Copper modified activated coke for mercury removal from coal-fired flue gas

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HIGHLIGHTS

- Different preparation conditions of CuO/AC-H will have an impact on the efficiency of mercury removal.
- 8%CuO/AC-H with 300 °C calcination performs the highest mercury removal efficiency at 160 °C.
- Gas components (O_2 and NO) all could improve the efficiency of mercury removal.
- Mechanism of mercury removal over CuO/AC-H is a combination of adsorption and catalytic oxidation.

ARTICLE INFO

ABSTRACT

A series of copper modified activated coke were prepared by an impregnation method to evaluate their efficiency of mercury removal in a simulated coal-fired flue gas. Effect of factors (including active component, copper loading value, calcinations temperature, reaction temperature and partial flue gas components) were studied. Results showed that the efficiency of raw coke could be enhanced by HNO_3 pretreatment its dual functions of dirty cleaning and surface functional group modifying. The sample with 8% Cu loading value and 300 °C calcination for 3 h was found to be the optimal material for mercury removal, achieving around 73% average efficiency at 120 °C. Meanwhile, the increase of reaction temperature would enhance the removal efficiency when it was below 160 °C, but had a negative effect with further increase. Besides, experimental results also revealed that O_2 and NO all had a positive effect on mercury removal. Various means (SEM, FTIR, BET, XRD, TGA) in this work were used to characterize samples. Results indicated that copper modification could change surface functional groups of activated coke, while calcination temperature would have an impact on the species of decomposition product. $Cu(NO_3)_2$ would decompose into CuO at lower calcination temperature, while partly into Cu_2O at higher temperature. Moreover, the BET results revealed that metal modification broadened pore distribution of AC, which favored mercury removal. The two peaks in TG curve could be ascribed to elemental mercury (Hg^0) and HgO, which testified that the mechanism of mercury removal over CuO/AC-H was the combination of adsorption and catalytic oxidation.

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1. Introduction

Coal, as a major primary energy in China, still reigns supreme (about 70% in energy structure) for decades under the background of rising energy demands in economic transformation period [1]. However, the combustion of coal inexorably leads to various pollutants, such as SO_x, NO_x, PM, and heavy metals (Hg, Pb, As etc.) [2,3], which are responsible for a series of environmental accidents. As one of trace elements in coal, the average mercury concentration in China was only 0.22 mg/kg [4]. However, China is the largest

coal consumption country around the world, and as a result, amount of mercury will be released into atmosphere after coal burning, which will cause great damage to environmental and human body. Recently, mercury has drawn more and more attention of society and enterprises because of its toxicity, volatility, bioaccumulation in environment [5,6] and the adverse influence on people's nervous system [7,8].

Natural release and anthropogenic discharge are the two main sources of Hg emissions [9]. Of all the anthropogenic discharge, almost 1/3 emission comes from coal burning in China. According to Streets et al. [10], China released about 537 ± 236t anthropogenic mercury in 1990, in which coal combustion accounted for about 38%. Coal-fired power plant has been regarded as the

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largest anthropogenic sources of mercury emissions. There are three forms of mercury in flue gas: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particulate-bound mercury (Hg^p) [11]. The concentration of different kinds of mercury in fuel gas depends on coal rank and operation conditions of boiler. Among them, Hg^{2+} can be easily to be removed through wet flue gas desulfurization (WFGD) because it is soluble, while Hg^p can be captured efficiently from flue gas by electrostatic precipitator (ESP) or fabric filter (FF). However, Hg^0 is relatively difficult to be removed through existing air pollution control devices (APCDs) because of its highly volatility, stability and insolubility in water.

Lots of methods have been investigated to cope with the mercury emission into atmosphere, including catalytic oxidation, activated carbon injection (ACI), photochemical oxidation, absorption, adsorption et al. [12–19]. Among these, ACI, which was ever considered to be the most efficient method for mercury control, has already been applied for mercury removal in some power plants. Nevertheless, some disadvantages of ACI, such as higher operation cost, poor adsorption capacity and much difficulties in separating from fly ash, had limited its later development [20,21]. Hence, it had tremendous value to develop new adsorbents and methods.

As a carbon based production, AC (activated coke) has attracted many researchers' attention to the study of Hg removal [22,23] because of its lower special area (150–300 m^2/g), better mechanical strength, regeneration and lower price compared with activated carbon and its higher ability in simultaneous removal of SO_x and NO_x. In order to improve the activity of adsorbents, many active components has been supported on AC to removal mercury from flue gas, including CeO_2, MnO_x, Fe_2O_3, V_2O_5 and so on. As a result, they all perform excellent mercury removal efficiency. Moreover, as one of low-cost transition metal oxides, CuO has been reported to be a good active component for NO reduction [24], Deacon Process, CO oxidation [25], and catalytic oxidation of Hg^0 [26,27]. However, there have been few papers involving in the activity and mechanism of removal mercury over copper loaded activated coke. In this study, the effect of different metal modification on mercury removal was investigated, so were the effects of preparation conditions and reaction conditions or copper modified AC. Furthermore, SEM, FTIR, BET, XRD and TGA were applied to characterize samples and the mechanism of mercury removal over CuO/AC was discussed according to the experimental and characterization results.

2. Materials and methods

2.1. Samples preparation

AC for adsorbents was purchased from Inner Mongolia Taixi Group Xingtai Coal Chemistry Co., Ltd. Equivalent-volume impregnation was chosen as method to prepare all the adsorbents as following steps: (1) The granular coke was ground and sieved into 40–60 mesh size small particles, then cleaned the surface ash and dirt using ultrapure water and dried in a drying oven at 110 °C for 8 h. (2) of the power AC was put into a solution of 6 wt% HNO_3 and treated in water bath at 75 °C for 3 h, then washed with ultrapure water until the pH had no change and dried in oven at 110 °C for 8 h. The materials were denoted as AC-H, which H represent HNO_3 pretreatment. (3) AC-H was impregnated in the solution of a certain concentration of precursors with ultrasonic assistance for 30 min and dried at 110 °C for 8 h. (4) The materials were calcined in muffle furnace under air atmosphere at a necessary temperature for 3 h. The samples were denoted as y%MO_x/AC-Hz (thereinto, M represented one metal, y represented mass ratio of MO_x to adsorbents, and z represented calcination temperature).

2.2. Characterization of samples

The surface appearance and structure of the samples was obtained by a Evo18 scanning electron microscopy (SEM). All samples should be plated carbon film for a better electrical conductivity. Fourier transform infrared (FTIR) spectroscopy was recorded on a Thermo Nicolet NEXUS 670 FTIR. The special surface area of the samples was determined using Brunauer–Emmett–Teller (BET) method on a Quadrasorb SI analyzer by N_2 adsorption. Pore sizes and pore volume were calculated by Horvath–Kawazoe method. The crystallinity information of copper species on the surface of samples was obtained on a TTRIII multifunctional X-ray diffraction (XRD) using a Cu kα radiation source (λ = 1.5406 Å, 35 kV voltage, 30 mA electric current and 2θ range from 10° to 90° at 5 °/min scanning speed). Finally, Thermogravimetric analysis (TGA) was used on a HCT-3 analyzer (Beijing Heven Scientific Instrument Factory) to observe the relationship between weight of the spent sample with temperature changes under N_2 atmosphere.

2.3. Experimental setup

The test rig was divided into four sections (Fig. 1): gas generation and control system, reaction system, sampling and detecting system and exhaust gas purification system. Hg^0 was generated through a mercury permeation tube (VICI Metronics of USA), which could release a constant weight of Hg^0 at an invariable temperature. Mass flow controllers were used to control the flux of individual gas provided by cylinder gases, thus the total flow rate was able to be limited to 300 ml/min, corresponding to a gas hourly space velocity (GHSV) of 23,000 h^{-1}. Basic Gas (BG) consisted of balance N_2, 50 $\mu g/m^3$ Hg^0, 5% O_2. A certain concentration of NO was added as necessary. All flue gas components were mixed and introduced into a fix-bed reactor, which was composed of 7 mm inner diameter by 300 mm long quartz tube and a constant temperature furnace. About 0.35 g adsorbent was used for each test. All the gas pipes after water bath had to be heated to 95 °C to prevent deposition of Hg^0. A cold vapor atomic absorption spectrometry mercury analyzer (JKG-203, Jilin institute of science and technology, Jilin, China) was used to detect the inlet and outlet total mercury concentration. The detection range and detection limit was 0–100 $\mu g/L$ and 0.003 $\mu g/L$, respectively. The correlation coefficient of standard curve must be above 0.999 needed before the first test. For each sampling, absorption solution (0.4% H_2SO_4 + 0.02 wt% $KMnO_4$) was poured into device to absorb mercury in flue gas, then 15 wt% $SnCl_2$ was added into the solution to reduced Hg^{2+} to Hg^0 before it was conducted into analyzer. The mercury concentration in simulate flue gas then could be calculated indirectly according to the data of analyzer. Finally, a carbon trap was used to clean exhaust gas before discharged into atmosphere.

In this work, Mercury RE (mercury removal efficiency) was calculated by comparison between inlet and outlet total mercury concentration as following equation:

$$\eta = \frac{\Delta Hg}{Hg_{inlet}} = \frac{Hg_{inlet} - Hg_{outlet}}{Hg_{inlet}} \times 100\% \tag{1}$$

where η is Mercury RE (%); Hg_{inlet} ($\mu g/m^3$) and Hg_{outlet} ($\mu g/m^3$) represented the inlet and outlet concentration of mercury (Hg^0 + Hg^{2+}), respectively.

All sets of experiments and the parameters were listed in Table 1. It was divided into six sections: in set 1, the effect of different pretreatment methods (including water treatment and HNO_3 pretreatment) on Mercury RE was investigated under BG atmosphere at 120 °C; set 2 was prepared to conduct the effect of different metal doping on mercury removal; set 3 was prepared to study the effect of copper loading value on Mercury RE; set 4