



## Research article

# Study on the effects of carrier and modifier on mercury adsorption behavior over halides modified sorbents using temperature programmed desorption method

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## ABSTRACT

Halides modified sorbents injection equipped with dust removal units is considered as the most promising technology for elemental mercury ( $\text{Hg}^0$ ) removal from coal-fired flue gas. However,  $\text{Hg}^0$  adsorption behavior over different halides modified sorbents remains controversial. In this study, the effects of carriers (activated carbon and neutral  $\text{Al}_2\text{O}_3$ ) and modifiers ( $\text{NaCl}$ ,  $\text{NaBr}$ ,  $\text{CuCl}_2$ , and  $\text{CuBr}_2$ ) on the behavior of  $\text{Hg}^0$  adsorption over modified sorbents were investigated using temperature programmed desorption (TPD) method. Both mercury adsorption experiments and TPD experiments were conducted in the bench-scale fixed bed. The results indicated that  $\text{CuBr}_2$ -modified activated carbon (AC) showed the best mercury removal performance due to the lower bond energy of  $\text{CuBr}_2$ . The decomposition temperature of mercury compounds generated on AC was different from that on neutral  $\text{Al}_2\text{O}_3$ . Further analysis indicated that the modifiers with lower bond energy could release halogens during modification. The released halogens could react with AC to form active C–Cl or C–Br group. Moreover, the lower bond energy of modifiers made it easier for halogens to release. But  $\text{Al}_2\text{O}_3$  carrier could not react with modifiers to form active group during modification. The  $\text{Hg}^0$  adsorption process over modified  $\text{Al}_2\text{O}_3$  could be explained by Langmuir–Hinshelwood mechanism.

## 1. Introduction

Mercury has strong toxicity to animals and humans through food-chain [1, 2]. According to statistics, coal-fired power plants have become one of the biggest anthropogenic sources of mercury emissions in the world [3–6]. Mercury has three basic chemical forms in coal-fired flue gas: particulate mercury ( $\text{Hg}^p$ ), oxidized mercury ( $\text{Hg}^{2+}$ ) and elemental mercury ( $\text{Hg}^0$ ) [7–10].  $\text{Hg}^p$  can be captured by dust control units and  $\text{Hg}^{2+}$  can be removed by wet flue gas desulfurization due to its good water-solubility [11–13]. However,  $\text{Hg}^0$  is insufficiently removed by the existing air pollution control devices because of its high volatility and low solubility in water [14–16]. Therefore, great efforts have been focused on the removal of  $\text{Hg}^0$  from coal combustion flue gas. The general method for controlling mercury emission fall into two categories: (1)  $\text{Hg}^0$  is converted into  $\text{Hg}^p$  through sorbents injection [17–20] and (2)  $\text{Hg}^0$  is oxidized into  $\text{Hg}^{2+}$  using strong oxidants or catalysts [21–24].

Among them, halides modified sorbents injection equipped with dust removal units is considered as the most promising technology for  $\text{Hg}^0$  removal from flue gas [25–29]. The mercury removal efficiency of

sorbents varies from the kind of activated carbon, flue gas composition, flue gas temperature, etc. In coal-fired power plants, the used sorbents after mercury adsorption are often processed together with fly ash. An inappropriate method for disposing fly ash may cause the secondary release of mercury [30]. Thus it is necessary to identify the mercury species on the used sorbents. This could provide guidance for inhibiting mercury emission during fly ash disposal. However, the amount of mercury adsorbed on sorbents was too small to reach the detection limits of measuring instruments. Temperature programmed desorption (TPD) method has been widely adopted to identify mercury species in solids due to its low detection limit and high accuracy [31–33]. TPD method is based on the fact that mercury compounds with different stability decomposed at different temperatures. In this case, mercury species can be judged from the decomposition temperatures. Lopez-Anton et al. have successfully identified and quantified mercury species in fly ash via TPD analysis [34]. Wu et al. used TPD to investigate the reactivity of  $\text{Hg}^0$  pretreated by HCl and  $\text{SO}_2$  [25]. In our previous studies [35, 36], TPD method was used to identify mercury occurrence in coal and  $\text{Hg}^0$  adsorption mechanism over AC's oxygen functional groups. Although TPD is an effective method for identifying the

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mercury species in solids, few literatures have focused on the effects of carriers and modifiers on the TPD characteristic of halides modified sorbents. And  $\text{Hg}^0$  adsorption behavior over different halides modified sorbents remains controversial [37–40], which needs for further research.

In this study, we investigated the TPD characteristic of mercury compounds generated on various modified sorbents after  $\text{Hg}^0$  adsorption. AC and neutral  $\text{Al}_2\text{O}_3$  were selected as carriers while NaCl, NaBr,  $\text{CuCl}_2$ , and  $\text{CuBr}_2$  were selected as modifiers. Combined with XPS analysis, the effects of carriers and modifiers on the TPD peaks were explained. The  $\text{Hg}^0$  adsorption mechanisms over halides modified sorbents were also revealed.

## 2. Material and methods

### 2.1. Sample preparation and characterization

NaCl,  $\text{CuCl}_2$ , NaBr, and  $\text{CuBr}_2$  were selected to modify activated carbon. Non-carbonaceous neutral  $\text{Al}_2\text{O}_3$  was also chosen to investigate the effects of carriers on the behavior of  $\text{Hg}^0$  adsorption. Neutral  $\text{Al}_2\text{O}_3$  was demonstrated to be a good carrier of mercury sorbents due to its large specific surface area. Modified sorbents were prepared by chemical impregnation method and the halogen loading ratio was 2 wt%. The specific surface area, pore sizes and pore volumes of various sorbents were measured using  $\text{N}_2$  adsorption at 77 K. XPS technique was used to analyze the change in surface chemistry after impregnation and mercury removal process.

### 2.2. Experimental apparatus and procedure

The schematic of the fixed-bed reactor system used for  $\text{Hg}^0$  adsorption was similar to that in our previous research [41].  $\text{N}_2$  was used as carrier gas and the total flow rate was kept as 1 L/min. The sorbents (0.5 g) were packed in the quartz tube reactor (internal diameter 2 cm), which was heated by a temperature controlled electric furnace. The corresponding gas hourly space velocity was  $50,956 \text{ h}^{-1}$ . The  $\text{Hg}^0$  concentration was measured by the mercury analyzer (VM3000, Germany) and recorded by a computer continuously.

In the  $\text{Hg}^0$  adsorption experiments, a stable flow rate of  $\text{Hg}^0$  vapor ( $120 \mu\text{g}/\text{m}^3$ ) was generated by mercury permeation tube and then introduced into the quartz reactor. All mercury adsorption tests were carried out at 20 °C and 130 °C for 1 h. The  $\text{Hg}^0$  removal efficiency ( $\eta$ ) of halogens-modified sorbents was calculated according to the following formula:

$$\eta = (1 - C_{\text{out}}/C_{\text{in}}) \times 100\% \quad (1)$$

where  $C_{\text{out}}$  and  $C_{\text{in}}$  represent the inlet and outlet  $\text{Hg}^0$  concentration ( $\mu\text{g}/\text{m}^3$ ), respectively.

TPD experiments were carried out after  $\text{Hg}^0$  adsorption experiments. The experiments were also performed in a fixed-bed reactor system, as shown in Fig. 1. The experimental setup was consisted of two horizontal electrical furnaces. The first electric furnace was served to heat the solid samples so that mercury was released from the sorbents. In each test, the solid sample (0.5 g) was heated from 50 °C to 600 °C with a liner heating rate of 10 °C/min. The oxygen carriers ( $\text{NiO}$  and  $\text{Fe}_2\text{O}_3$ ) were placed in the second quartz reactor to eliminate interference components, such as aromatic hydrocarbons. This was mainly because the measuring principle of the mercury analyzer (VM3000) is that elemental mercury atoms can absorb ultraviolet (UV) wavelength 253.7 nm light. However, the aromatic hydrocarbons emitted from carrier (i.e. activated carbon) during the TPD experiments can also absorb UV 253.7 nm, which had negative effects on the measurement of mercury concentration. According our previous study [42], aromatic hydrocarbons could react with oxygen carrier and then  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were generated. In such a case, the adverse effect caused by aromatic hydrocarbons was eliminated. The mercury concentration desorbed

from the used sorbents was measured by the VM3000. Finally, the mercury concentration as a function of temperature could be obtained via TPD experiments.

## 3. Results and discussions

### 3.1. Samples characterization

$\text{Hg}^0$  physisorption mainly depends on the specific area surface and pore size of sorbents. Therefore, BET tests were carried out and the results are listed in Table 1. The pore volumes and average pore sizes of the modified AC were decreased compared to the virgin AC. Similarly, the pore volumes and average pore sizes of the modified  $\text{Al}_2\text{O}_3$  were noticeably smaller than that of raw  $\text{Al}_2\text{O}_3$ . This phenomenon could be attributed to the blockage of internal porosity by modifiers during modification. It could also be found that raw AC has larger BET surface area and pore size than raw  $\text{Al}_2\text{O}_3$ , which was favorable to mercury physisorption [43].

### 3.2. $\text{Hg}^0$ removal performance of various sorbents

The mercury removal efficiencies of various sorbents as a function of adsorption temperature are shown in Fig. 2. As shown in Fig. 2a, the mercury removal efficiency of raw AC tested at 20 °C was about 40%. This might be caused by the reaction between  $\text{Hg}^0$  and the oxygen functional groups on the surface of raw AC, especially the carbonyl groups and ester groups [36]. However, less than 20% of  $\text{Hg}^0$  was removed when the temperature was increased to 130 °C. In addition, the  $\text{Hg}^0$  removal performance of modified ACs were entirely different from each other even though the halogen loading ratio was the same (2 wt %). For NaCl-AC and NaBr-AC, the mercury removal efficiencies tested at 20 °C were higher than raw AC. This indicated that the modifiers could enhance the  $\text{Hg}^0$  adsorption performance. But mercury adsorption was suppressed with the further increase of adsorption temperature to 130 °C. In this case, it was inferred that physisorption dominated the  $\text{Hg}^0$  removal process. Meanwhile, the mercury removal performance of NaCl-AC was inferior to NaBr-AC. It might be because the bond energy of NaCl (412 kJ/mol) is higher than NaBr (367 kJ/mol) (Fig. 3) [44–46]. This caused Cl more difficult to be released from modifier and reacted with  $\text{Hg}^0$ . In this case, the adsorption performance of NaBr-AC was higher than NaCl-AC. For  $\text{CuCl}_2$ -AC and  $\text{CuBr}_2$ -AC, the mercury removal efficiencies increased significantly compared to raw AC. And the increase in adsorption temperature had a positive effect on mercury adsorption. In particular,  $\text{Hg}^0$  removal efficiency of  $\text{CuBr}_2$ -AC tested at 130 °C could reach above 99% within 1 h. This indicated that  $\text{CuCl}_2$ -AC and  $\text{CuBr}_2$ -AC mainly adsorbed elemental mercury via chemisorption. As the temperature increasing, the chemical adsorption strengthened and then the mercury adsorption efficiency increased [19]. However, it was worth mentioning that the mercury removal efficiency increased in the order: NaCl-AC < NaBr-AC <  $\text{CuCl}_2$ -AC <  $\text{CuBr}_2$ -AC. This sequence was in the reverse order of the bond energy of modifiers (Fig. 3). This was mainly because the lower the bond energy of modifiers, the easier it is for the halogens to release. NaCl was more stable than other modifiers, which led to Cl ion harder to be released from modifiers. Thus  $\text{CuBr}_2$ -AC could provide more Br ions during mercury adsorption, which could significantly promote  $\text{Hg}^0$  removal.

Further investigation on the effects of the sorbents' carrier on mercury removal performance was also examined. Pure  $\text{Al}_2\text{O}_3$  and  $\text{CuCl}_2$ - $\text{Al}_2\text{O}_3$  were selected to test the mercury removal performance at 20 °C and 130 °C for comparison and the results are shown in Fig. 2b. The untreated  $\text{Al}_2\text{O}_3$  captured negligible elemental mercury at 20 °C and 130 °C. It might be due to the lack of the active site on the surface of  $\text{Al}_2\text{O}_3$ . On the contrary, the modified  $\text{CuCl}_2$ - $\text{Al}_2\text{O}_3$  showed good mercury removal efficiency, especially at 130 °C. However, the treated  $\text{CuCl}_2$ - $\text{Al}_2\text{O}_3$  did not perform as well as  $\text{CuCl}_2$ -AC. This observation suggested that the sorbents' carrier has an important role in mercury

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