash compositions should be investigated.

3.2. Mercury oxidation and adsorption mechanism

To investigate the mercury species on the fly ashes after adsorption in a N₂ atmosphere and to further understand the mechanisms of mercury oxidation, TPDT was employed in this study. Different pure model mercury compounds, which were the most likely to appear on the fly ashes in the coal combustion process, were mixed

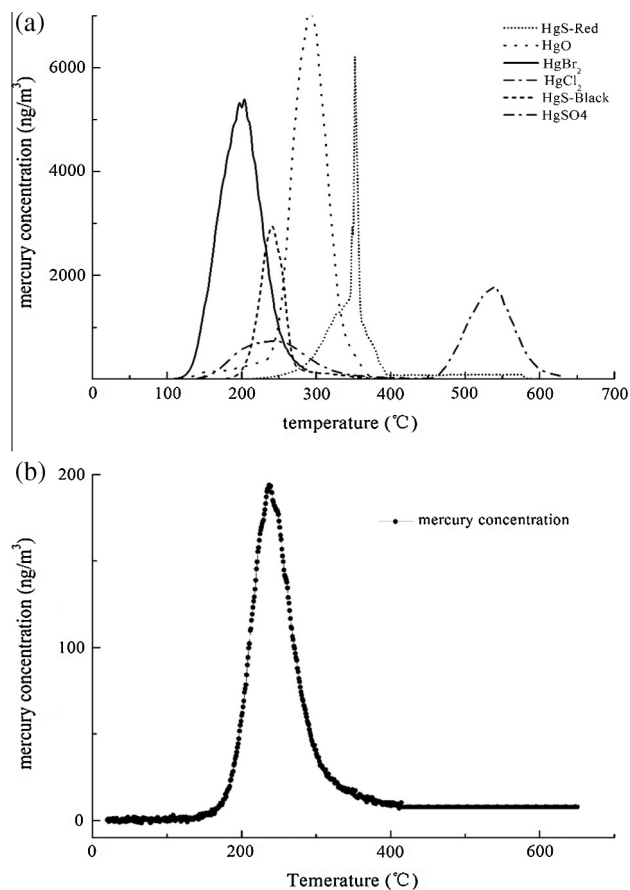


Fig. 2. Mercury species identification after adsorption in a N_2 atmosphere: (a) thermo decomposition profile of model mercury compounds in a matrix fly ash; (b) thermo decomposition profile of fly ashes after adsorption in a N_2 atmosphere.

with pretreated mercury-removed fly ashes. The mixtures were then heated to obtain the standard thermo decomposition curves. The thermo decomposition profiles of the model mercury compounds are shown in Fig. 2(a). The temperature appearance of the model mercury compounds is arranged in an increasing order of $HgBr_2 < HgCl_2 < HgS$ (Black) $< HgO < HgS$ (Red) $< HgSO_4$. The peak temperatures for the thermo decomposition for the different mercury compounds in this study are compared with those in other studies in Table 2. The majority of peak temperatures are close between the different studies. The noted differences are considered to be mainly caused by the variations between the experimental conditions in these studies, such as the basic materials. The mercury species on the fly ashes after mercury adsorption in a N_2 atmosphere was determined and presented in Fig. 2(b). The peak temperature was 237 °C, which is closest to the standard profile of $HgCl_2$. Therefore, the pretreatment process of fly ashes, as mentioned before, could not remove the Cl element from the surface of the fly ashes; however, other mercury compounds were vaporized and decomposed. The residual Cl element contributed to the mercury oxidation in a N_2 atmosphere. The oxidation process finished after approximately 1 h because no Cl was supplied. The Cl residue might also contribute to the mercury adsorption on fly ashes, as discussed in previous studies; these previous studies were mainly conducted on activated carbon [33,34]. In order to confirm this point, the chlorine content of the fly ashes pretreated in muffle furnace was determined to be $2.03 \pm 0.77 \mu\text{g/g}$. It can be seen that there was still chlorine remaining on the fly ashes though the fly ashes was pretreated under the temperature of 650 °C for

Table 2

Comparison of the peak temperatures of the thermo decomposition for different mercury compounds.

Mercury compound	Peak temperature in this study (°C)	Peak temperature in other studies (°C)
$HgBr_2$	220	110 [47]
Hg_2Cl_2	–	170 [17]
$HgCl_2$	240	85 [17]
HgS (Black)	259	265 [17]
HgO	312	430 [17], 340 [48]
HgS (Red)	350	290 [17], 310–330 [47]
$HgSO_4$	540	570 [17], 450–500 [49]

Note: “–” indicates not available.

4 h. This was consistent with the experiment results of TPDT experiments.

The TPDT results also indicated that elemental mercury was not physically adsorbed on the surface of the fly ashes at 140 °C and that the chemisorption occurred only at the Cl-sites. Therefore, the heterogeneous reaction between mercury and HCl may follow the Eley–Rideal (E–R) mechanism. To further confirm this mechanism, a series of experiments was designed and conducted. First, HCl was introduced into the fixed-bed for 4 h. In this step, HCl was adsorbed onto the surface of the fly ashes. The mercury species were then determined at the outlet of the fixed-bed when the N_2 carrying mercury passed through the bed, as exhibited in Fig. 3(a). Finally HCl was introduced into the system for the second time. The mercury concentration displayed a high peak and then declined to zero, as presented in Fig. 3(b). The mercury was almost entirely present in oxidized forms, indicating that mercury oxida-

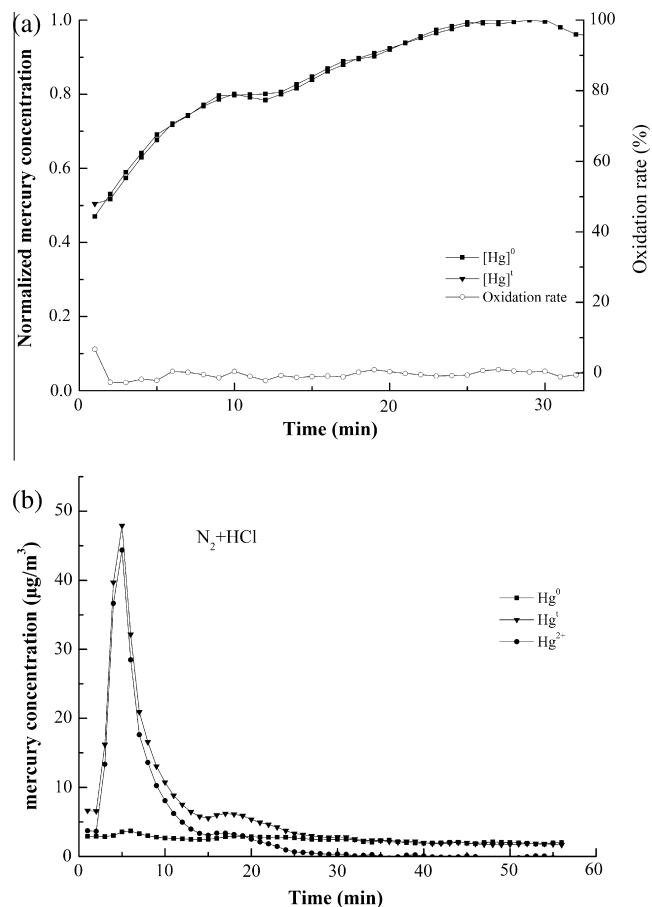
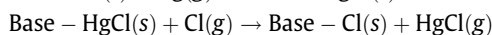
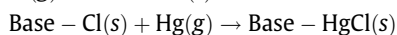


Fig. 3. E–R mercury oxidation mechanism (a) Hg and (b) HCl.

tion occurred. According to the E–R mechanism, the above results can be interpreted by the flowing equations:



3.3. Composition analyses of the fly ashes

The fly ashes consist of UBC and inorganic components; the inorganic components are mainly metallic oxides. The contents of the UBC and inorganic components are exhibited in Table 3. The UBC was determined by heating the fly ashes to a consistent weight at more than 850 °C. The fly ashes in this study have a high UBC content (5.82%) compared to other studies [20,24,35]. The inorganic components of the fly ash appeared in the decreasing proportion order of $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{CaO} > \text{TiO}_2 > \text{K}_2\text{O} > \text{MgO} > \text{MnO} > \text{SO}_3$. The inorganic components of this fly ash are consistent with previous studies [24]. SiO_2 accounts for more than half of the fly ash. Fe_2O_3 was demonstrated to be a catalyst for mercury oxidation [12,21], and the proportion of Fe_2O_3 is 9.21%. CaO is often regarded as a potential sorbent for mercury adsorption [36,37], and the proportion of CaO is 4.13%. Al_2O_3 accounts for a high proportion of 21.77%. Although TiO_2 and MnO display relatively low proportions (3.15% and 0.88%, respectively), previous studies focused on their mercury catalysis efficiencies [38,39]. In this study, the adsorption and catalytic oxidation of the UBC and five potential metallic oxides are investigated by using their pure substance as substitutes to understand the mechanisms of mercury adsorption and oxidation.

3.4. The role of UBC in fly ashes

Activated carbon injection (ACI) has been shown to be an efficient technology for mercury removal from coal combustion flue gases [40–42]. In this study, activated carbon was used as a substitute for UBC in the fly ashes. The adsorption and oxidation experiments were conducted in three stages according to the atmosphere differences presented in Fig. 4. Elemental mercury in a N_2 atmosphere was introduced into the fixed-bed in the first stage. The mercury concentration curve in the first stage is similar to the curve in Fig. 1(a). The normalized mercury concentration rose to nearly 1 in approximately 20 min, indicating that the activated carbon reached its adsorption capacity. The activated carbon in this study displayed a relatively low adsorption capacity when considering the identical experimental conditions conducted for the fly ashes. The oxidation rate also declined from approximately 20% to zero in 10 min. This can also be explained by the residual elements on the surface of the activated carbon, similar to the fly ashes experiment. The mercury adsorption and oxidation curves on the fly ashes and activated carbon are consistent in our study.

Table 3
Composition analyses of the fly ashes.

	Valence	Percentage
UBC	–	5.82
SiO_2	+4	52.31
Al_2O_3	+3	21.77
Fe_2O_3	+3	9.21
CaO	+2	4.13
TiO_2	+4	3.15
K_2O	+1	1.30
MgO	+2	0.88
SO_3	+6	0.40
MnO	+2	0.08

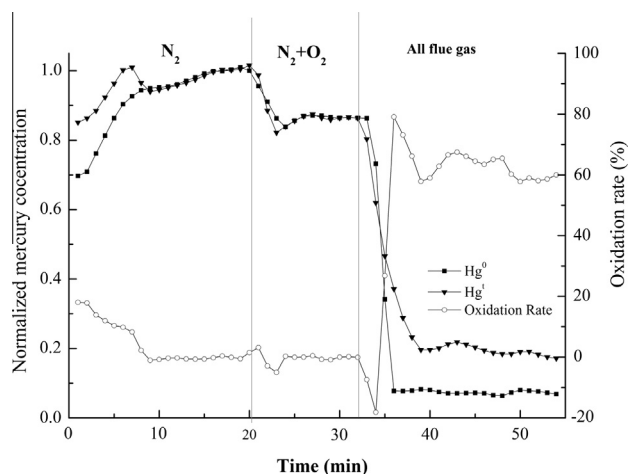


Fig. 4. Mercury oxidation and adsorption by the activated carbon.

The UBC may play a significant role in the mercury adsorption and oxidation on fly ashes. This result is confirmed by a previous study [20].

In the second stage, the normalized total mercury concentration rapidly dropped from 1 to approximately 0.85 after O_2 was added into the experimental gas. O_2 promoted the mercury adsorption on the activated carbon. The chemisorption of mercury on the adsorption sites formed by O_2 was considered to be the main reason for the higher adsorption. However, the oxidation rate remained zero during the entire stage, indicating that under these experimental conditions, minimal mercury oxidation, including heterogeneous oxidation, was noted. In the third stage, the mercury adsorption and oxidation in the simulated flue gas, which simulated the realistic flue gas in coal-fired power plants, were tested. The normalized Hg^{T} concentration declined from approximately 0.85 to 0.2. The mercury adsorption on the activated carbon increased after the addition of an acid flue gas, such as HCl , NO , SO_2 and CO_2 . HCl and SO_2 were illustrated to promote the adsorption on activated carbon, whereas the role of NO was shown to be complex. NO inhibited Hg^{T} adsorption in the presence of 50 ppm of HCl [43]. In the third stage, the oxidation rate increased to 60%, showing that the activated carbon significantly promoted the mercury oxidation. Generally, the oxidation is directly related to mercury chemisorption. Thus the efficient catalytic oxidation also contributed to mercury adsorption. Overall, the surface of the UBC in the fly ashes, substituted by activated carbon in this study, may be an important location for mercury heterogeneous reactions and mercury adsorption. Considering the possible memory effects and overlapping of mercury adsorption and oxidation in different atmospheres, these experiments were also conducted individually in this study. The results are presented in Supporting Information, and found to be similar with the experiment results when conducting consecutively.

3.5. The role of inorganic compositions in fly ashes

According to the composition analysis of the fly ashes, the mercury oxidation and adsorption of five metallic oxides representing the main fly ash components, Al_2O_3 , Fe_2O_3 , TiO_2 , CaO and MgO , were studied in three different atmospheres. The results are shown in Fig. 5. The three different atmospheres were N_2 , $\text{N}_2 + \text{O}_2$ and the simulated flue gas. Among the five metallic oxides, only three oxides, Al_2O_3 , Fe_2O_3 and TiO_2 , displayed the ability to absorb mercury, whereas the other two metallic oxides, CaO and MgO , displayed little adsorption capacity. Al_2O_3 displayed the highest adsorption

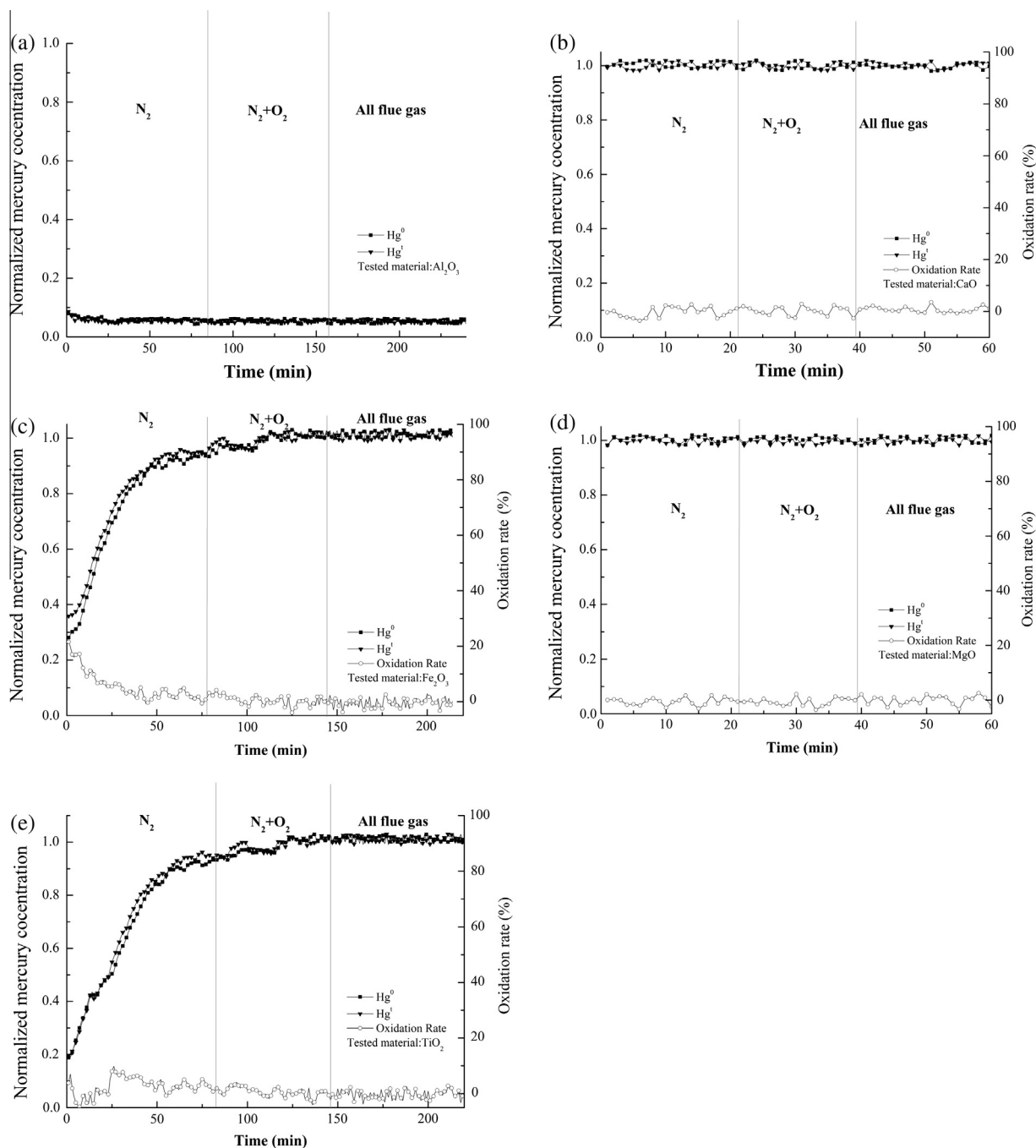


Fig. 5. Mercury oxidation and adsorption of the simulated fly ash compositions: (a) Al_2O_3 ; (b) CaO ; (c) Fe_2O_3 ; (d) MgO ; and (e) TiO_2 .

capacity. For more than 4 h, the mercury breakthrough concentration remained approximately zero. The flue gas changes had little effects on the adsorption process. Fe_2O_3 and TiO_2 presented similar breakthrough curves to the fly ashes. The normalized mercury concentration increased from 0.2 to 0.3 to more than 0.9 in the N_2 atmosphere for approximately 1 h. The adsorption capacity displayed minimal increases in the $\text{N}_2 + \text{O}_2$ and simulated flue gas. Iron-base sorbents have been developed to remove elemental mercury from coal combustion flue gas [44–46]. But according to this study, Al-based sorbents may be more efficient than that of iron-based sorbents. More studies should be conducted to investigate the mercury adsorption of Al-based sorbent. The normalized mercury concentration in the flue gas through CaO and MgO was approximately 1 in all three atmospheres, indicating that no

adsorption process occurred. Changes in the flue gas also did not influence the adsorption process. The oxidation rates for all of the five metallic oxides remained approximately zero in the three atmospheres, indicating that no oxidation process occurred on the surface of the five metallic oxides. Therefore, select metallic oxides, including Al_2O_3 , Fe_2O_3 and TiO_2 , played important roles in the mercury adsorption onto the fly ashes; however, no metallic oxides were found to be able to catalyze mercury oxidation.

4. Conclusions

In this study, we discussed the mercury adsorption/oxidation mechanisms on the surface of fly ashes and the different roles of organic and inorganic components. A fixed-bed reactor and TPDD

were employed in this study. The results are summarized as follows. (1) The fly ashes in this study presented an adsorption ability in a N₂ atmosphere and an oxidation rate of 60% in the simulated flue gas. (2) The mercury oxidation that lasted for a short time in the N₂ atmosphere was attributed to the fly ashes. Further, the TPDD results indicated that the residual Cl element on the surface of the fly ashes contributed to the oxidation and adsorption of mercury. (3) The heterogeneous oxidation process in this study was confirmed to be an Eley–Rideal mechanism. HCl is first adsorbed onto the surface of the fly ashes, and mercury in the gaseous phase reacts with the adsorbed Cl to produce chlorides. (4) The UBC, substituted by activated carbon, played a significant role in the oxidation and adsorption of mercury. O₂ promoted mercury adsorption, and the fly ashes displayed a larger adsorption capacity in the simulated flue gas. The oxidation rate in the simulated flue gas was 60%. (5) Al₂O₃, Fe₂O₃ and TiO₂ were able to adsorb mercury. Among these components, Al₂O₃ displayed the largest adsorption capacity. Mercury adsorption did not occur on the surfaces of CaO or MgO. The flue gas compositions exhibited no influence on the adsorption capacity for the five metallic oxides. No metallic oxides catalyzed mercury oxidation regardless of the flue gas composition.

Future studies should focus on a quantitative model for mercury oxidation based on the E–R mechanisms confirmed in this study. Additional studies should investigate the oxidation and adsorption mechanisms for mercury in varying flue gas compositions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2015.09.065>.

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