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Regeneration mechanism of CeO_2-TiO_2 sorbents for elemental mercury capture from syngas

Kunzan Qiu, Wenhui Hou, Jinsong Zhou†, Shuaiqi Meng, and Xiang Gao

State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, P. R. China

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Abstract–The characteristics of mercury desorption on spent CeO_2-TiO_2 (CeTi) sorbents were investigated to improve the cyclic regeneration removal activity. Mercury was significantly released in the form of elemental mercury at temperatures ranging from 250 to 280 °C. Mercury desorption had a significant correlation with regeneration temperature, but was independent of the heating rate and regeneration conditions. The optimal regeneration temperature was 500 °C. The CeTi sorbents could be easily restored by simple heating and exhibited superior activity over several capture-regeneration cycles. The amount of released mercury almost equaled the adsorbed mercury on the surface of the CeTi sorbent, indicating that most of the adsorbed mercury was released during the heating process.

Keywords: Mercury, Regeneration, Syngas, Removal, CeO_2

INTRODUCTION

Mercury, a heavy metal, is the only global pollutant that can be transmitted over long distances in a gaseous form [1,2]. In the 1950s, the sensational event of "minamata disease" occurred at Minamata Bay in Japan. Early this century, millions of women were tested with excessive mercury levels in their bodies, which showed that mercury pollution is a widespread concern in the international community and has become one of the hot fields of environmental pollution research worldwide. Because of the serious dangers of mercury emissions to humans and the environment, America, Canada, the European Union and many other countries and regions in the world have formulated relevant laws and regulations [3,4].

Coal gasification is a promising coal conversion technology that is a source of electrical power generation. In the gasification process, most of the mercury in the coal is released in the form of elemental mercury. With the rapid development of coal gasification technology, it is very important to develop effective mercury control technology.

In our previous research, the CeTi sorbent was developed to remove Hg^0 and exhibited high activity for mercury removal from syngas [5,6]. However, the high cost of CeTi sorbents is a current limitation for developing this technology. Regeneration can restore the mercury removal ability of sorbents, so it is beneficial to decrease the adsorption cost. For industrial applications, the structure of the sorbent will degrade if products accumulate on the surface or the gaps of the sorbent, and its absorption capacity will decrease. Therefore, the durability of sorbents is limited. The performance of a sorbent after recycling is an important factor to assess, assuming that few changes have been made to the structure of the sorbent.

There are a few effective regeneration methods, such as thermal regeneration, washed regeneration, chemical regeneration, photocatalysis regeneration, and super-critical extraction. Different regeneration methods indicate different reaction mechanisms. In general, once the adsorption product is desorbed, active sites will be vacated, which is a prerequisite for the adsorption progress to continue. Thermal regeneration can improve the vibration energy of adsorption molecules by heating the sorbent at a temperature higher than the pollutant adsorption temperature, and it is a favorable way to release adsorption sites. Thermal regeneration is easy to manipulate under high temperature and inert gas atmospheric conditions. Thermal regeneration has the advantages of easy collection of desorbed mercury, high regeneration efficiency and minimal effects on the activity of the adsorbent; therefore, it has been widely studied [7-9]. Investigated the regeneration performance of Au and Ag. Their results showed that the mercury removal ability of noble metals could be recovered by the thermal regeneration method, greatly reducing the cost of mercury removal.

In this work, the mechanism of mercury desorption under different heating modes was studied. Additionally, the effect of regeneration conditions on the mercury removal activity of CeTi sorbents was investigated. Finally, the regenerability of the CeTi sorbent over several adsorption-regeneration cycles was evaluated. Our purpose was to develop a promising sorbent and to lay the theoretical foundation for its industrial application.

EXPERIMENTAL SECTION

The fixed-bed test system used in the present experiments has been described in our previous publication [5]. The Hg^0 concentration in the gas flow was recorded by a mercury continuous emissions monitor (MS-1A/DM-6B, Nippon Instrument Corporation, Japan). Please refer to Ref. 8 for further details. In each regeneration test, only 0.05 g of the spent sorbent was placed on the quartz wool inside the quartz tube, the temperature of which was con-

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†To whom correspondence should be addressed.
E-mail: zhoujs@zju.edu.cn

Table 1. Experimental conditions

Experiments	Sample	Gas components (1 L·min^{-1})	Temperature (°C)	Heating rate (°C/min)
Set I	Ce0.2Ti	N_2	400/600	5
Set II	Ce0.2Ti	N_2	600	10/15
Set III	Ce0.2Ti	N_2	400/500/600	10
Set IV	Ce0.2Ti	N_2+20% O_2	500	10
Set V	Ce0.2Ti	N_2	500	10

trolled by the tubular furnace. A gas flow rate of 1.0 L·min^{-1} was utilized.

The operating conditions of different sets of regeneration experiments are listed in Table 1. The experiments from set I to set IV were implemented to investigate the effect of the heating mode, regeneration temperature, and regeneration atmosphere on the mercury removal ability of the sorbent. The set V experiment was completed to evaluate the removal performance of the CeTi sorbent over several regeneration cycles. The adsorption experiments were performed under simulated syngas consisting of 30% H_2, 20% CO, 100 ppm H_2S and 1 ppm HCl at 150 °C. The initial concentration of Hg^0 was maintained at 70 μg/m^3.

RESULTS AND DISCUSSION

1. The Characteristics of Mercury Desorption under Different Heating Modes

This set of experiments investigated the law of mercury desorption under two different heating modes: one sample was heated from room temperature to 400 °C and then the heat was preserved, while another sample was heated from room temperature to 600 °C. Both of the sample heating rates were 5 °C/min. As shown in Fig. 1, when the heating temperature was increased gradually, mercury desorption occurred in both heating modes. The main mercury desorption peak appeared at approximately 600 °C, and almost no Hg^{2+} was detected in the experiment; the vast majority of the desorbed mercury existed in the form of elemental mercury. The results showed that HgS, attached to the surface of the sorbent in a chemical adsorption manner, had decomposed and was removed by the carrier gas. The significant amount of HgS decomposition at 260 °C was consistent with the results found by Ozaki et al. [10]. The decomposition reaction is shown in Eq. (1). In addition, for the first heating mode, when the temperature exceeded 400 °C, a

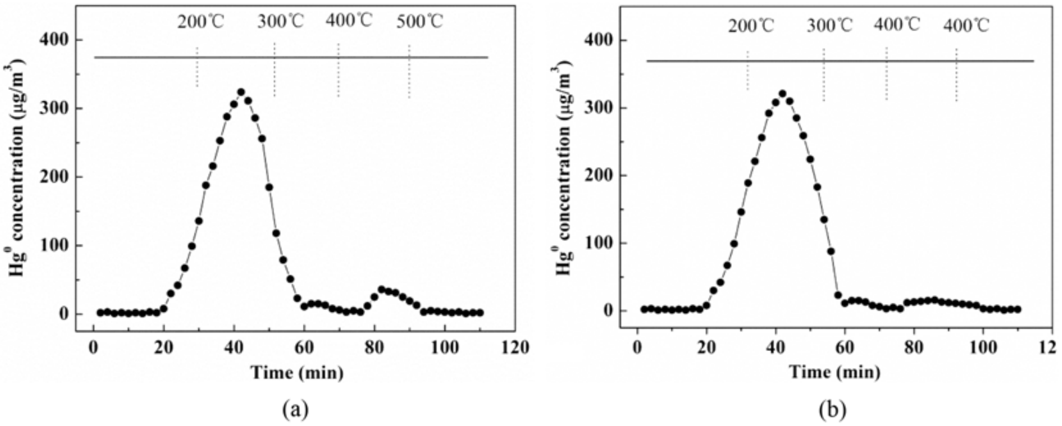


Fig. 1. Characteristic of mercury desorption under different heating mode ((a) Heating from room temperature to 600 °C, (b) heating from room temperature to 400 °C and then heat preservation, both of the heating rate are 5 °C/min).

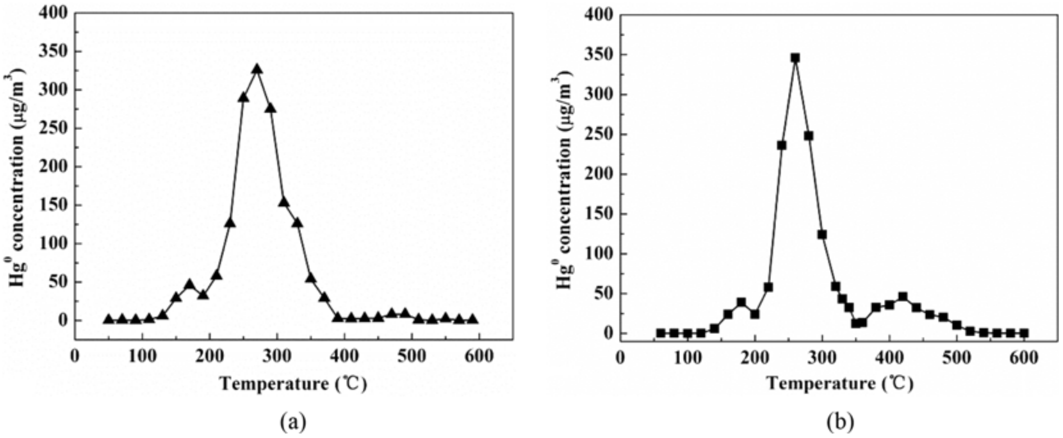


Fig. 2. Characteristic of mercury desorption under different heating rates ((a) Heating rate is 10 °C/min, (b) heating rate is 5 °C/min).

relatively weak mercury desorption peak was also detected; this peak was likely caused by the decomposition of $HgCl_2$ on the surface of the sorbent [64]. Note that research on the decomposition law of $HgCl_2$ is scarce, and therefore the decomposition characteristics are not very clear and further research needs to be conducted.

$$HgS \rightarrow Hg^0 + (1/x)S_x \tag{1}$$

For a more comprehensive evaluation of mercury precipitation characteristics on the CeTi sorbent, a second set of experiments investigated desorption of mercury under different heating rates (10 °C/min and 15 °C/min), the results of which are shown in Fig. 2. As the figure shows, the heating rates had little impact on the precipitation of mercury on the CeTi sorbent. The main mercury desorption peak appeared at approximately 260 °C, and the regeneration efficiencies of the sorbents were almost consistent (greater than 90%) using either heating rate. The results showed that desorption of mercury on the CeTi sorbent is related to the heating temperature and heating rates have insignificant effects. The mercury desorption peak appeared at approximately 170 °C due to a small amount of elemental mercury that remained on the surface of the sorbent as a result of van der Waals forces, causing physical adsorption and precipitation under low heating temperatures [11,12].

2. The Effect of Regeneration Temperature

The regeneration temperature is a key factor for the industrial application of sorbents. Three regeneration temperatures were evaluated in this experiment 300, 400, and 500 °C (Fig. 3). When the regeneration temperature was 300 °C, E_{cap} was 45.3%. When the regeneration temperature was increased to 500 °C, E_{cap} increased to 54.5%. Most of the mercury on the surface of the CeTi sorbent was released at approximately 260 °C. Mercury desorption would be more complete at higher temperatures, and thus, higher temperatures could result in higher mercury removal efficiencies. Further increasing the temperature will cause sulfur to enter the pores of the sorbent and decrease the degree of CeO_2 dispersion on the surface of the TiO_2 support, inhibiting mercury removal [13,14]. Therefore, temperatures higher than 500 °C were not investigated in this study.

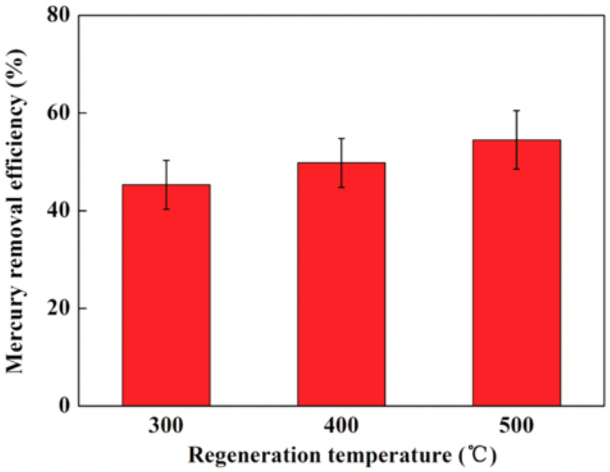


Fig. 3. Effect of regeneration temperature on mercury removal activity.

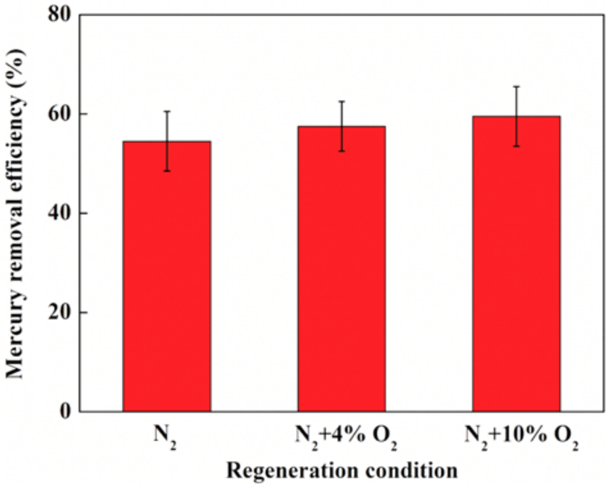


Fig. 4. Effect of regeneration atmosphere on mercury removal activity.

3. Effect of Regeneration Atmosphere

As the research in the third section shows, the CeTi adsorbent consumes its surface storage of oxygen (lattice oxygen and chemisorbed oxygen) to adsorb mercury. If the consumed oxygen can be supplemented during the regeneration process, the regeneration rate of the adsorbent will be greatly improved [15,16]. Therefore, we studied the mercury removal activity of the CeTi adsorbent in the presence of oxygen (Fig. 4). As seen, the presence of oxygen promoted limited regeneration activity of the CeTi adsorbent. After the CeTi adsorbent regenerated under the condition of a 4% O_2 atmosphere, E_{cap} increased from 54.5 to 57.4%. However, when 10% O_2 was added to the regeneration atmosphere again, E_{cap} was almost unchanged. The regeneration process of CeTi was not sensitive to gas phase oxygen, which indicated that the stored oxygen on the adsorbent was superfluous with respect to mercury and that little oxygen is consumed during the mercury adsorption process. Covering the active sites was responsible for degradation of the CeTi sorbent removal performance [17].

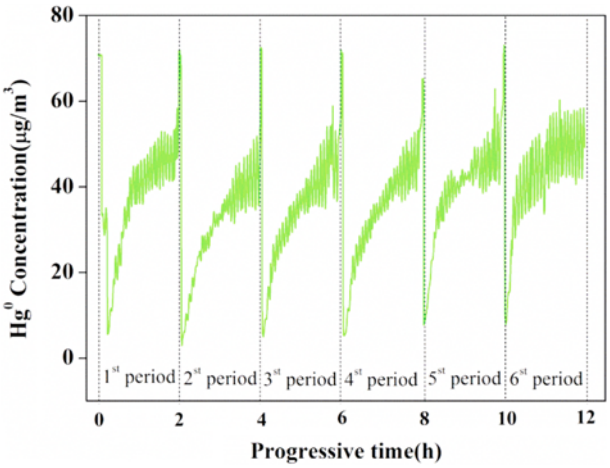


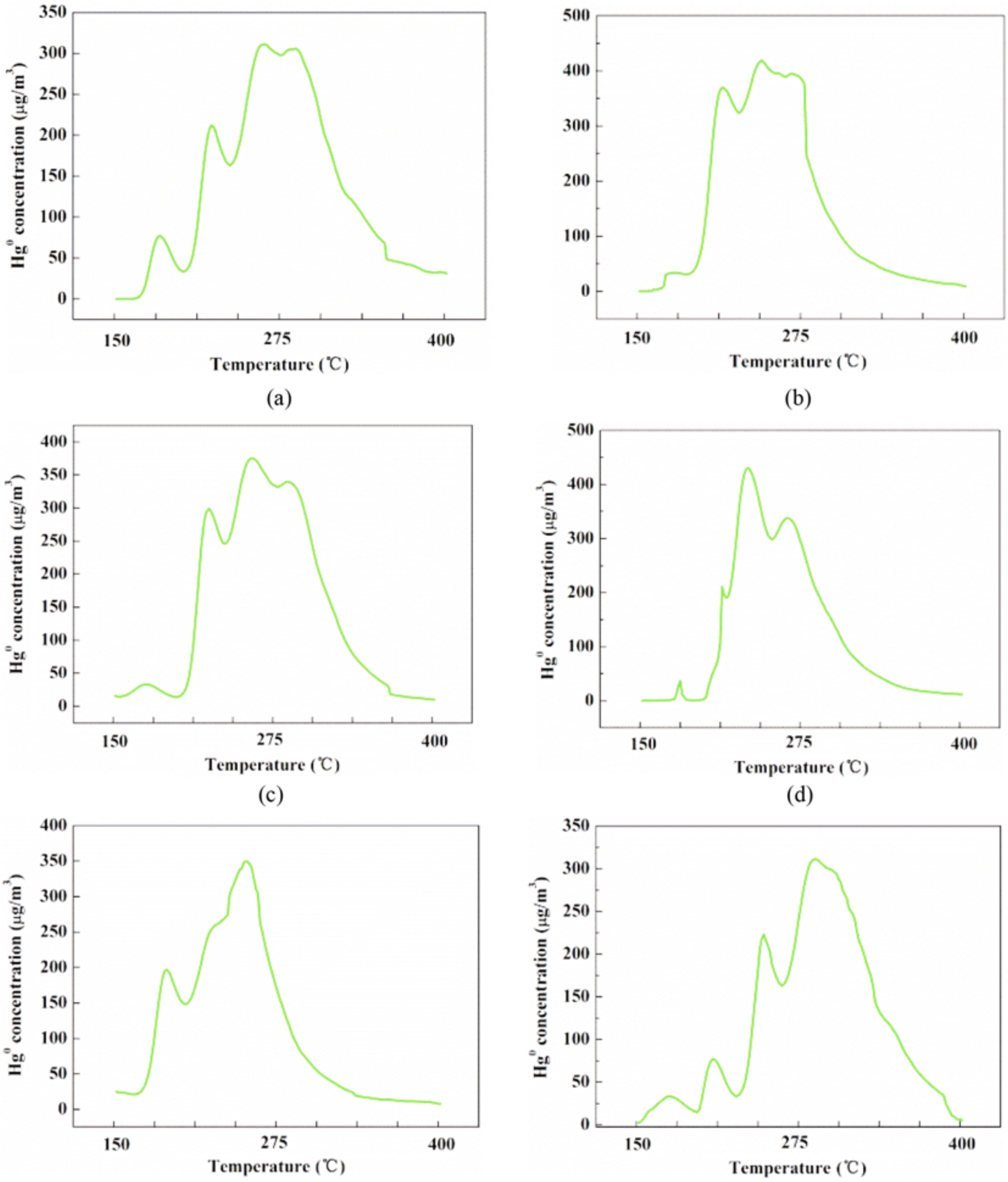
Fig. 5. Mercury penetration curves of CeTi sorbent over several capture-regeneration cycles under N_2 condition.

4. Effect of Regeneration Cycles

The recycling and regeneration performance of the sorbent is an important factor that determines whether the sorbent can be applied to large-scale industry. This set of experiments investigated the mercury removal efficiency of the CeTi sorbent at 150 °C after several adsorption and desorption cycles. The adsorption time was 2 h, and the results are shown in Fig. 5. Fresh sorbent samples and the mercury break-through curve after five regeneration cycles are shown in the sixth stage of the figure. As seen in the figure, the mercury concentration of the reactor outlet gradually increased with the adsorption time. To investigate the mercury removal performance of the sorbent, three parameters were set in this group

Table 2. Activity of CeTi sorbent over five regeneration cycles

Performance parameters	Fresh sample	1st Cycle	2st Cycle	3st Cycle	4st Cycle	5st Cycle
20% Break-through (min)	22	18	11	13	8	6
80% Vreak-through (min)	116	119	118	119	116	86
Hg removal efficiency (%)	50.1	60.5	55.4	54.6	49.8	45.9



(a) (b)

(c) (d)

(e) (f)

Fig. 6. Release characteristics of mercury over several regeneration cycles ((a)-(f) Represents 1st-6st adsorption cycle).

of experiments, including a 20% break-through time (mercury concentration of the reactor outlet was 20 percent of the mercury concentration of the reactor inlet), 80% break-through time (mercury concentration of the reactor outlet was 80 percent of the mercury concentration of the reactor inlet) and the average adsorption efficiency of Hg (E_{cap}).

Table 2 shows the mercury removal performance of the CeTi sorbent over several regeneration cycles. As seen, the 20% mercury break-through threshold condition shifted to an earlier time in the second cycle. However, no obvious fluctuation in the 80% mercury break-through threshold was observed except in the fifth cycle. A mercury removal efficiency higher than that of fresh samples was even observed before the third cycle, e.g., approximately 60.5% mercury removal for the CeTi sorbent at 150 °C. This significant improvement in the mercury removal activity can be attributed to the conversion of oxygen from lattice oxygen to chemical adsorption oxygen [18,19]. Following the fourth cycle, the mercury removal efficiency remained higher than 45%, indicating that CeTi sorbents were good candidates for mercury capture and can be easily restored by simple heating. The decrease in the mercury removal efficiency can be attributed to the accumulation of adsorption product on the active site. In addition, some mercury compounds ($HgCl_x$) were not completely released, which can also inhibit the regeneration activity of CeTi sorbents [20,21].

The release characteristics of mercury in absorption cycles 1-6 are presented in Fig. 6. The CeTi sorbent after adsorption significantly released mercury from 250-280 °C. No obvious Hg^{2+} was observed during the entire regeneration process, indicating that mercury compounds were decomposed at high temperatures [22,23]. Note that a desorption peak was also detected at temperatures lower than 200 °C, which could be due to the release of weakly bound mercury species [24,25]. The adsorption and desorption masses of mercury on the sorbent surface were calculated to evaluate the mass balance of mercury between the adsorption and desorption experiments. As seen in Fig. 7, the amount of released mercury almost equaled the adsorbed mercury on the surface of the CeTi sorbent, indicating that most of the adsorbed mercury except for a small amount of $HgCl_x$ was released by simple heating.

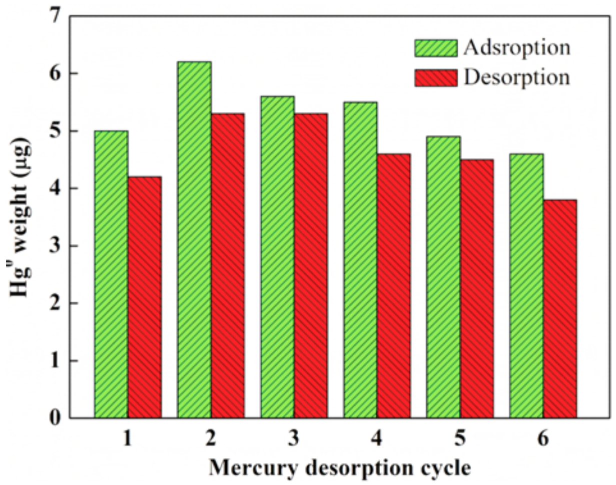


Fig. 7. Amount of adsorbed and desorbed mercury.

CONCLUSIONS

The characteristics of mercury desorption on spent CeO_2-TiO_2 (CeTi) sorbents were investigated to improve the cyclic regeneration removal activity. Mercury was significantly released in the form of elemental mercury at temperatures ranging from 250-280 °C. Mercury desorption had a significant correlation with regeneration temperature, but was independent of the heating rate and regeneration conditions. The optimal regeneration temperature was 500 °C. The CeTi sorbents could be easily restored by simple heating and exhibited superior activity over several capture-regeneration cycles. The amount of released mercury almost equaled the adsorbed mercury on the surface of the CeTi sorbent, indicating that most of the adsorbed mercury was released during the heating process.

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