

Plasma-assisted adsorption of elemental mercury on CeO₂/TiO₂ at low temperatures

Lu Liu¹, Chenghang Zheng², Xiang Gao^{2,*}

¹ School of Energy and Power Engineering, Jiangsu University, Zhenjiang 212013, PR China

² State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, PR China

E-mail: lliuenergy@ujs.edu.cn; xgao1@zju.edu.cn

Abstract. Mercury is a kind of pollutants contained in flue gas which is hazardous for human beings. In this work, CeO₂ was packed in the discharge zone of a plasma reactor to adsorb elemental mercury at low temperatures. Plasma-catalyst reactor can remove Hg⁰ efficiently with CeO₂/TiO₂ catalysts packed in the discharge zone. The Hg⁰ concentration continued to decrease gradually when the plasma was turned on, but not sank rapidly. This tendency was different with other catalysts. The treatment of plasma to CeO₂/TiO₂ catalysts has a promotion effect on the adsorption of Hg⁰. Plasma has the effect of changing the surface properties of the catalysts and the changes would reconstitute if the condition changed. The long-running test demonstrated that this method is an effective way to remove Hg⁰. The removal efficiency remained at above 99% throughout 12 hours when plasma had been turned on (15kV, 0.5 g packed CeO₂/TiO₂).

1. Introduction

Mercury is a kind of pollutants contained in the flue gas [1]. It is hazardous for human beings and easy to accumulate in the organisms [2]. With decades of studies, a variety of technologies has been proposed to remove elemental mercury (Hg⁰) from flue gas [3-5]. Among these technologies, adsorption of mercury on adsorbent is the most efficient one.

Various manganese oxides and ceria were selected for Hg⁰ removal because of their high activity, low price and environmental friendliness, making them possible for the application [6-8]. Ma et al. [3] synthesized MnO₂/CeO₂-MnO₂ hierarchical binary oxides that exhibited excellent Hg⁰ removal performance, 89% at 150 °C under 4% O₂. MnO₂ was the primary active site for Hg⁰ catalytic oxidation. Fan et al. [8] reported that impregnation with CeO₂ significantly enhanced the Hg⁰ removal ability of activated carbon fibre, particularly with the loading value of 6%. Guo et al. [9] used MnOx as the main catalytic component, with Mo and/or Ru to improve the catalytic activity, to convert Hg⁰ to its oxidized form at low temperatures (around 150 °C) and the conversion efficiency of Hg⁰ reached 95% with Mo-Ru-Mn catalyst and 8 ppmv HCl.

Non-thermal plasma provided an innovative approach to the solution of air pollutants reduction [10, 11]. In our previous study, we found non-thermal plasma has promotion effect on mercury removal by catalysts. The plasma-catalyst system displays a much higher elemental mercury adsorption efficiency than a catalyst only or plasma only system at low temperatures. MnO₂, V₂O₅, Co₃O₄, Fe₂O₃, CuO, and NiO were supported on TiO₂ and used as the packed catalysts [12]. Recently, we found CeO₂/TiO₂ presents a different tendency from the above catalysts. In this work, CeO₂ was packed in the discharge



zone of a plasma reactor to adsorb elemental mercury at low temperatures. Compared with other kinds of catalysts, a different tendency was observed when $\text{CeO}_2/\text{TiO}_2$ packed in the discharge zone.

2. Experimental

The experimental setup for the mercury adsorption contains three parts: the gas generating system, the plasma-catalyst reactor and the detecting system, the same as in Ref. [12]. A mercury permeation device (VICI Metronics) was used to provide a constant feed of Hg^0 concentration. The gas flow was 1.2 L min^{-1} . The gas mixtures for Hg^0 adsorption contained $55\sim 65 \mu\text{g m}^{-3} \text{Hg}^0$ and balance N_2 . The non-thermal plasma was generated by dielectric barrier discharge (DBD). The power supply of the DBD reactor was an AC high voltage power with a frequency of 50 Hz. A MS-1A/DM-6B Hg analyzer (Nippon Inc.) was used to measure the Hg^0 concentrations at both the inlet and outlet of the reactor. All the tests were performed at room temperature and atmospheric pressure. The $\text{CeO}_2/\text{TiO}_2$ catalysts were prepared by an impregnation method as stated in Ref. [12]. The loading amount is only 1% wt. The BET surface area of the $\text{CeO}_2/\text{TiO}_2$ is $77.0 \text{ m}^2/\text{g}$, similar to TiO_2 ($77.5 \text{ m}^2/\text{g}$).

3. Results and discussion

Usually, after the gas flow passing through the plasma-catalyst reactor and the plasma being turned on, the outlet Hg^0 concentration would stay at a certain value within 60 min, for example, Hg^0 adsorption with TiO_2 catalysts packed in the discharge zone, as shown in Figure 1. However, when $\text{CeO}_2/\text{TiO}_2$ packed in the discharge zone, it presented a different tendency (Figure 1). The Hg^0 concentration continued to decrease gradually even 120 min after the plasma being turned on, until the concentration was close to zero. Besides, when the discharge voltage increased, the concentration has no obvious decline, but still decrease gradually with a higher speed, as shown in Figure 2. Ceria has unique oxygen storage capacity. The results above indicate that the oxygen atoms in ceria take part in the reaction gradually, but not at once.

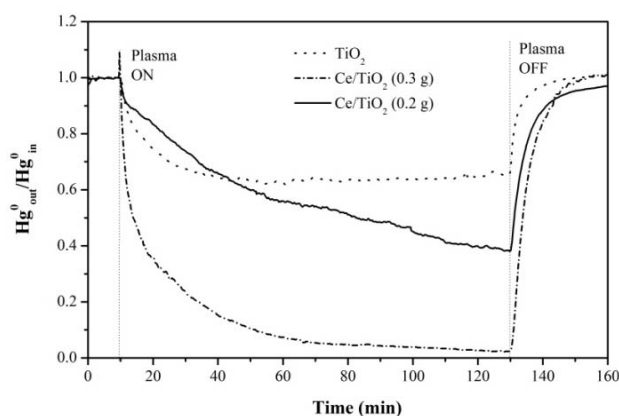


Figure 1. Hg^0 adsorption with TiO_2 and $\text{CeO}_2/\text{TiO}_2$ catalysts packed in the discharge zone (14 kV, 0.2 g packed catalyst).

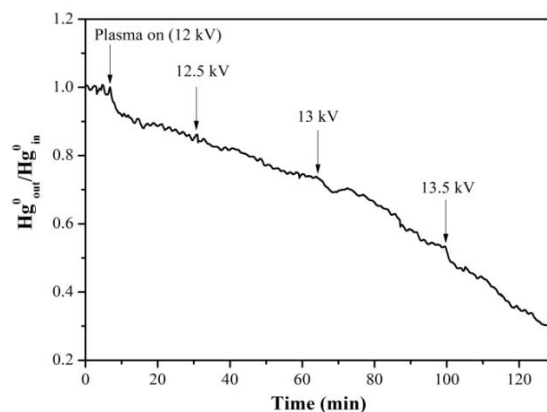


Figure 2. Effect of discharge voltage on Hg^0 adsorption with $\text{CeO}_2/\text{TiO}_2$ catalysts packed in the discharge zone (0.05 g packed catalyst).

Figure 3 shows the Hg^0 adsorption in the second period in a plasma-catalyst system. After the catalyst exposed in N_2 , the adsorption curve did not decrease gradually anymore and the adsorption efficiency was higher than in the period. However, after the catalyst was exposed in air, the adsorption efficiency was much lower. Regarding the first period as a treatment of the plasma, this result indicate that plasma has the effect of changing the surface properties of the catalysts and the changes would reconstitute if the condition changed.

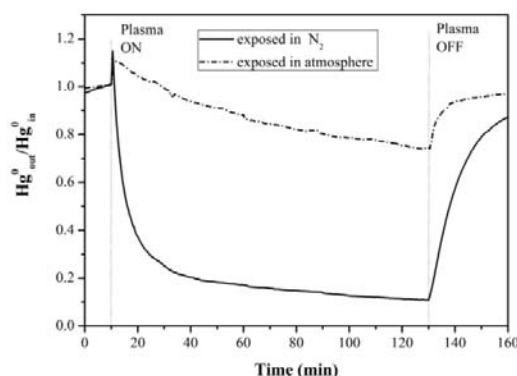


Figure 3. Hg^0 adsorption of the second period in a plasma-catalyst system (14 kV, 0.2 g packed catalyst).

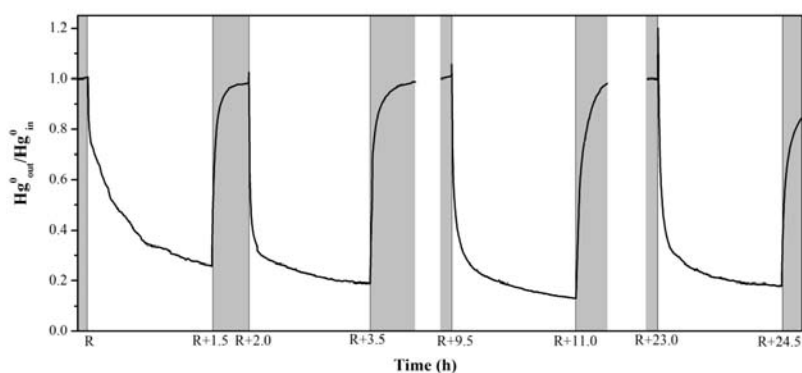


Figure 4. Repeated test of Hg^0 adsorption with $\text{CeO}_2/\text{TiO}_2$ catalysts packed in the discharge zone (14 kV, 0.2 g packed catalyst).

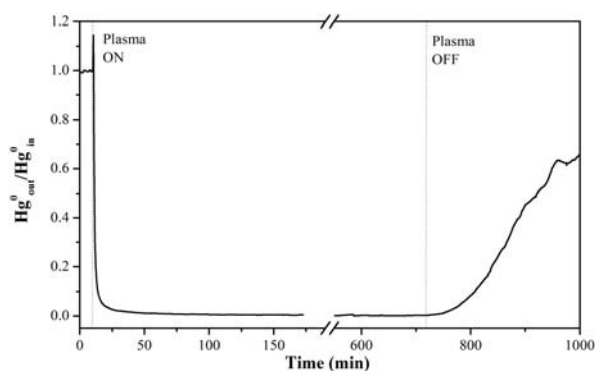


Figure 5. Long-running test of Hg^0 adsorption with $\text{CeO}_2/\text{TiO}_2$ catalysts packed in the discharge zone (15 kV, 0.5 g packed catalyst).

The treatment of plasma to $\text{CeO}_2/\text{TiO}_2$ catalysts has a promotion effect on the adsorption of Hg^0 . As shown in Figure 4, the adsorption efficiency in the second period was higher than in the first period. After 6 hours' exposure in N_2 atmosphere, the adsorption efficiency in the third period was still higher than in the second period. After 12 hours' exposure in N_2 atmosphere, the adsorption efficiency in the fourth period became a little lower.

The adsorption capacity of the plasma-catalyst system is particularly high, compared with the catalyst only system. Figure 5 shows the result of a 12-hour long-running test of Hg^0 adsorption with

CeO₂/TiO₂ catalysts packed plasma-catalyst system. The removal efficiency remained at above 99% throughout the period when plasma had been turned on. When the plasma was turned off, the Hg⁰ concentration went up with a very slow speed, whereas it returned to its initial value rapidly after 1.5 hour's discharge (Figure 1, Figure 3 and Figure 4). This result demonstrated that with CeO₂/TiO₂ catalysts packed in the discharge zone, the method of plasma-assisted adsorption is an effective way to remove Hg⁰.

4. Conclusions

Plasma-catalyst reactor can remove Hg⁰ efficiently with CeO₂/TiO₂ catalysts packed in the discharge zone. The Hg⁰ concentration continued to decrease gradually when the plasma was turned on, but not sank rapidly. This tendency was different with other catalysts. The treatment of plasma to CeO₂/TiO₂ catalysts has a promotion effect on the adsorption of Hg⁰. The long-running test demonstrated that this method is an effective way to remove Hg⁰.

Acknowledgments

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