Journal of Hazardous Materials 402 (2021) 123502

Contents lists available at ScienceDirect

Journal of Hazardous Materials

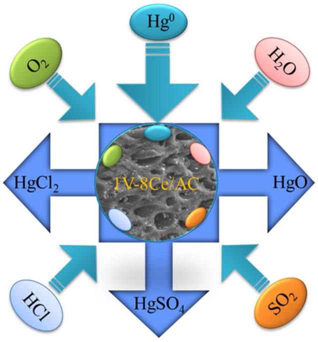
journal homepage: www.elsevier.com/locate/jhazmat

Insight into the effect of SO_2 on the Hg^0 removal performance over a 1V-8Ce/AC sorbent at low temperatures

Youcai Zhu, Caiting Li*, Yue Lyu, Shanhong Li*, Yindi Zhang, Xueyu Du, Yunbo Zhai

College of Environmental Science and Engineering, Key Laboratory of Environmental Biology and Pollution Control (Ministry of Education), Hunan University, Changsha, 410082, PR China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Elemental mercury
1V-8Ce/AC
Adsorption
Catalytic oxidation
SO_2

ABSTRACT

The influences of SO_2 on Hg° removal over the 1V-8Ce/AC sorbent were systematically investigated at low temperatures. The experimental results showed that SO_2 has a dual effect on Hg° removal, that is, SO_2 has both a promoting effect and an inhibiting effect on Hg° removal. The SO_2 transient response experiment indicated that SO_2 could not only react with Hg° to promote the removal of Hg° but also react with the active components and poison the sorbent. O_2 is indispensable for the removal of Hg°, which can offset the adverse effects caused by SO_2 and H_2O. HCl exhibited an obvious promoting effect on Hg° removal in the presence of SO_2. The 1V-8Ce/AC sorbent exhibited good sulfur resistance and excellent stability (E_{Hg} = 90.04 %) after a 24 h reaction performed under the 1000 ppm SO_2 condition at 150 °C. In addition, the Hg-TPD and XPS methods were used to assist in studying the effect of SO_2 on Hg° removal over the 1V-8Ce/AC sorbent. Finally, the mechanism of Hg° removal in an SO_2 atmosphere was also explored, which showed that Hg° was removed by two possible pathways over the 1V-8Ce/AC sorbent.

1. Introduction

In recent years, with the rapid development of modern industry, environmental pollution has become increasingly prominent (Streets et al., 2011). However, with people's yearning for a better life, environmental problems, especially air pollution, have been increasingly emphasized. Mercury, a natural trace element found in coal, is released after burning and mainly comes in three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particulate mercury (Hg^P) (Galbreath and Zygarlicke, 1996). Among them, Hg^{2+} and Hg^P

---

* Corresponding author.
E-mail addresses: ctli@hnu.edu.cn (C. Li), lsh-17208@hnu.edu.cn (S. Li).

https://doi.org/10.1016/j.jhazmat.2020.123502
Received 6 February 2020; Received in revised form 8 July 2020; Accepted 9 July 2020

can be easily controlled by air pollution control devices (APCDs), such as electrostatic precipitators (ESPs), fabric filters (FFs) and wet flue gas desulfurization equipment (WFGD) (Chen et al., 2018). However, only Hg^0 is difficult to be effectively removed due to its high volatility and poor water-solubility (Gao et al., 2013). Generally, selective catalytic reduction (SCR) is usually used in conjunction with a desulfurization unit, which results in a large investment and high operating costs. Furthermore, although Hg^{2+} in flue gas can be effectively captured and enriched in slurry during the WFGD process, it can also cause secondary pollution (Xu et al., 2017; Gustin and Ladwig, 2010; Presto and Granite, 2006). Therefore, determining how to effectively control the release of Hg^0 into the air has become a hot and difficult research topic.

Currently, activated carbon (AC) is widely used as an sorbent due to its large specific surface area, developed pore structure, and great mechanical strength (Diamantopoulou et al., 2010; Wu et al., 2015; Xie et al., 2015). Previous studies have found that AC has a large specific surface area and has a certain adsorption effect on Hg°, after the modification of AC by V and Ce, it can significantly improve the removal performance of Hg° (Zhu et al., 2018). Although brominated activated carbon has shown excellent performance in the removal of Hg° (Saha, 2014; Zhou et al., 2015), the study of economic, environmental, and efficient sorbents (or catalysts) are still focused. By modifying AC, V-Ce/AC sorbent has both adsorption and oxidation properties on Hg°, which can further improve the removal performance of various pollutants without causing secondary pollution. What's more, the dry simultaneous removal technologies used to remove multi-pollutants from coal-fired flue gas by using carbon-based sorbents have achieved zero water consumption based on their high efficiency and low energy.

As a global pollutant, mercury has attracted increasing attention, and the emission requirements of pollutants emitted from coal-fired power stations have also become more strict (China, 2011; United States Environmental Protection Agency (U.S. EPA), 2013). Under such conditions, effectively controlling the removal of Hg^0 without causing secondary pollution has become a more environmentally friendly research method. As we all know, flue gas compositions, especially those containing acidic gases (such as HCl and SO_2), have different effects on Hg^0 removal. It is generally believed that HCl improves Hg^0 removal due to the role of active chlorine species [Cl] (Tong et al., 2015; Li et al., 2012). However, the effect of SO_2 on Hg^0 removal has been controversial (Xu et al., 2017; Li et al., 2013), and the effect of SO_2 on the Hg^0 removal performance over a V-Ce/AC sorbent is rarely studied. Therefore, it is necessary to conduct a comprehensive and in-depth study on the effect of SO_2 on the Hg^0 removal performance over a V-Ce/AC sorbent.

In this paper, a systematic study was performed to determine the influence of SO_2 on the Hg° removal performance over the 1V-8Ce/AC sorbent at low temperatures, which included studying the role of the concentration of SO_2, the effect of the temperature (100 − 220 °C), and the interaction of SO_2 with other flue gas components (including O_2, H_2O, and HCl). Moreover, the possible reaction pathways were also proposed using techniques such as XPS and Hg-TPD. The ultimate goal is to fully understand the mechanism of Hg° removal under the SO_2 atmosphere. This knowledge will play a guiding role in effectively controlling mercury emissions from coal-fired power plants.

2. Experimental

2.1. Chemicals and reagents

Activated carbon (AC) was supplied by Xinhua Chemical Ltd., China. All the reagents used in this work were analytical pure grade (AR), including: Cerium nitrate in hexahydrate (99.0 %, Sinopharm Chemical Reagent Co., Ltd), ammonium metavanadate (99.0 %, Kemiou Chemical Reagent Co., Ltd) and Oxalic acid (99.5 %, Sinopharm Chemical Reagent Co., Ltd). Ultrapure water was used for preparing the required solutions.

2.2. Catalyst preparation

AC was used as the catalyst support. The V-Ce/AC sorbent was synthesized by an ultrasound-assisted impregnation method. The details of a similar synthetic procedure are available in our previous research (Zhu et al., 2018).

2.3. Catalyst characterization

The X-ray photoelectron spectroscopy (XPS) analysis was conducted with an Escalab 250Xi instrument (Thermo Fisher Scientific Corporation, USA) using monochromatic Al K-Alpha radiation as the excitation source. The spectra were corrected by the C 1s binding energy value of 284.6 eV.

The temperature-programmed desorption experiments of Hg (Hg-TPD) were carried out in a quartz reactor with 0.10 g of the samples (fresh or spent), which were heated from 60 °C to 660 °C with a heating rate of 5 °C/min and exposed to 80 mL/min pure N_2. The outlet Hg° concentration was continuously measured by an on-line RA-915 M mercury analyzer (Lumex Co., Ltd., Russia).

2.4. Catalyst activity test

As shown in Figure S1, the activity of the catalyst was tested using a bench-scale fixed-bed reactor that consists of several parts, including the flue gas simulation system, temperature control system, reaction system, online analysis system, and exhaust treatment system. During each test, 0.10 g of the samples were packed into the quartz reactor. The total flow rate was 240 mL/min. All the simulated flue gas components, including N_2, O_2, SO_2, H_2O, and HCl, were precisely controlled by a mass flow controller (MFC). Among these flue gas components, the N_2 flow was used for two purposes: one purpose was used to carry water vapor into the flue gas system, and another purpose was to carry the Hg° vapor. Before and after each test, the concentrations of the feed gases were precisely detected.

The concentrations of Hg° and SO_2 were detected by an RA-915 M mercury analyzer and a KM9506 flue gas analyzer (KANE International Limited, U.K), respectively.

The Hg^0 removal efficiency (E_{Hg}) is defined as follows:

$$E_{Hg}(\%) = \frac{Hg^0_{in} - Hg^0_{out}}{Hg^0_{in}} \times 100\% \tag{1}$$

where Hg^0_{in} and Hg^0_{out} are the inlet and outlet Hg^0 concentrations of the fixed-bed reactor, respectively (μg/m^3).

3. Results and discussion

3.1. Effect of different flue gas components on Hg° removal

The Hg° removal performance of the 1V-8Ce/AC sorbent was investigated under the different flue gas component conditions. It can be clearly seen from Fig. 1 that the E_{Hg} varies significantly under the different atmospheres. The E_{Hg} in pure N_2 was only 70.59 %. After 6 vol % O_2 was added into the gas stream, the E_{Hg} obviously increased to 93.76 %. However, when 1000 ppm SO_2 or 8 vol% H_2O was added into pure N_2, which showed an obvious downward trend and only 3.64 % or 17.55 % was achieved, respectively. This may be due to the competitive adsorption between Hg° and SO_2 (or H_2O) (Wen et al., 2011; Xu et al., 2015). After 1000 ppm SO_2 was added into the $N_2 + O_2$ atmosphere, the E_{Hg} declined to 84.35 %. Similarly, when 8 vol% H_2O was added into the $N_2 + O_2$ atmosphere, the E_{Hg} declined to 62.80 %. However, when 1000 ppm SO_2 and 8 vol% H_2O were added together into pure N_2, the E_{Hg} seriously declined to only 4.37 %. After 6 vol% O_2 was added into

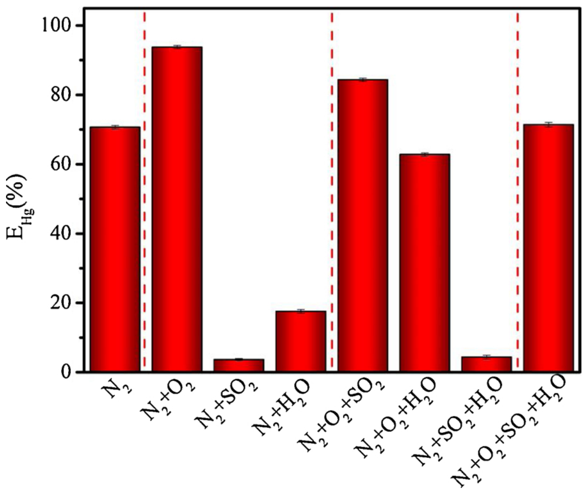


Fig. 1. Effect of different flue gas components on Hg° removal over the 1V-8Ce/AC sorbent at 150 °C (reaction conditions: O_2 = 6 vol%, Hg° = 240 μg/m^3, SO_2 = 1000 ppm, H_2O = 8 vol%, N_2 as balance, GHSV = 80,000 h^{-1}).

the $N_2+SO_2+H_2O$ atmosphere, the E_{Hg} increased back to 71.39 %. This increase indicated that SO_2 and H_2O could inhibit the removal of Hg°, while O_2 had an obvious promoting effect on Hg° removal, and the addition of O_2 could offset the inhibition of SO_2 and H_2O (Zhu et al., 2018; Zhang et al., 2014).

Based on the abovementioned studies about the effects of the various gases on Hg° removal, an O_2 transient response experiment was conducted over the 1V-8Ce/AC sorbent in the presence of SO_2. As shown in Figure S2, the E_{Hg} of the 1V-8Ce/AC sorbent in the simulated flue gas (Hg°$+H_2O$ + SO_2) without added O_2 was maintained at approximately 5% for 60 min. However, when 6 vol% O_2 was added to the simulated flue gas, the E_{Hg} increased rapidly and remained at approximately 66 %. When 6 vol% O_2 was cut off again at the 180th min, the E_{Hg} decreased rapidly from 64.13 % to 6.19 % within 20 min and remained at very low efficiency. The results indicated that O_2 can offset the adverse effects caused by SO_2 and H_2O in the removal of Hg°.

3.2. Effect of H_2O concentrations on Hg° removal

Water vapor, an important component in flue gas, was also investigated under the 1000 ppm SO_2 condition. As shown in Fig. 2, adding 6 vol% H_2O into the simulated flue gas significantly impacted the activities of the 1V-8Ce/AC sorbent and caused the E_{Hg} to significantly declined from 84.35% to 66.18%, and the E_{Hg} continued to decreased from 58.89 % to 52.43 % with increasing the H_2O content (from 8 vol% to 15 vol%). This indicated that the addition of H_2O has an obvious inhibitory effect on the removal of Hg°, and the inhibitory effect is more obvious with increasing H_2O contents.

To comprehensively understand the relationship between H_2O and Hg° under the SO_2 atmosphere condition, the transient response of H_2O was evaluated. As seen from Figure S3, the E_{Hg} significantly decreased from 89.98 % to 70.40 % after 8 vol% H_2O was added at the 60th min, but the E_{Hg} could be recovered to 89.59 % when 8 vol% H_2O was removed from the simulated flue gas system at the 120th min. This indicated that there is an obvious competitive adsorption relationship between H_2O and Hg° on the surface of the 1V-8Ce/AC sorbent (Zhang et al., 2014; Zhou et al., 2016), and this temporary deactivation can be stopped and the original level restored when the H_2O supply was cut off.

3.3. Effect of temperature on Hg° removal in the presence of SO_2

To investigate the effect of different temperatures on Hg° removal in the presence of SO_2, 1000 ppm SO_2 was added into the simulated flue gas, and the experiments were conducted at a temperature range of 100 − 220 °C.

As shown in Fig. 3, when the reaction temperature was adjusted to 100 °C, the highest removal efficiency was obtained (E_{Hg} = 94.93 %). By continuing to increase the reaction temperature to 120 °C, 150 °C, 180 °C, and 200 °C, the obtained E_{Hg} was 91.01 %, 85.87 %, 68.5 %, and 56.84 %, respectively. Note that the E_{Hg} dropped significantly, and an E_{Hg} of only 31.58 % was obtained after further increasing the temperature to 220 °C. This indicated that the reaction temperature has an obvious influence on the Hg° removal reaction, and higher temperatures were more unfavorable for Hg° removal under the SO_2 condition. According to the abovementioned experimental results, two possible reasons might explain this inhibition trend. The first reason is that the temperature increase is not conducive to the adsorption of Hg° (limiting the first step of the Hg° removal reaction) (Zhu et al., 2019). The second reason is that the reaction temperature increase accelerated the toxicity of the catalyst, where SO_2 could react with the active components to form sulfate and the caused partial deactivation of the 1V-8Ce/AC sorbent (Xu et al., 2015; Ma et al., 2008; He et al., 2016a).

3.4. Effect of HCl on Hg° removal in the presence of SO_2

As shown in Fig. 4, the effect of HCl on Hg° removal over the 1V-8Ce/AC sorbent at 150 °C was experimentally studied. When 25 ppm HCl was added to the simulated flue gas, the E_{Hg} increased from 85.87% to 93.82%. After that, when the concentration of HCl was further

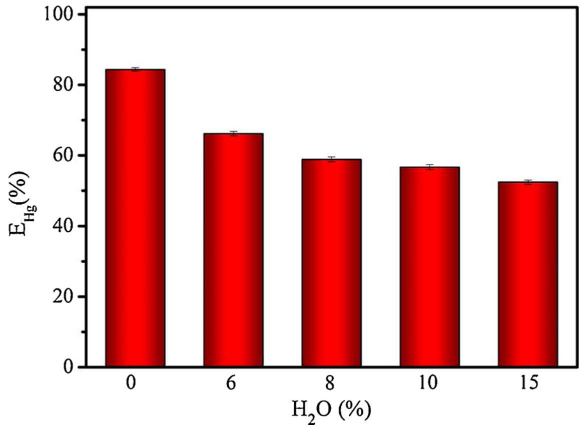


Fig. 2. Effects of different H_2O concentrations on Hg° removal at 150 °C (reaction conditions: O_2 = 6 vol%, Hg° = 240 μg/m^3, H_2O = 0-15 vol%, SO_2 = 1000 ppm, N_2 as balance, GHSV = 80,000 h^{-1}).

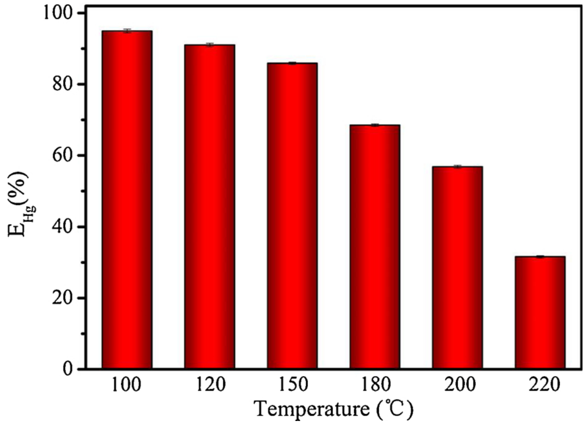


Fig. 3. Effect of temperature on Hg° removal in the presence of SO_2 (reaction conditions: O_2 = 6 vol%, Hg° = 240 μg/m^3, SO_2 = 1000 ppm, N_2 as balance, T = 100-220 °C, GHSV = 80,000 h^{-1}).

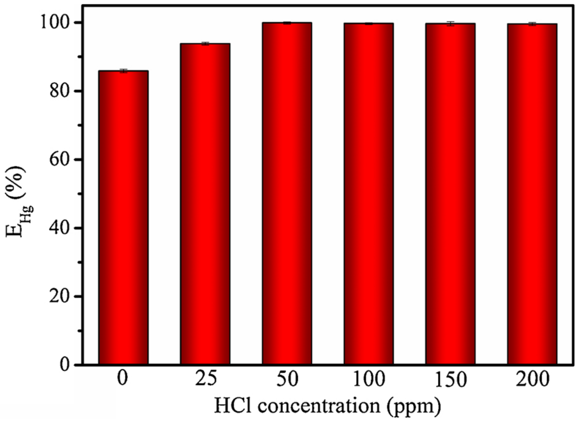


Fig. 4. Effect of different HCl concentrations over the 1V-8Ce/AC sorbent (reaction conditions: O_2 = 6 vol%, Hg° = 240 μg/m^3, HCl = 0-200 ppm, SO_2 = 1000 ppm, N_2 as balance, T =150 °C, GHSV = 80,000 h^{-1}).

increased to 200 ppm, the E_{Hg} almost remained at 99.93 %. This indicated that HCl has an obvious promoting effect on Hg° removal (Niu et al., 2015).

Subsequently, we continued to study the lifetime of the 1V-8Ce/AC sorbent under the 100 ppm HCl condition. The results are shown in Fig. 5. For the reaction without added HCl, the E_{Hg} of 1V-8Ce/AC gradually decreased as the experiment time was prolonged, and the E_{Hg} decreased to 91 % after 24 h. However, for the reaction where 100 ppm HCl was added to the simulated flue gas, the E_{Hg} of 1V-8Ce/AC was consistently maintained at approximately 99 % after 24 h. This indicated that the addition of HCl contributed to the stability of Hg° removal. In the presence of HCl and O_2, HCl can be oxidized to form active chlorine species that could react with Hg° to form $HgCl_2$ (Wen et al., 2011; Xu et al., 2015; Chen et al., 2016). Thus, the pathway for the reaction of HCl and Hg° over the 1V-8Ce/AC sorbent might be described as Eq. (2).

$$4HCl(ads) + O_2(ads) + 2Hg^0(ads) \rightarrow 2HgCl_2(ads) + 2H_2O(ads) \quad (2)$$

3.5. Effect of SO_2 concentrations on Hg° removal

The effect of SO_2 concentrations on Hg° removal is shown in Fig. 6. It can be seen that the E_{Hg} of 1V-8Ce/AC was 93.76 % without added SO_2. When 100 ppm SO_2 was added into the simulated flue gas stream, there was an obvious inhibitory trend, and the E_{Hg} decreased to 55.25 %. However, an interesting experimental phenomenon was observed, as

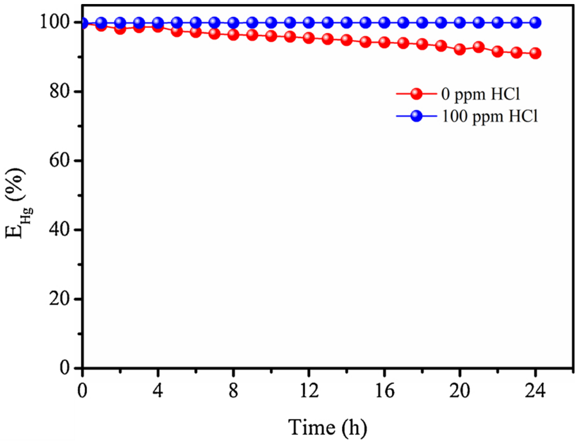


Fig. 5. The stability of 1V-8Ce/AC sorbent under the HCl atmosphere at 150 °C (reaction conditions: O_2 = 6%, Hg° = 240 μg/m^3, HCl = 100 ppm, N_2 as balance, GHSV = 80,000 h^{-1}).

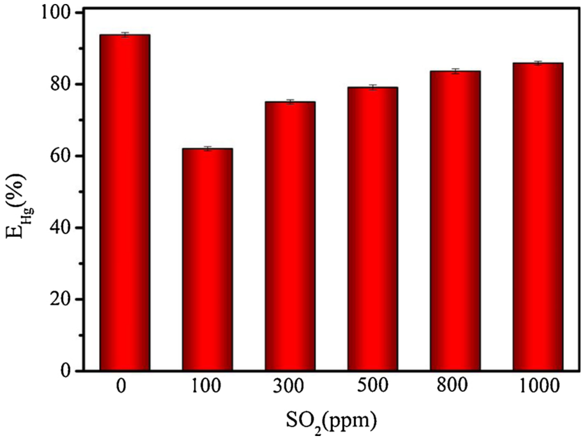


Fig. 6. Effect of different SO_2 concentrations on Hg° removal at 150 °C (reaction conditions: O_2 = 6 vol%, Hg° = 240 μg/m^3, SO_2 = 0-1000 ppm, N_2 as balance, GHSV = 80,000 h^{-1}).

the SO_2 concentration in the flue gas flow increased to 300 ppm, 500 ppm, and 800 ppm, the E_{Hg} gradually increased to 75.04 %, 79.09 %, and 83.61 % again, respectively. By further increasing the SO_2 concentration to 1000 ppm, the E_{Hg} was increased to 85.87 %. This indicated that SO_2 has a certain inhibitory effect on Hg° removal, but the inhibition trend slowed down with increasing SO_2 concentrations. The extent to which the SO_2 concentration affected Hg° removal differed depending on the SO_2 concentration, which might be attributed to SO_2 adsorbed on the surface of the sorbent, and a small part of SO_2 is oxidized to SO_3. With increasing SO_2 concentrations, the amount of SO_2 that oxidized to accumulated SO_3 gradually increases, and SO_3 can react with Hg° to generate $HgSO_4$ (Zhang et al., 2017; Li et al., 2011; Fan et al., 2012), thus reducing the extent to which SO_2 inhibited the Hg° removal process to a certain degree.

To further investigate the effect of SO_2 on the Hg^0 removal performance, the SO_2 transient response over the 1V-8Ce/AC sorbent and blank AC sample was evaluated experimentally. The results are shown in Fig. 7.

The SO_2 transient response experiment was first carried out over the blank AC and then performed with the 1V-8Ce/AC sorbent for comparison. It can be clearly seen from Fig. 7 that the E_{Hg} of the AC gradually decreased and was maintained at 4.90 % until 60 min. After 1000 ppm SO_2 was added into the gas stream at the 60th min, a promotion trend was observed, and the E_{Hg} increased from 4.90 % to 24.53 %. However, when the supply of SO_2 was cut off at the 120th min, the E_{Hg} decreased, but the E_{Hg} (approximately 11.98 %) was still higher

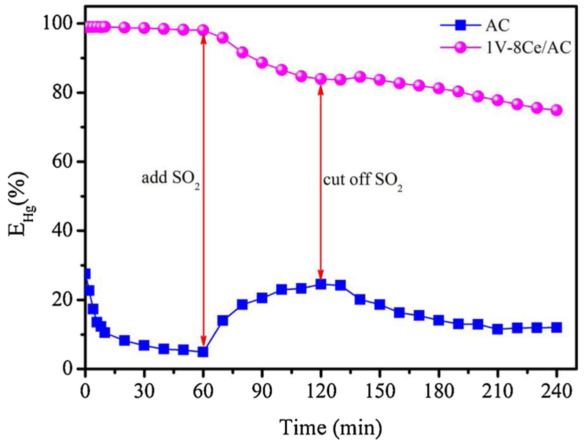


Fig. 7. Transient response of SO_2 (reaction conditions: O_2 = 6 vol%, Hg° = 240 μg/m^3, SO_2 = 1000 ppm, N_2 as balance, T =150 °C, GHSV = 80,000 h^{-1}).

than that observed before the addition of SO_2. This indicated that the addition of SO_2 is helpful for the removal of Hg°, and the SO_2 remaining on the surface of AC can continue to react with Hg°.

Similarly, the SO_2 transient response experiment was also conducted over the 1V-8Ce/AC sorbent. For the first 60 min, the E_{Hg} of the 1V-8Ce/AC sorbent was maintained at 98 % without added SO_2. When 1000 ppm SO_2 was added to the simulated flue gas at the 60th min, the E_{Hg} gradually decreased from 98.06% to 83.74%. However, the E_{Hg} was not restored but continued to declined to 74.84 % after 1000 ppm SO_2 was removed at the 120th min. Therefore, it can be inferred that the inhibitory role of SO_2 on mercury removal is due to the partial deactivation caused by the toxicity of SO_2 on the 1V-8Ce/AC sorbent. More importantly, it also can be seen that the toxicity of SO_2 on the 1V-8Ce/AC sorbent is irreversible.

By comparing the two abovementioned experimental groups, we can infer that the added SO_2 can react with Hg^0, which thus promoted Hg^0 removal to a certain extent (Li et al., 2013). The AC modified by active components (V_2O_5 and CeO_2) further improved the removal performance of Hg^0. However, the added SO_2 can also react with the active components of the catalyst, so the catalyst gradually lost its original activity. This may be due to the formation of metal sulfate during the reaction (Ma et al., 2008; Smirnov et al., 2014; He et al., 2016b). The process can be described as the following reaction in Eqs. (3) and (4).

$$2V_2O_5 + 4SO_2 + O_2 \rightarrow 4VOSO_4 \tag{3}$$

$$2CeO_2 + 3SO_2 + O_2 \rightarrow Ce_2(SO_4)_3 \tag{4}$$

To determine the chemical state of the different samples (fresh and spent 1V-8Ce/AC), the XPS analysis was conducted, and the S 2p and Hg 4f spectra are shown in Fig. 8.

The S 2p spectra are shown in Fig. 8(A). For the fresh 1V-8Ce/AC sorbent, no peak was attributed to S 2p. In contrast, for the spent 1V-8Ce/AC sorbent spectrum, there were two obvious peaks at approximately 164.6 eV and 169.15 eV, which can be attributed to SO_4^{2-} species, indicating that SO_2 can be oxidized to SO_4^{2-} (Ma et al., 2008; Yang et al., 2017). The spectra of Hg 4f are presented in Fig. 8(B); the two main peaks at approximately 101.75 eV and 102.25 eV corresponded to Si and Hg^{2+}, indicating that Hg^{2+} formed on the spent 1V-8Ce/AC sorbent under the SO_2 condition (Zhu et al., 2018; Zhang et al., 2017). However, the Hg° peak was not observed from the Hg 4f spectra, which might be due to the Hg° content on the spent 1V-8Ce/AC sorbent surface being lower than the detection limit of the XPS analysis (Wang et al., 2016).

As we all know, different mercury species have different boiling points. To obtain a better understanding of the mechanism of how SO_2 affects the Hg^0 removal process, the Hg-TPD profile is an important consideration, as Hg-TPD can be used to effectively identify the type of mercury species in samples. By comparing the decomposition temperature of the mercury species in the samples with that of the pure mercury compounds, the mercury species in the samples can be identified (Yang et al., 2017).

The Hg-TPD-O_2 experiment was carried out on the spent 1V-8Ce/AC samples (treated with 6 vol% O_2 + 240 μg/m^3 Hg°). As shown in Fig. 9(A), with increasing temperatures, different types of mercury species were desorbed from the spent 1V-8Ce/AC sorbent, and two peaks appeared at approximately 230 °C and 380 °C. The peak at 230 °C was attributed to chemical adsorbed Hg° and the peak at 380 °C can be ascribed to oxidized mercury (Zhou et al., 2017; Rumayor et al., 2015; Sun et al., 2017). It can be inferred that there are two types of mercury species (Hg° and HgO) in the spent 1V-8Ce/AC sorbent, and it is also confirmed that the mercury removal process is the result of adsorption and oxidation. As for the Hg-TPD-O_2+SO_2 experiment performed on the spent 1V-8Ce/AC samples (treated with 6 vol% O_2 + 1000 ppm SO_2 + 240 μg/m^3 Hg°) Fig.9(B) shows that three peaks can be observed at 250 °C, 370 °C, and 520 °C, respectively. The peak at 250 °C was attributed to chemical adsorbed Hg° and the peak at 370 °C can be classified as HgO. However, note that a peak at 520 °C is observed in Fig. 9(B) but not in Fig. 9(A). This new peak may be due to the formation of $HgSO_4$ on the surface of the catalyst after the addition of SO_2 during the reaction process (Tong et al., 2015; Zhou et al., 2017; Lopez-Anton et al., 2010). Based on the abovementioned experiments, we can infer the possible reactions as follows:

$$Hg^0(g) \rightarrow Hg^0(ads) \tag{5}$$

$$O_2(ads) + Hg^0(ads) \rightarrow HgO(ads) \tag{6}$$

$$O_2(ads) + SO_2(ads) + Hg^0(ads) \rightarrow HgSO_4(ads) \tag{7}$$

3.6. Mechanism of the Hg^0 removal process in the presence of SO_2

Combined with the abovementioned experimental and characterization results (Transient response of SO_2, Hg-TPD and XPS), the Hg^0 removal reaction with SO_2 over the 1V-8Ce/AC sorbent mainly consists of adsorption and oxidation, which can be divided into two pathways.

Path 1. Inhibiting effect pathway

The first pathway is the inhibition effect on Hg^0 removal (including the competitive adsorption and poisoning of the active sites). The inhibiting effect of water vapor may be due to the competitive adsorption of Hg^0 and H_2O on the sorbent surface, which is temporarily deactivated and can be restored when water vapor is removed from the simulated flue gas, the reaction is shown in Eq. (8).

$$H_2O(g) \rightarrow H_2O(ads) \tag{8}$$

However, the inhibiting effect of SO_2 may be caused by the reaction between the active components (V and Ce) and SO_2 (Ma et al., 2008; Smirnov et al., 2014; He et al., 2016b), so the sorbent gradually deactivates, and that's irreversible. The reaction is shown in Eqs. (3) and (4).

$$2V_2O_5 + 4SO_2 + O_2 \rightarrow 4VOSO_4 \tag{3}$$

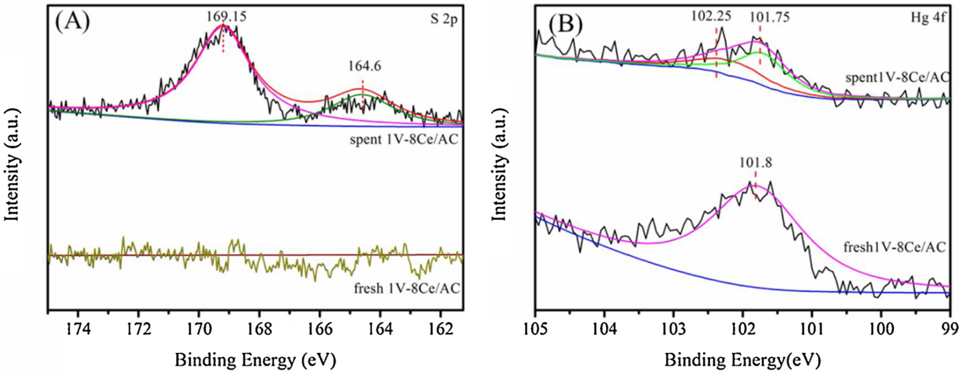


Fig. 8. S 2p (A) and Hg 4f (B) XPS spectra obtained for the fresh and spent 1V-8Ce/AC sorbent.

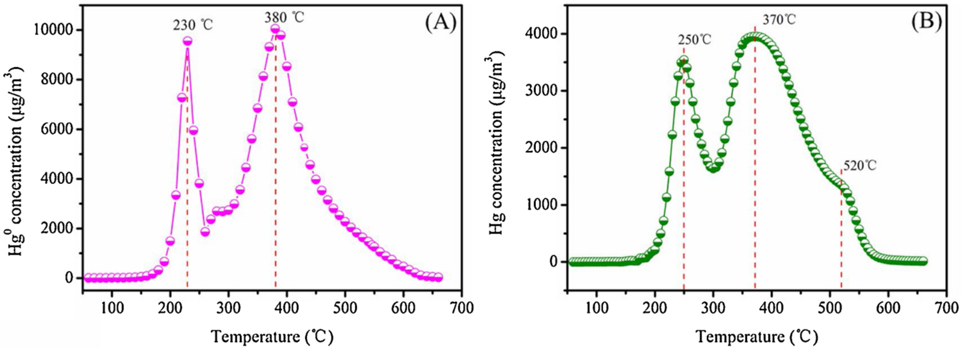


Fig. 9. Hg-TPD profiles: (A) Hg-TPD-O_2 and (B) Hg-TPD-$O_2 + SO_2$ (reaction conditions: N_2 = 80 mL, 5 °C/min, T = 60-660 °C).

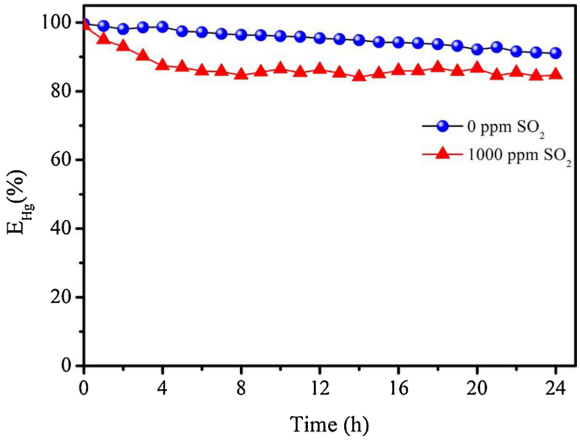


Fig. 10. Stability of the 1V-8Ce/AC sorbent in the presence of SO_2 (reaction conditions: O_2 = 6 vol%, Hg° = 240 μg/m^3, SO_2 = 1000 ppm, N_2 as balance, T = 150 °C, GHSV = 80,000 h^{-1}).

$$2CeO_2 + 3SO_2 + O_2 \rightarrow Ce_2(SO_4)_3 \tag{4}$$

Path 2. Promoting effect pathway

The second pathway is the promotion effect on Hg^0 removal (including adsorption and oxidation), as shown in Eqs. (2),(5),(6), and (7).

$$4HCl(ads) + O_2(ads) + 2Hg^0(ads) \rightarrow 2HgCl_2(ads) + 2H_2O(ads) \tag{2}$$

$$Hg^0(g) \rightarrow Hg^0(ads) \tag{5}$$

$$O_2(ads) + Hg^0(ads) \rightarrow HgO(ads) \tag{6}$$

$$O_2(ads) + SO_2(ads) + Hg^0(ads) \rightarrow HgSO_4(ads) \tag{7}$$

In the actual reaction process, the abovementioned two pathways will occur simultaneously. Therefore, the experimental phenomenon we finally observed is a balance of the results, in which the two pathways occurred simultaneously. What's more, the promoting effect is greater than the inhibiting effect in the presence of SO_2 at the low reaction temperature (below 200 °C). Therefore, the 1V-8Ce/AC sorbent exhibits good sulfur resistance and excellent mercury removal performance.

3.7. *The stability of the 1V-8Ce/AC sorbent under the SO_2 atmosphere*

Based on the abovementioned speculation, the experimental results we finally observed are the results of the two reaction pathways equilibrating. Thus, the stability of the 1V-8Ce/AC sorbent during the Hg° removal process was also studied. As shown in Fig. 10, for the reaction without added SO_2, the E_{Hg} gradually decreased, and an E_{Hg} of 91.06 % was obtained after 24 h. For the reaction with 1000 ppm SO_2 added, the E_{Hg} dropped to approximately 85 % during the first 4 h and gradually stabilized as the reaction time was prolonged. However, the E_{Hg} was still maintained at approximately 84.68 % after 24 h. This indicated that the 1V-8Ce/AC sorbent has a good sulfur resistance and excellent stability.

4. Conclusions

In summary, the 1V-8Ce/AC sorbents were prepared by the ultrasound-assisted impregnation method and systematically investigated the influences of SO_2 on Hg° removal at low temperatures. The experimental results indicated that SO_2 has both a promoting effect and an inhibiting effect on Hg° removal. In addition, the effect of other flue gas components (O_2, H_2O, and HCl) on Hg° removal was also investigated. O_2 is indispensable for the removal of Hg°, which can offset the adverse effects caused by SO_2 and H_2O. HCl has an obvious promoting effect on Hg° removal even in the presence of SO_2. The 1V-8Ce/AC sorbent exhibited good sulfur resistance and excellent stability (E_{Hg} = 90.04 %) in the presence of the 1000 ppm SO_2 at 150 °C. The Hg° removal mechanism in the presence of SO_2 was also explored by Hg-TPD and XPS methods, which showed that Hg° was removed by two possible pathways over the 1V-8Ce/AC sorbent.

CRediT authorship contribution statement

Youcai Zhu: Methodology, Formal analysis, Investigation, Writing - original draft, Data curation. **Caiting Li:** Supervision, Writing - review & editing. **Yue Lyu:** Writing - review & editing. **Shanhong Li:** Supervision, Writing - review & editing. **Yindi Zhang:** Writing - review & editing. **Xueyu Du:** Writing - review & editing. **Yunbo Zhai:** Supervision.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

Acknowledgements

This work was supported by the Key Research and Development Program of Hunan Province in China (2018SK2032) and the National Key Research and Development Program of China (2016YFC0204100).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2020.123502.

References

Chen, W., Pei, Y., Huang, W., Qu, Z., Hu, X., Yan, N., 2016. Novel effective catalyst for elemental mercury removal from coal-fired flue gas and the mechanism investigation. Environ. Sci. Technol. 50, 2564–2572.

Chen, L., Meng, J., Liang, S., Zhang, H., Zhang, W., Liu, M., Tong, Y., Wang, H., Wang, W., Wang, X., Shu, J., 2018. Trade-induced atmospheric mercury deposition over China and implications for demand-side controls. Environ. Sci. Technol. 52, 2036–2045.

China, S.E.P.Ao., 2011. Emission Standard of Air Pollutants for Thermal Power Plants, in, Beijing.

Diamantopoulou, I., Skodras, G., Sakellaropoulos, G., 2010. Sorption of mercury by activated carbon in the presence of flue gas components. Fuel Process. Technol. 91, 158–163.

Fan, X., Li, C., Zeng, G., Zhang, X., Tao, S., Lu, P., Tan, Y., Luo, D., 2012. Hg° removal from simulated flue gas over CeO_2/HZSM-5. Energy Fuels 26, 2082–2089.

Galbreath, K.C., Zygarlicke, C.J., 1996. Mercury speciation in coal combustion and gasification flue gases. Environ. Sci. Technol. 30, 2421–2426.

Gao, Y., Zhang, Z., Wu, J., Duan, L., Umar, A., Sun, L., Guo, Z., Wang, Q., 2013. A critical review on the heterogeneous catalytic oxidation of elemental mercury in flue gases. Environ. Sci. Technol. 47, 10813–10823.

Gustin, M., Ladwig, K., 2010. Laboratory investigation of Hg release from flue gas desulfurization products. Environ. Sci. Technol. 44, 4012–4018.

He, C., Shen, B., Li, F., 2016a. Effects of flue gas components on removal of elemental mercury over Ce–MnO_x/Ti-PILCs. J. Hazard. Mater. 304, 10–17.

He, C., Shen, B., Chi, G., Li, F., 2016b. Elemental mercury removal by CeO_2/TiO_2-PILCs under simulated coal-fired flue gas. Chem. Eng. J. 300, 1–8.

Li, H., Wu, C.-Y., Li, Y., Zhang, J., 2011. CeO_2-TiO_2 catalysts for catalytic oxidation of elemental mercury in low-rank coal combustion flue gas. Environ. Sci. Technol. 45, 7394–7400.

Li, H., Wu, C.-Y., Li, Y., Li, L., Zhao, Y., Zhang, J., 2012. Role of flue gas components in mercury oxidation over TiO_2 supported MnO_x-CeO_2 mixed-oxide at low temperature. J. Hazard. Mater. 243, 117–123.

Li, H., Wu, C.-Y., Li, Y., Li, L., Zhao, Y., Zhang, J., 2013. Impact of SO_2 on elemental mercury oxidation over CeO_2-TiO_2 catalyst. Chem.Eng. J. 219, 319–326.

Lopez-Anton, M.A., Yuan, Y., Perry, R., Maroto-Valer, M.M., 2010. Analysis of mercury species present during coal combustion by thermal desorption. Fuel 89, 629–634.

Ma, J., Liu, Z., Liu, Q., Guo, S., Huang, Z., Xiao, Y., 2008. SO_2 and NO removal from flue gas over V_2O_5/AC at lower temperatures—role of V_2O_5 on SO_2 removal. Fuel Process. Technol. 89, 242–248.

Niu, Q., Luo, J., Sun, S., Chen, Q., Lu, J., 2015. Effects of flue gas components on the oxidation of gaseous Hg° by dielectric barrier discharge plasma. Fuel 150, 619–624.

Presto, A.A., Granite, E.J., 2006. Survey of catalysts for oxidation of mercury in flue gas. Environ. Sci. Technol. 40, 5601–5609.

Rumayor, M., Fernandez-Miranda, N., Lopez-Anton, M.A., Diaz-Somoano, M., Martinez-Tarazona, M.R., 2015. Application of mercury temperature programmed desorption (Hg-TPD) to ascertain mercury/char interactions. Fuel Process. Technol. 132, 9–14.

Saha, A., 2014. Investigation of changes in surface chemistries on virgin and brominated activated carbon sorbents during mercury capture: before and after regeneration. Energy Fuels 28, 4021–4027.

Smirnov, M.Y., Kalinkin, A.V., Pashis, A.V., Prosvirin, I.P., Bukhtiyarov, V.I., 2014. Interaction of SO_2 with Pt model supported catalysts studied by XPS. J. Phys. Chem. C 118, 22120–22135.

Streets, D.G., Devane, M.K., Lu, Z., Bond, T.C., Sunderland, E.M., Jacob, D.J., 2011. All-time releases of mercury to the atmosphere from human activities. Environ. Sci. Technol. 45, 10485–10491.

Sun, P., Zhang, B., Zeng, X., Luo, G., Li, X., Yao, H., Zheng, C., 2017. Deep study on effects of activated carbon's oxygen functional groups for elemental mercury adsorption using temperature programmed desorption method. Fuel 200, 100–106.

Tong, L., Xu, W., Zhou, X., Liu, R., Zhu, T., 2015. Effects of multi-component flue gases on Hg° removal over HNO_3-Modified activated carbon. Energy Fuels 29, 5231–5236.

United States Environmental Protection Agency (U.S. EPA), 2013. Mercury and Air Toxics Standards. U.S. EPA, Washington, D.C. http://www.epa.gov/mats/actions.html.

Wang, Y., Li, C., Zhao, L., Xie, Ye., Zhang, X., Zeng, G., Wu, H., Zhang, J., 2016. Study on the removal of elemental mercury from simulated flue gas by Fe_2O_3-CeO_2/AC at low temperature. Environ. Sci. Pollut. Res. 23, 5099–5110.

Wen, X., Li, C., Fan, X., Gao, H., Zhang, W., Chen, L., Zeng, G., Zhao, Y., 2011. Experimental study of gaseous elemental mercury removal with CeO_2/γ-Al_2O_3. Energy Fuels 25, 2939–2944.

Wu, Sj., Katayama, R., Uddin, M.A., Sasaoka, E., Xie, Z.-m., 2015. Study on reactivity of HgO over activated carbon with HCI and SO_2 in the presence of moisture by temperature-programmed decomposition desorption mass spectrometry. Energy Fuels 29, 6598–6604.

Xie, Y., Li, C., Zhao, L., Zhang, J., Zeng, G., Zhang, X., Zhang, W., Tao, S., 2015. Experimental study on Hg° removal from flue gas over columnar MnO_x-CeO_2/activated coke. Appl. Surf. Sci. 333, 59–67.

Xu, W., Tong, L., Qi, H., Zhou, X., Wang, J., Zhu, T., 2015. Effect of flue gas components on Hg° oxidation over Fe/HZSM-5 catalyst. Ind. Eng. Chem. Res. 54, 146–152.

Xu, H., Ma, Y., Huang, W., Mei, J., Zhao, S., Qu, Z., Yan, N., 2017. Stabilization of mercury over Mn-based oxides: speciation and reactivity by temperature programmed desorption analysis. J. Hazard. Mater. 321, 745–752.

Yang, J., Ma, S., Zhao, Y., Zhang, J., Liu, Z., Zhang, S., Yi, Z., Liu, Y., Feng, Y., Kai, X., 2017. Mercury emission and speciation in fly ash from a 35 MW th large pilot boiler of oxyfuel combustion with different flue gas recycle. Fuel 195, 174–181.

Zhang, A., Zheng, W., Song, J., Hu, S., Liu, Z., Xiang, J., 2014. Cobalt manganese oxides modified titania catalysts for oxidation of elemental mercury at low flue gas temperature. Chem.Eng. J. 236, 29–38.

Zhang, X., Li, Z., Wang, J., Tan, B., Cui, Y., He, G., 2017. Reaction mechanism for the influence of SO_2 on Hg° adsorption and oxidation with $Ce_{0.1}$-Zr-MnO_2. Fuel 203, 308–315.

Zhou, Q., Duan, Y.-F., Hong, Y.G., Zhu, C., She, M., Zhang, J., Wei, H.Q., 2015. Experimental and kinetic studies of gas-phase mercury adsorption by raw and bromine modified activated carbon. Fuel Process. Technol. 134, 325–332.

Zhou, Z., Liu, X., Zhao, B., Shao, H., Xu, Y., Xu, M., 2016. Elemental mercury oxidation over manganese-based perovskite-type catalyst at low temperature. Chem.Eng. J. 288, 701–710.

Zhou, Q., Duan, Y., Chen, M., Liu, M., Lu, P., 2017. Studies on mercury adsorption species and equilibrium on activated carbon surface. Energy Fuels 31, 14211–14218.

Zhu, Y., Han, X., Huang, Z., Hou, Y., Guo, Y., Wu, M., 2018. Superior activity of CeO_2 modified V_2O_5/AC catalyst for mercury removal at low temperature. Chem. Eng. J. 337, 741–749.

Zhu, Y., Hou, Y., Wang, J., Guo, Y., Huang, Z., Han, X., 2019. Effect of SCR atmosphere on the removal of Hg° by a V_2O_5-CeO_2/AC catalyst at low temperature. Environ. Sci. Technol. 53, 5521–5527.