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# Experimental Study of Gaseous Elemental Mercury Removal with $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$

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**ABSTRACT:** The  $\text{Hg}^0$  removal ability of  $\gamma\text{-Al}_2\text{O}_3$  impregnated with cerium dioxide ( $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ ) was tested in the experimental flue gas of  $\text{N}_2 + \text{O}_2 + \text{NO} + \text{SO}_2 + \text{H}_2\text{O}$ . Brunauer–Emmett–Teller (BET), X-ray diffractogram (XRD), and thermogravimetric (TG) analyses were used to characterize the samples. The effects of  $\text{CeO}_2$  loading values, reaction temperatures, reaction time, and individual flue gas components, including  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}(\text{g})$ , on the  $\text{Hg}^0$  removal efficiency were investigated. The results show that the  $\text{Hg}^0$  removal efficiency of  $\gamma\text{-Al}_2\text{O}_3$  can be greatly improved by  $\text{CeO}_2$  and, at a test temperature of 350 °C, the best suitable loaded mass percentage of  $\text{CeO}_2$  is 9%. In the temperature range from 150 to 350 °C, the  $\text{Hg}^0$  removal efficiency using  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  increases with the increase of the temperature and then decreases above 350 °C, except virgin  $\gamma\text{-Al}_2\text{O}_3$ . In addition, the presence of  $\text{O}_2$  and  $\text{NO}$  have positive effects on the  $\text{Hg}^0$  removal efficiency, while the presence of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  inhibited it. Furthermore, prolonging the reaction time had a small negative effect on the  $\text{Hg}^0$  removal performance, indicating that the catalyst of  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  possesses thermostability.

## 1. INTRODUCTION

Mercury has been a well-known environmental pollutant for several decades, because it has detrimental effects on human health and the environment because of its volatility, persistence, bioaccumulation, and toxicity.<sup>1–3</sup> Consequently, mercury emissions are receiving more and more attention over recent years. The United Nations Environment Program<sup>4</sup> proposed a global legally binding paper on mercury emissions in 2010, and global mercury pollution control is becoming a topic of increasing legislative and scientific focus.

According to refs 5–7, there are mainly three forms of mercury in coal-fired flue gas: elemental mercury ( $\text{Hg}^0$ ), oxidized mercury ( $\text{Hg}^{2+}$ ), and particle-bound mercury ( $\text{Hg}^{\text{p}}$ ). Different forms of mercury have different physical and chemical properties. Specifically,  $\text{Hg}^{2+}$  is water-soluble and can be removed by the wet flue gas desulfurization (WFGD) system;  $\text{Hg}^{\text{p}}$  can be captured by a dust removal device, e.g., electrostatic precipitators (ESPs). However, in terms of  $\text{Hg}^0$ , it is insufficiently captured because of its high volatility and low solubility in water. Hence, the study on  $\text{Hg}^0$  removal from flue gas is becoming a scientific focus. Several methods, such as the particulate adsorption method, oxidation–reduction method, and chemical sedimentation method, have been proposed for control of  $\text{Hg}^0$  emissions and evaluated from bench to pilot scale in the past few decades.<sup>8–11</sup> Among those schemes, the major drawbacks of the particulate adsorbent are high costs, poor capacity, narrow temperature range of application, and slow regeneration and adsorption rates,<sup>12</sup> and therefore, the oxidation–reduction method exhibits a promising future. In this method, the catalyst is the most important element because it plays a dominant role in the operating costs and  $\text{Hg}^0$  removal performance.

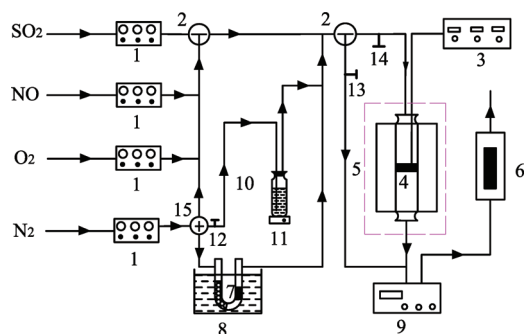
At present, many catalysts, such as  $\text{V}_2\text{O}_5/\text{AC}$ ,  $\text{MnO}_2/\text{AC}$ , and  $\text{Fe}_2\text{O}_3/\text{TiO}_2$ , have been used in the oxidation–reduction

method and proven to be effective for  $\text{Hg}^0$  removal.<sup>13–16</sup> However, it was seldom reported that  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  was used as a catalyst in the  $\text{Hg}^0$  oxidation–reduction or capture process. As reported, cerium oxide ( $\text{CeO}_2$ ), as a nontoxic, abundant, and inexpensive rare earth material, attracted considerable attention for its potential application as fast ion conductors, oxygen-storage capacitors, catalysts, ultraviolet (UV) blockers, and polishing materials.<sup>17–19</sup> Most importantly, it was also reported that  $\text{CeO}_2$  can enhance the  $\text{Hg}^0$  removal efficiency of many catalysts.<sup>20,21</sup> Nevertheless, pure ceria has poor thermal stability, and it undergoes a rapid sintering at higher temperatures, thereby losing oxygen storage capacity (OSC), which would lead to the deactivation of the catalysts. Therefore, many efforts have been devoted to the chemical synthesis of metal oxides impregnated with  $\text{CeO}_2$ . The mixing of two different oxides offers an opportunity not only to improve the performance of the involved metal oxide but also to form new stable compounds that may lead to totally different physicochemical properties and catalytic behavior from the individual components.<sup>22</sup>  $\gamma\text{-Al}_2\text{O}_3$  has important applications as an industrial catalyst support, catalyst, adsorbent, or ceramic raw material, because of its low costs, high surface area and porosity, good thermal stability, high mechanical strength, and extensive variability of acid–base properties.<sup>23–26</sup> Hence, the major objective of present study is to perform an experimental study to investigate the  $\text{Hg}^0$  removal using  $\text{CeO}_2$  supported by  $\gamma\text{-Al}_2\text{O}_3$  ( $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ ) as the catalyst. Experimental studies were carried out on a lab-scale fixed-bed system. The simulated flue gas system included  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{H}_2\text{O}$ , and gaseous  $\text{Hg}^0$ . During the course of the study, different operating conditions, including loading values of  $\text{CeO}_2$ , reaction

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**Figure 1.** Flow diagram of the experimental setup for  $\text{Hg}^0$  removal: (1) mass flow controller, (2) three-way valve, (3) temperature controller, (4) catalyst, (5) fixed-bed reactor, (6) exhaust gas collector, (7)  $\text{Hg}^0$  permeation tube, (8) water bath, (9) Hg analyzer, (10) water bubbler, (11) heating plate, (12–14) valves, and (15) four-way valve.

temperatures, reaction time, and flue gas components on the removal efficiency were discussed.

## 2. EXPERIMENTAL SECTION

**2.1. Catalyst Preparation.** First, the commercially available  $\gamma\text{-Al}_2\text{O}_3$  was ground, then washed with deionized water, and dried in an electric blast drying oven at  $90^\circ\text{C}$  for 24 h. After that, the sample was stored in a desiccator for future use.

Samples of  $\gamma\text{-Al}_2\text{O}_3$  impregnated with  $\text{CeO}_2$  (loading values were 3, 6, 9, 12, and 15 wt %) were prepared by the thermal decomposition of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  loaded on  $\gamma\text{-Al}_2\text{O}_3$  as follows: At first,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was dissolved in deionized water to form the solution. Then,  $\gamma\text{-Al}_2\text{O}_3$  was added to the solution with stirring in a proportion corresponding to different loading values varied from 3 to 15 wt %. Next, the samples were dried in an electric blast drying oven at  $100^\circ\text{C}$  for 12 h. After this, the dried samples of  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  were calcined in a muffle furnace at  $500^\circ\text{C}$  for 4 h and then cooled to ambient temperature. At last, the samples were stored in a desiccator for future use.

**2.2. Catalyst Characterization.** X-ray diffractogram (XRD) measurements were carried out with a diffractometer to determine the crystal species distribution of the catalyst. The Rigaku Rotaflex D/Max-C system has Cu  $K\alpha$  radiation as the X-ray source. The accelerating voltage and the applied current were 35 kV and 30 mA, respectively.

The Brunauer–Emmett–Teller (BET) theory was used to calculate the surface area, total pore volume, and pore size of the catalysts from the measured nitrogen adsorption isotherm at  $-196^\circ\text{C}$  obtained with a Micromeritics ASAP 2010 analyzer. All of the  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  powders were degassed at  $120^\circ\text{C}$  prior to BET measurements.

The thermogravimetric (TG) analyses of samples were performed with a TG analyzer (STA-409PC/PG). For each test, approximately 10 mg of sample was heated from  $80$  to  $800^\circ\text{C}$  at the heating rate of  $10^\circ\text{C min}^{-1}$ .

**2.3. Experimental Setup and Procedure.** Research on the  $\text{Hg}^0$  removal was carried out in a specially designed system (Figure 1). The simulated flue gas consisted of five major gases:  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$ . Thereinto, the  $\text{N}_2$  flow was distributed into three branches. The first stream converged with the individual stream of  $\text{SO}_2$ ,  $\text{NO}$ , and  $\text{O}_2$  and formed the main gas flow. The second  $\text{N}_2$  stream passed through a heated water bubbler (10) (with an inner diameter of 5 cm) to introduce  $\text{H}_2\text{O}(\text{g})$  into the simulated flue gas system. The third  $\text{N}_2$  stream was used as  $\text{Hg}^0$ -laden gas stream by passing through the  $\text{Hg}^0$  permeation tube (7). To guarantee a constant permeation concentration, the  $\text{Hg}^0$  permeation tube was placed in a U-shaped glass tube, which was immersed in a constant temperature ( $45 \pm 0.5^\circ\text{C}$ ) water bath (8). The gas flow rate was controlled in each experiment by mass flow

**Table 1.** Porous Structure Parameters of the Samples

sample	BET surface area ( $\text{m}^2/\text{g}$ )	total pore volume ( $\text{cm}^3/\text{g}$ )	pore size (nm)
$\gamma\text{-Al}_2\text{O}_3$	141.66	0.43	12.06
3% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$	128.71	0.40	11.81
6% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$	111.86	0.39	11.64
9% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$	103.25	0.38	11.53
15% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$	75.12	0.35	11.24

controllers (MFCs) (1), and their concentrations in the system were designed according to the range of basal coal-fired flue gas composition:  $20.02 \mu\text{g}/\text{m}^3$   $\text{Hg}^0$ , 5%  $\text{O}_2$ , 800 ppm  $\text{NO}$ , 1000 ppm  $\text{SO}_2$ , 10%  $\text{H}_2\text{O}(\text{g})$ , and balanced with  $\text{N}_2$  in the system. The total flux of gas was 1 L/min, and the space velocity (SV) was around  $7.6 \times 10^3 \text{ h}^{-1}$ . The fixed-bed reactor (5) is comprised of a digital temperature controller (3) and a quartz tube with an inner diameter of 10 mm. About 1.0 g of catalyst (4) is packed in the quartz tube, which has been demonstrated to have good chemical resistance and inertness toward mercury. The digital temperature controller (3) was employed to keep the fixed-bed reactor at the desired temperature. The exhaust gas from the mercury analyzer was introduced into the activated carbon trap (6) before being expelled into the atmosphere.

During the experiments, the inlet and outlet  $\text{Hg}^0$  concentrations were measured online by the portable mercury analyzer (9) (model QM201G), which was based on cold-vapor atomic fluorescence spectroscopy. The detection limit was  $0.001 \mu\text{g}/\text{m}^3$ , and the nominal range was  $0.01\text{--}100 \mu\text{g}/\text{m}^3$ . In the  $\text{Hg}^0$  analyzer, the sample gas was first dehumidified by silica gel and then entered into the mercury collector, where  $\text{Hg}^0$  was collected by the gold film. After collection, the gold film was heated to the desired high temperature to release  $\text{Hg}^0$ . Throughout the monitoring processes, the mercury analyzer provided a real-time response every 3 min.

In our study, the inlet  $\text{Hg}^0$  concentration was fixed. The experiments were carried out in a batch mode. Before each run, the inlet  $\text{Hg}^0$  concentration was measured by closing the valve (14). Then, after opening the valve (14) and closing the valve (13), the gas flowed through the fixed-bed reactor. At this moment, the value of mercury analyzer was the outlet  $\text{Hg}^0$  concentration. According to the literature, the  $\text{Hg}^0$  removal efficiency ( $\eta$ ) is defined as<sup>27</sup>

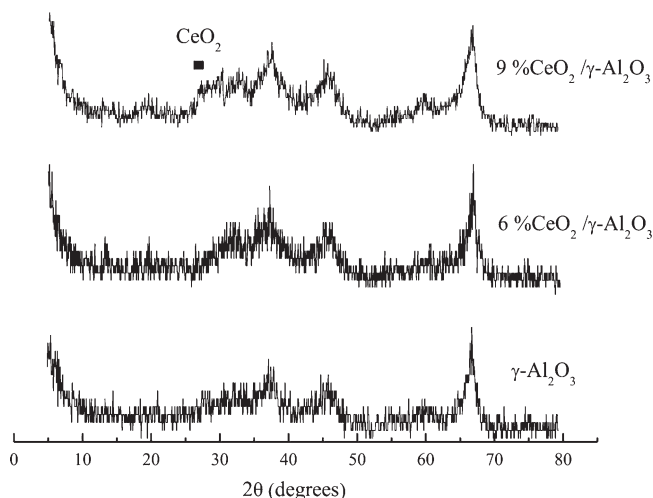
$$\eta = \frac{\text{Hg}_{\text{in}}^0 - \text{Hg}_{\text{out}}^0}{\text{Hg}_{\text{in}}^0} \times 100\% \quad (1)$$

where  $\text{Hg}_{\text{in}}^0$  and  $\text{Hg}_{\text{out}}^0$  are the  $\text{Hg}^0$  inlet and outlet concentrations, respectively.

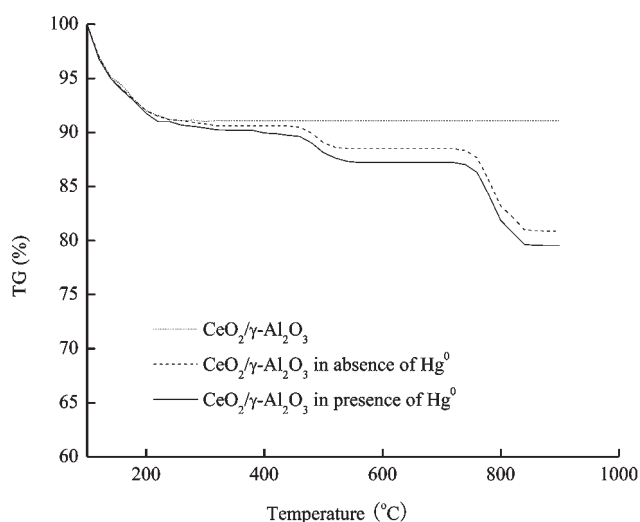
The error of experiment is inevitable. Hence, the mercury removal points in the figures are the average of three experimental data. The relative errors of experimental results were controlled below 1%.

## 3. RESULTS AND DISCUSSION

**3.1. Characteristics of the Sample.** The pore structure parameters of the samples are shown in Table 1. It is obvious that the virgin  $\gamma\text{-Al}_2\text{O}_3$  has the highest BET surface area (approximately  $141.66 \text{ m}^2/\text{g}$ ) and largest pore size (approximately 12.06 nm). However, the BET surface area, total pore volume, and pore size of the samples decrease with the increase of the  $\text{CeO}_2$  loading value. Especially, when the  $\text{CeO}_2$  loading value reaches 15%, the BET surface area is sharply reduced from 141.66 to  $75.12 \text{ m}^2/\text{g}$ , the total pore volume is reduced from 0.43 to  $0.35 \text{ m}^3/\text{g}$ , and the pore size changes from 12.06 to 11.24 nm. The reason may be that the active



**Figure 2.** XRD comparison between samples of virgin  $\gamma$ - $\text{Al}_2\text{O}_3$ , 6%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ , and 9%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ .

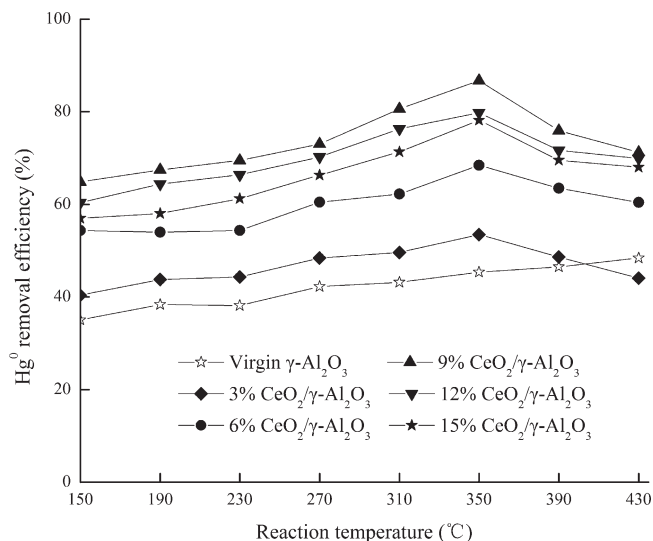


**Figure 3.** TG analyses of the samples.

component,  $\text{CeO}_2$ , is impregnated on the surface of  $\gamma\text{-Al}_2\text{O}_3$  and blocked its pores.<sup>28</sup>

Figure 2 shows the XRD patterns of virgin  $\gamma\text{-Al}_2\text{O}_3$ , 6%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ , and 9%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ . The peaks at the ranges of  $2\theta = 36\text{--}40^\circ$ ,  $44\text{--}48^\circ$ , and  $65\text{--}70^\circ$  in the XRD pattern are corresponding to the characteristic peaks of  $\gamma\text{-Al}_2\text{O}_3$ , which can be detected in these three samples. Furthermore, there is no  $\text{CeO}_2$  characteristic peak for 6%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ . According to the monolayer dispersion theory,<sup>29</sup> an oxide like  $\text{CeO}_2$  has a trend of spontaneous dispersion on the carrier surface and forms a monolayer or sub-monolayer. This is because, when the oxide content is in the range of the threshold value, the oxide is in a monolayer dispersion state and, when the content of oxide is more than the threshold value, the oxide is in a crystalline phase. The XRD pattern of 9%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  shows a weak crystal phase of  $\text{CeO}_2$ , powerfully indicating that the surface of  $\gamma\text{-Al}_2\text{O}_3$  is occupied by  $\text{CeO}_2$ .

TG analyses of fresh  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  and 9%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ , which was used at  $350^\circ\text{C}$  in the presence and absence of  $\text{Hg}^0$  in the flue gas, are shown in Figure 3. There is a quick mass loss as

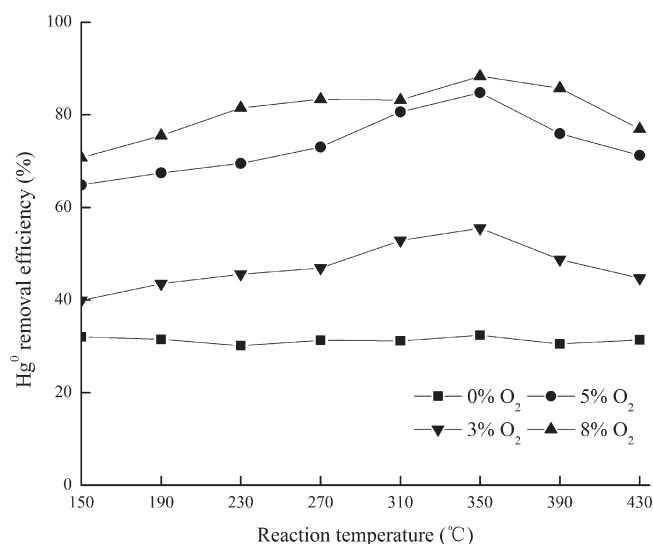


**Figure 4.** Relationship between the  $\text{Hg}^0$  removal efficiency and  $\text{CeO}_2$  loading value supported on  $\gamma\text{-Al}_2\text{O}_3$  at different reaction temperatures (reaction time of 1 h).

the temperature increases up to  $200^\circ\text{C}$  for the three curves, which corresponds to the evaporation of adsorbed water. As for the TG curve of used 9%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  in the presence of  $\text{Hg}^0$  in the flue gas, the small weight loss that occurred at  $400^\circ\text{C}$  can be ascribed to  $\text{HgO}$ .<sup>30</sup> As the pyrolysis temperature increases to  $450^\circ\text{C}$ , the weight losses of used 9%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ , which was used at  $350^\circ\text{C}$  in the presence and absence of  $\text{Hg}^0$  in the flue gas, can be attributed to the decomposition of  $\text{Ce}(\text{SO}_4)_2$  and their weight loss at  $750^\circ\text{C}$  can be ascribed to the decomposition of  $\text{Ce}_2(\text{SO}_4)_3$  according to the related research.<sup>31</sup>

**3.2. Effects of the Loading Value and Reaction Temperature.** Figure 4 presents the relationship between the  $\text{Hg}^0$  removal efficiency and  $\text{CeO}_2$  loading value supported on  $\gamma\text{-Al}_2\text{O}_3$  at different reaction temperatures (reaction time = 1 h). As shown in this figure,  $\gamma\text{-Al}_2\text{O}_3$ -loaded 9%  $\text{CeO}_2$  shows significantly higher  $\text{Hg}^0$  removal efficiency. At the temperature of  $350^\circ\text{C}$ , with the loading value of  $\text{CeO}_2$  changing from 0 to 9 wt %,  $\text{Hg}^0$  removal efficiency increases from 45.36 to 86.76%, which indicates that  $\text{CeO}_2$  has an obvious accelerative effect on  $\text{Hg}^0$  removal. Figure 3 illustrates that  $\text{HgO}$  is the major product of the  $\text{Hg}^0$  removal reaction over  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ , indicating that  $\text{CeO}_2$  can catalyze the oxidation reaction of  $\text{Hg}^0$ .<sup>19</sup> The processes can be described as follows: First,  $\text{Hg}^0$  in the flue gas collides with the catalyst and is adsorbed onto its surface. Then, the adsorbed  $\text{Hg}^0$  is oxidized by the active constituent on the sample surface, leading to the formation of  $\text{Hg}^{2+}$  presented as  $\text{HgO}$ . Therefore, the more the  $\text{CeO}_2$  loading value, the higher the  $\text{Hg}^0$  removal efficiency of  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ . However, the  $\text{Hg}^0$  removal efficiency does not enhance consistently but decreases when the  $\text{CeO}_2$  loading value increases above 9 wt %. Especially with a loading value of 15 wt %, the  $\text{Hg}^0$  removal efficiency decreases to 78.17%. The possible reason can be ascribed to the fact that the surface area, total pore volume, and pore size of  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  decrease with the increase of  $\text{CeO}_2$ , as shown in Table 1. The decrease of the surface area prevents the valid collision between  $\text{Hg}^0$  and  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ .<sup>32</sup> Although  $\text{CeO}_2$  can promote the  $\text{Hg}^0$  removal, its positive effect is weaker than its side effect when the  $\text{CeO}_2$  loading is higher than 9 wt %. Therefore, the loading value

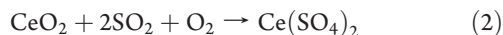




**Figure 5.** Effect of the O<sub>2</sub> concentration on Hg<sup>0</sup> removal efficiency at different reaction temperatures (9% CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and reaction time of 1 h).

of CeO<sub>2</sub> supported on γ-Al<sub>2</sub>O<sub>3</sub> possesses an optimum value (9 wt % in this paper).

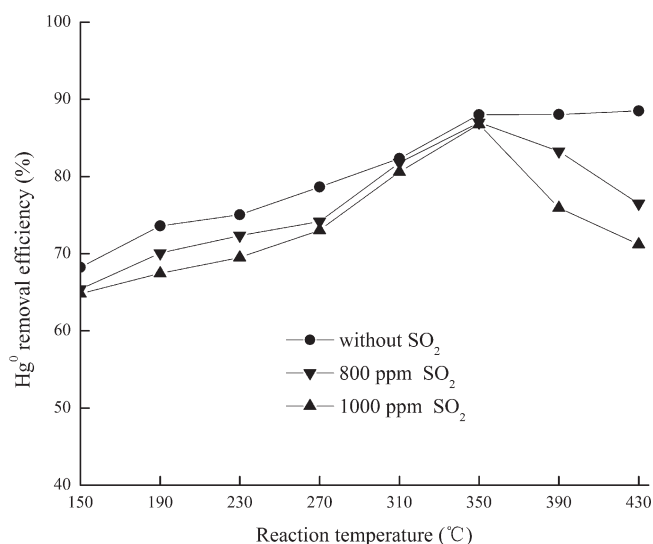
On the other hand, when the CeO<sub>2</sub> loading value is kept constant, the Hg<sup>0</sup> removal efficiencies increase continuously with the temperature increasing in the range of 150–350 °C. However, when the temperature is over 350 °C, Hg<sup>0</sup> removal efficiencies decrease slowly, except that of virgin γ-Al<sub>2</sub>O<sub>3</sub>. This is because, when the temperature exceeds 300 °C, the excessive CeO<sub>2</sub> would react with SO<sub>2</sub> and O<sub>2</sub>, forming Ce(SO<sub>4</sub>)<sub>2</sub>, expressed as<sup>33</sup>



The generated Ce(SO<sub>4</sub>)<sub>2</sub> covers the surface of γ-Al<sub>2</sub>O<sub>3</sub> and blocks its micropores, preventing Hg<sup>0</sup> from contacting CeO<sub>2</sub>. Moreover, with the temperature increasing, the cell size of crystal CeO<sub>2</sub> becomes larger and can also block the pores of γ-Al<sub>2</sub>O<sub>3</sub>.<sup>34</sup> These changes lead to a decrease of Hg<sup>0</sup> removal efficiency. The Hg<sup>0</sup> removal efficiency of virgin γ-Al<sub>2</sub>O<sub>3</sub> still increases after 300 °C because, as the experimental temperature rises, reactants can obtain more kinetic energy, which enhances the catalytic activity of the samples for the oxidation of Hg<sup>0</sup>.

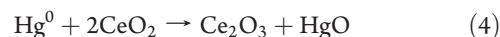
**3.3. Effect of O<sub>2</sub>.** Figure 5 shows the effects of O<sub>2</sub> on Hg<sup>0</sup> removal when 0, 3, 5, and 8% O<sub>2</sub> were individually added to the flue gas system of N<sub>2</sub> + O<sub>2</sub> + NO + SO<sub>2</sub> + H<sub>2</sub>O (reaction time = 1 h). The results indicate that, in the absence of O<sub>2</sub>, only about 30% Hg<sup>0</sup> removal efficiency is achieved and even lower than that of virgin γ-Al<sub>2</sub>O<sub>3</sub> in Figure 4. When O<sub>2</sub> is added to the flue gas, the Hg<sup>0</sup> removal enhances. The higher concentration of O<sub>2</sub>, the higher the removal efficiency. For example, as the O<sub>2</sub> concentration increases to 8%, the Hg<sup>0</sup> removal efficiency of CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> is the highest over the full operating temperature range.

Combining the results of Figures 3 and 5, it is easy to draw a conclusion that O<sub>2</sub> may be the principal active constituent oxidant of the Hg<sup>0</sup> removal reaction. In the process, a proportion of Hg<sup>0</sup> is adsorbed by CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and then oxidized directly by O<sub>2</sub> through reaction 3. Another part of Hg<sup>0</sup> is oxidized by the lattice oxygen stored in CeO<sub>2</sub> through reactions 4 and 5.<sup>35</sup> On the basis of Figure 4, the oxidation of Hg<sup>0</sup> took place mainly



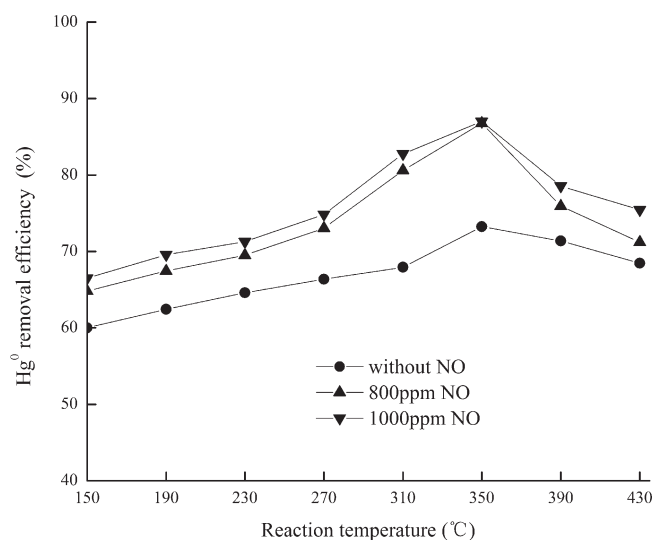
**Figure 6.** Effect of SO<sub>2</sub> on Hg<sup>0</sup> removal efficiency at different reaction temperatures (9% CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and reaction time of 1 h).

through reactions 4 and 5 in the presence of CeO<sub>2</sub> because of its catalyst role.



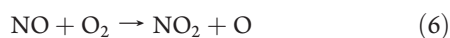
**3.4. Effect of SO<sub>2</sub>.** Figure 6 gives the effects of SO<sub>2</sub> on the Hg<sup>0</sup> removal efficiency of 9% CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> at different reaction temperatures (reaction time = 1 h). The results reveal that SO<sub>2</sub> has an inhibitory effect on Hg<sup>0</sup> removal of CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, especially when the reaction temperature exceeds 350 °C. At the reaction temperature of 430 °C, the Hg<sup>0</sup> removal efficiency without SO<sub>2</sub> can reach 88.5% but decreases to 72.1% with 1000 ppm SO<sub>2</sub> in the flue gas system of N<sub>2</sub> + O<sub>2</sub> + NO + H<sub>2</sub>O. This is because the competitive adsorption between Hg<sup>0</sup> and SO<sub>2</sub> on the CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> surface will occur, and it has an adverse effect on the Hg<sup>0</sup> removal efficiency. Moreover, when the reaction temperature is below 300 °C, the adsorbed SO<sub>2</sub> could react with O<sub>2</sub> and H<sub>2</sub>O to form H<sub>2</sub>SO<sub>4</sub>, and when the reaction temperature is above 300 °C, reaction 2 can be at work. Both H<sub>2</sub>SO<sub>4</sub> and Ce(SO<sub>4</sub>)<sub>2</sub> can cover the surface of γ-Al<sub>2</sub>O<sub>3</sub> and go against the Hg<sup>0</sup> removal. Additionally, the result is somewhat different from that by Fan et al.<sup>20</sup> and Zhou et al.,<sup>36</sup> who reported that the presence of SO<sub>2</sub> can promote Hg<sup>0</sup> removal. Likely, this difference resulted from different operation conditions. For example, there was no H<sub>2</sub>O in their experimental flue gas, which could react with O<sub>2</sub> and SO<sub>2</sub> to form H<sub>2</sub>SO<sub>4</sub>. Ce(SO<sub>4</sub>)<sub>2</sub> was hard to form in the experiment by Fan et al. because of the lower operation temperature (<300 °C). On the other hand, adsorbed SO<sub>2</sub> could react with O<sub>2</sub> to form SO<sub>3</sub>, which had strong oxidation ability on Hg<sup>0</sup>; therefore, SO<sub>2</sub> could promote the Hg<sup>0</sup> removal in their experiments.

**3.5. Effect of NO.** To investigate the effects of NO on the Hg<sup>0</sup> removal efficiency, the experiments were carried out with different NO concentrations (0, 800, and 1000 ppm) in the flue gas system of N<sub>2</sub> + O<sub>2</sub> + SO<sub>2</sub> + H<sub>2</sub>O using 9% CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> at different reaction temperatures. With the reaction time equal to 1 h, the results are presented in Figure 7.



**Figure 7.** Effect of NO on  $\text{Hg}^0$  removal efficiency at different reaction temperatures (9%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  and reaction time of 1 h).

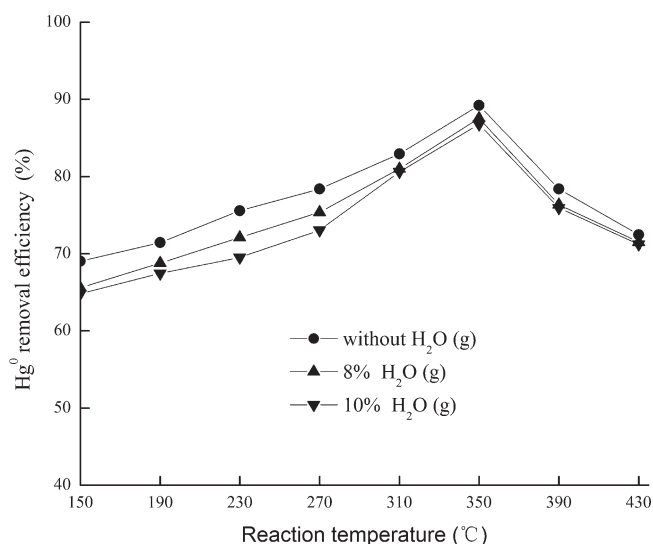
When NO is 1000 ppm in the flue gas system, the  $\text{Hg}^0$  removal efficiency of 9%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  increases from 73.24 to 86.99% at 350 °C. It indicates that NO has a promotional effect on  $\text{Hg}^0$  removal. The possible reason can be ascribed to the following mechanism: Both  $\text{Hg}^0(\text{g})$  and NO can be adsorbed by  $\gamma\text{-Al}_2\text{O}_3$ , but the competition of the two for similar active sites on the surface is minimized.<sup>37</sup> In the oxidizing atmosphere, NO is absorbed on the  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  surface and catalyzed by  $\text{CeO}_2$  to form  $\text{NO}_2$  and O. Meanwhile,  $\text{Hg}^0(\text{g})$  can also react with active O and  $\text{NO}_2$  to produce  $\text{HgO}$ .<sup>36,38–41</sup> The series of reactions can be described as



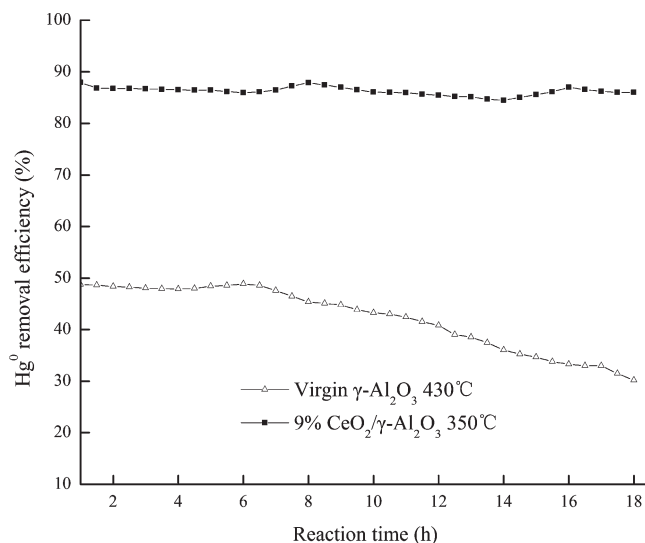
**3.6. Effect of  $\text{H}_2\text{O}(\text{g})$ .** Experiments about effects of  $\text{H}_2\text{O}(\text{g})$  on  $\text{Hg}^0$  removal were conducted in a relatively dry condition bypassing the water bubbler and in humid conditions. The results are presented in Figure 8 (reaction time = 1 h). Generally speaking,  $\text{H}_2\text{O}$  has a slight inhibitory effect on  $\text{Hg}^0$  removal, which agrees with that by Li et al.<sup>40</sup> As the concentration of  $\text{H}_2\text{O}(\text{g})$  increases to 10%, the  $\text{Hg}^0$  removal efficiency decreases about 3.51% and even up to 6.07% at 230 °C. The inhibition of  $\text{H}_2\text{O}$  is attributed first to competitive adsorption between  $\text{Hg}^0$  and  $\text{H}_2\text{O}$  on the  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  surface. On the other hand, adsorbed  $\text{H}_2\text{O}$  could react with  $\text{SO}_3$  to form  $\text{H}_2\text{SO}_4$ , which covered the surface of  $\gamma\text{-Al}_2\text{O}_3$ , and go against the  $\text{Hg}^0$  removal, but this inhibition would weaken when the reaction temperature is above 320 °C because of the pyrolysis of  $\text{H}_2\text{SO}_4$ .<sup>42</sup>

**3.7. Effect of the Reaction Time.** According to the results of section 3.2,  $\text{Hg}^0$  removal efficiencies are highest when using 9%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  at 350 °C and virgin  $\gamma\text{-Al}_2\text{O}_3$  at 430 °C. Therefore, the effect of the reaction time on  $\text{Hg}^0$  removal efficiency is studied under these conditions. The results are shown in Figure 9.

As shown in the figure, the  $\text{Hg}^0$  removal efficiency of 9%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  remains constant (about 85%) within 18 h. However, for virgin  $\gamma\text{-Al}_2\text{O}_3$ , when the reaction time is more than 6 h, its  $\text{Hg}^0$  removal efficiency begins to decrease and is about 33.5% at the

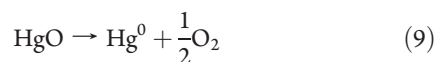


**Figure 8.** Effects of  $\text{H}_2\text{O}(\text{g})$  on  $\text{Hg}^0$  removal at different reaction temperatures (9%  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ ).



**Figure 9.** Effect of the reaction time on  $\text{Hg}^0$  removal efficiency.

reaction time of 18 h. When the reaction temperature exceeds 400 °C, the reaction 9 is supposed to take place slowly and is heavily dependent upon the amount of  $\text{HgO}$  on the catalyst surface.<sup>31</sup> Therefore, the inhibition of reaction 9 is smaller on the  $\text{Hg}^0$  removal efficiency of  $\gamma\text{-Al}_2\text{O}_3$  at the initial time because of a small quantity of  $\text{HgO}$  on the surface of the catalyst. With the prolonging of reaction times, more and more  $\text{HgO}$  is produced, which enhances the inhibition of reaction 9. Therefore, the  $\text{Hg}^0$  removal efficiency of virgin  $\gamma\text{-Al}_2\text{O}_3$  decreases with the reaction time, especially when the reaction time exceeded 6 h.



## 4. CONCLUSION

In this work, the removal of  $\text{Hg}^0$  was conducted in a lab-scale fixed-bed system over  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  at different reaction

temperatures. The experimental results show that  $\text{CeO}_2$  could catalyze the  $\text{Hg}^0$  removal reaction and the  $\text{Hg}^0$  removal efficiency of  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  increases with the increase of the  $\text{CeO}_2$  loading value. However, when the  $\text{CeO}_2$  loading exceeds 9%, the  $\text{Hg}$  removal efficiency began to decrease. BET analysis shows that the surface area of  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  will decrease with the increase of  $\text{CeO}_2$  loading values, which prevents the valid collision between  $\text{Hg}^0$  and  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  and, thereby, the decrease of  $\text{Hg}^0$  removal efficiency. Therefore, the most suitable loaded mass percentage of  $\text{CeO}_2$  is 9%. Moreover, the reaction temperature is an important factor on the  $\text{Hg}^0$  removal of  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ . With the rise of the experimental temperature, the  $\text{Hg}^0$  removal efficiency increases and then decreases after the reaction temperature is above 350 °C because of the generation of  $\text{Ce}(\text{SO}_4)_2$ , which can prevent  $\text{Hg}^0$  further contacting  $\text{CeO}_2$ . In the flue gas system of  $\text{N}_2 + \text{O}_2 + \text{NO} + \text{SO}_2 + \text{H}_2\text{O}$ , the presence of  $\text{O}_2$  and  $\text{NO}$  has positive effects on the  $\text{Hg}^0$  removal efficiency, while the presence of  $\text{SO}_2$  and  $\text{H}_2\text{O}(\text{g})$  has inhibitory effects on the  $\text{Hg}^0$  removal efficiency. Meanwhile, the results testify that the catalyst of  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$  possesses excellent thermostability within the studied life span.

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