Elemental Mercury Removal over CeO$_2$/TiO$_2$ Catalyst Prepared by Sol–Gel Method

Qiang Lv $^1$, Chang’an Wang $^1$, Yang He $^1$, Ming Cai $^{1,2}$ and Defu Che $^{1,*}$

$^1$ State Key Laboratory of Multiphase Flow in Power Engineering, School of Energy and Power Engineering, Xi’an Jiaotong University, Xi’an 710049, China; lv20610@hotmail.com (Q.L.); changanwang@mail.xjtu.edu.cn (C.W.); hylx199498@163.com (Y.H.); caiming@tpri.com.cn (M.C.)

$^2$ Xi’an Thermal Power Research Institute Limited Company, Xi’an 710032, China

* Correspondence: dfche@mail.xjtu.edu.cn; Tel.: +86-029-82668703

Received: 20 March 2020; Accepted: 11 April 2020; Published: 14 April 2020

Abstract: Elemental mercury (Hg$^0$) emitted from a coal-fired boiler is a serious menace and challenge to humans. Using high-efficiency CeO$_2$/TiO$_2$ catalysts to enhance the conversion from elemental mercury to oxidized mercury is a promising approach to reducing Hg$^0$ emission. However, most of the CeO$_2$/TiO$_2$ catalysts were prepared by impregnation method or coprecipitation method while little attention has been paid to sol–gel method, which has many advantages in material production. In this study, a series of catalysts were synthesized through the sol–gel method to remove the gaseous Hg$^0$ from simulated flue gas. The effect of vanadium (V) on Hg$^0$ removal efficiency and the simultaneous removal of Hg$^0$ and NO were also investigated. The results showed the optimal temperature for Hg$^0$ removal over the CeO$_2$/TiO$_2$ catalysts was 350 °C. The oxidation of Hg$^0$ could be promoted by O$_2$, HCl, and NO, but inhibited by NH$_3$ and SO$_2$. The addition of vanadium could enhance the Hg$^0$ removal performance and the resistance to NH$_3$ and SO$_2$. A synergetic effect was found during the simultaneous removal of Hg$^0$ and NO. The high redox reaction reactivity of Ce$^{4+}$/Ce$^{3+}$ and V$^{5+}$/V$^{4+}$ should take the credit for the oxidation of Hg$^0$ and the removal of NO. Based upon the performance tests and the characterization experiments of the samples, the detailed mechanisms of the Hg$^0$ and NO removal over the catalysts were proposed.

Keywords: elemental mercury; cerium; vanadium; sol–gel; nitrogen oxide; mechanism

1. Introduction

Mercury (Hg), a severe global concern to human health, is derived from both natural sources and anthropogenic pollution [1–3]. The natural portion mainly comes from volcanic eruption, forest burning, geogenic activity, soil and vegetation, etc. As for the anthropogenic part, according to the latest Global Mercury Assessment published by United Nations Environment Programme (UNEP) in 2019, about 2200 tons of mercury is emitted into the air as a result of human activities each year [4]. This number is 20% higher than that reported in 2010. In comparison, most of the mercury pollution is released from anthropogenic activities, which results in a 450% increase of mercury concentration in the air. In terms of regional contributions, a declining trend has shown up in the anthropogenic mercury pollution in Europe and North America due to the effective implementation of mercury emission regulations. However, global mercury pollution is still serious because of the continuing growth of mercury emissions from developing countries. At present, nearly half (49%) of all anthropogenic mercury emission around the world occurs in Asia, especially in East and South-East Asia. Besides, South America and Sub-Saharan Africa are also facing serious mercury pollution problems. If the anthropogenic mercury results are classified by industry, it can be found that small-scale gold mining and the combustion of fossil fuels are the main sources, followed by non-ferrous metal production and
cement production. Moreover, mercury emission from coal combustion makes up approximately 88% of all mercury emission from fossil fuel combustion. As a result, reducing mercury emission from coal combustion is of great significance for the global mercury pollution control.

Mercury can be divided into three forms in the coal-fired boiler flue gas: elemental mercury (Hg$^0$), oxidized mercury (Hg$^{2+}$), and particulate-bound mercury (Hg$p$) [5,6]. Among them, oxidized mercury and particulate-bound mercury can be effectively removed by air pollution control devices (APCDs), such as wet flue gas desulfurization (WFGD) and particulate matter control devices (PMCDs) [7,8]. On the contrary, elemental mercury is difficult to be controlled directly and has attracted broad attention among laboratories [9]. In addition, the atmospheric lifetimes of Hg$^{2+}$ and Hg$p$ are relatively short because of the high solubility and gravity, respectively. However, unlike other mercury species, gaseous Hg$^0$ can be carried globally before being deposited onto waters or lands. Hence, the excellent atmospheric transport ability of Hg$^0$ is another critical factor for assessing its environmental impact.

Cerium (Ce) is the most abundant rare earth element. More importantly, due to the superior oxygen storage capacity and the existence of the Ce$^{3+}$/Ce$^{4+}$ couple, high elemental mercury removal efficiency could be obtained by using the catalysts or sorbents with the addition of Ce [10–12]. According to our previous study, Ce modification could improve the Hg$^0$ removal performance of a honeycomb selective catalytic reduction (SCR) catalyst [8]. The preparation approach adopted in [8] was wet impregnation. A disadvantage of this approach is that it is hard to control the loading value of cerium oxides in the catalyst accurately and actively. Changing the concentration of the precursor (cerium nitrate) solution could only adjust the relative content of Ce. Besides, various catalysts and sorbents were synthesized by impregnation or ultrasonic-assisted impregnation to remove the elemental mercury from the flue gas. E.g., the Mo-Ce/cylindrical activated coke prepared by Liu et al. [13], and the Mn-Ce modified wheat straw chars made by Yang et al. In addition, coprecipitation method was employed by Zhao et al. to prepare the novel V/ZrCe-x catalyst [14].

Different preparation methods could result in different performances of the catalysts. Compared with the wet impregnation method, the sol–gel method has the advantage of studying the influence of Ce loading value on Hg$^0$ removal efficiency due to its ability to control the elemental content precisely. Moreover, different components can be mixed more evenly at the molecular level through the sol–gel method. Nevertheless, the study on Hg$^0$ removal efficiency of novel CeO$_2$/TiO$_2$ catalyst prepared by sol–gel method is still insufficient. Moreover, it has been reported that the interaction between vanadium (V) oxides and cerium oxides could further promote the simultaneous removal efficiency of NO and Hg$^0$ [15,16]. Considering this and the toxicity of vanadium oxides, it is necessary to study the effect of vanadium addition on the elemental mercury removal efficiency of the CeO$_2$/TiO$_2$ catalyst prepared by sol–gel.

In this study, a series of CeO$_2$/TiO$_2$ catalysts with various Ce loading values was synthesized by sol–gel. Besides, a V$_2$O$_5$-CeO$_2$/TiO$_2$ catalyst was also prepared. The elemental mercury removal performances of all catalysts were tested in the laboratory-scale experimental system. Firstly, each flue gas component was fed into the system. The effect of reaction temperature on the catalyst performance was studied in the simulated flue gas. Then, in an atmosphere with oxygen (O$_2$), carbon dioxide (CO$_2$), and hydrogen chloride (HCl), the effects of each flue gas component and the ratio of ammonia (NH$_3$) to nitric oxide (NO) were investigated. Besides, the performances of CeO$_2$/TiO$_2$ catalyst and V$_2$O$_5$-CeO$_2$/TiO$_2$ catalyst were compared under various conditions. The simultaneous removal efficiency of Hg$^0$ and NO was also studied. At last, the Hg$^0$ removal mechanisms of the catalysts were proposed after conducting the characterization experiments. The results provided valuable information for better understanding the elemental mercury removal process over the catalyst prepared by sol–gel.
2. Materials and Methods

2.1. Catalyst Preparation

Sol–gel is a widely used technology for producing metal oxides or other solid compounds from small organic or inorganic molecules. Sol is a colloidal suspension liquid and it could then turn into a gel-like material through gelatification. The porous gel can be purified by a chemical method or high temperature treatment in order to obtain oxides with high purity. In this study, a series of novel powdery Ce/Ti catalysts was synthesized in order to remove the elemental mercury from the coal-fired boiler flue gas. The detailed operation procedures are shown in Figure 1. Butyl titanate (C_{16}H_{36}O_{4}Ti) and cerium nitrate (Ce(NO_{3})_{3}·6H_{2}O) were employed as the precursors of Ti and Ce, respectively. A certain amount of butyl titanate was mixed with absolute ethanol to obtain Solution 1. Besides, cerium nitrate, absolute ethanol, nitric acid, and deionized water were mixed together to obtain Solution 2. Solution 1 was pumped into Solution 2 at the speed of 2 mL·min^{-1} by a peristaltic pump. Then, the pale yellow sol could be obtained after a 3-h magnetic stirring. The pale yellow sol would be put into a drying oven at 105 °C for 48 h. Before being calcined in a 500 °C muffle furnace for 5 h, the sol had been grounded and sieved into 60–100 mesh. After all these procedures, the powdery CeO_{2}/TiO_{2} catalysts were eventually synthesized. As mentioned in the introduction part, the addition of vanadium could improve the performance of the catalyst. Considering this, vanadium trisopropoxy oxide (C_{9}H_{21}O_{4}V) was taken as the precursor of V, which would be mixed together with absolute ethanol, nitric acid, hydrochloric acid, and deionized water to obtain Solution 3. Solution 3 was slowly added to the pale yellow sol at 2 mL·min^{-1} by using a peristaltic pump. After the same drying, grounding, sieving, and calcination processes, the powdery V_{2}O_{5}-CeO_{2}/TiO_{2} catalyst was obtained. The flow chart of the sample preparation is shown in Figure 1. Five CeO_{2}/TiO_{2} catalysts and one V_{2}O_{5}-CeO_{2}/TiO_{2} catalyst were synthesized in this study, including pure TiO_{2}, Ce0.1Ti, Ce0.2Ti, Ce0.5Ti, Ce1.0Ti, and Ce0.5Ti-V. The number in the name of the catalyst represents the mass ratio of cerium dioxide to titanium dioxide. For example, Ce0.1T1 refers to the catalyst whose mass ratio of cerium dioxide to titanium dioxide is 0.1. The mass fraction of vanadium pentoxide is 0.5% in Ce0.5Ti-V. For each catalyst, 10 g sample was prepared by sol–gel method. The amounts of the precursors used in the preparation process for all samples were listed in Table 1.

![Figure 1. Operation procedures of catalyst preparation by sol–gel method.](image-url)
2.2. Catalyst Performance Test and Characterization

A laboratory-scale elemental mercury removal system was used in this study. The schematic of the setup is shown in Figure 2. The removal efficiency of Hg\(_0\) (\(\eta\)) and NO (\(\eta'\)) could be calculated from the following equations:

\[
\eta = \frac{C_0 - C}{C_0} \times 100, \%
\]

\[
\eta' = \frac{C_0' - C'}{C_0'} \times 100, \%
\]

where \(C_0\) represents the inlet Hg\(_0\) concentration (\(\mu\)g-m\(^{-3}\)), \(C\) represents the outlet Hg\(_0\) concentration (\(\mu\)g-m\(^{-3}\)), \(C_0'\) represents the inlet NO concentration (\(\mu\)L-L\(^{-1}\)), and \(C'\) represents the outlet NO concentration (\(\mu\)L-L\(^{-1}\)). It is noteworthy that both adsorption and oxidation of Hg\(_0\) may happen over the catalyst. Therefore, reducing agents and a conversion system before Hg\(_0\) analyzer would be needed for calculating the oxidation efficiency and adsorption efficiency of the catalysts. However, neither the adsorbed Hg nor the gaseous Hg\(_{2+}\) could emit into the atmosphere, since the gaseous Hg\(_{2+}\) would be removed later (for example, in WFGD). In other words, only the Hg\(_0\) downstream of the catalyst should be considered as the mercury emission from the power plant in a practical situation. As a result, the removal efficiency of Hg\(_0\) defined by Equation (1) is used in this paper.

From Section 3.1 to Section 3.3, the effects of reaction temperature and flue gas components on the Hg\(_0\) removal efficiency are investigated. In Section 3.4, the simultaneous removal performance of Hg\(_0\) and NO is studied at various reaction temperatures; 0.500 g catalyst was placed into the quartz reactor whose diameter was 8 mm. The total flow rate of the simulated flue gas was 1.0 L-min\(^{-1}\). The space velocity during the experiments was about 120,000 h\(^{-1}\), which has the same order of magnitude as many other studies [14,17]. All the experimental conditions are presented in Table 2.

### Table 1. The amounts of the precursors used in the preparation process.

| Catalyst  | \(\text{C}_16\text{H}_36\text{O}_4\text{Ti/mL}\) | \(\text{Ce(NO}_3)_3\cdot 6\text{H}_2\text{O/g}\) | \(\text{C}_3\text{H}_21\text{O}_4\text{V/g}\) |
|-----------|---------------------------------|---------------------------------|---------------------------------|
| pure TiO\(_2\) | 44.00                          | -                               | -                               |
| Ce0.1Ti   | 40.00                          | 2.29                            | -                               |
| Ce0.2Ti   | 36.67                          | 4.21                            | -                               |
| Ce0.5Ti   | 29.33                          | 8.41                            | -                               |
| Ce1.0Ti   | 22.00                          | 12.62                           | -                               |
| Ce0.5Ti-V | 29.18                          | 8.37                            | 1.34                            |

### Table 2. Experimental conditions.

| Variable | Temperature/°C | Flue Gas Components                                                                 |
|----------|----------------|--------------------------------------------------------------------------------------|
| Temperature | 150, 200, 250, 300, 350, 400, 450 | \(\text{BG} + 6\% \text{O}_2 + 45 \mu\text{L-L}^{-1} \text{HCl} + 200 \mu\text{L-L}^{-1} \text{NO} + 200 \mu\text{L-L}^{-1} \text{NH}_3 + 500 \mu\text{L-L}^{-1} \text{SO}_2\) |
| \(\text{O}_2\) | 350 | \(\text{BG} + 45 \mu\text{L-L}^{-1} \text{HCl} + \text{O}_2 (0, 3\%, 6\%, 9\%)\) |
| HCl       | 350 | \(\text{BG} + 6\% \text{O}_2 + \text{HCl} (0, 15, 30, 45 \mu\text{L-L}^{-1})\) |
| NO and \(\text{NH}_3\) | 350 | \(\text{BG} + 45 \mu\text{L-L}^{-1} \text{HCl} + 6\% \text{O}_2 + (\text{NO} + \text{NH}_3) (0, 200, 400, 600 \mu\text{L-L}^{-1})\) |
| \(\text{NH}_3/\text{NO}\) | 350 | \(\text{BG} + 45 \mu\text{L-L}^{-1} \text{HCl} + 6\% \text{O}_2 + 200 \mu\text{L-L}^{-1} \text{NO} + \text{NH}_3 (0, 160, 180, 200, 220, 240 \mu\text{L-L}^{-1})\) |
| \(\text{SO}_2\) | 350 | \(\text{BG} + 45 \mu\text{L-L}^{-1} \text{HCl} + 6\% \text{O}_2 + \text{SO}_2 (0, 250, 500, 750 \mu\text{L-L}^{-1})\) |

*BG—basic gas (\(\text{N}_2 + 50 \mu\text{g-m}^{-3} \text{Hg}_0 + 15\% \text{CO}_2\)).
Table 1. The amounts of the precursors used in the preparation process.

| Catalyst     | C 16H36O4Ti/mL | Ce(NO 3)3·6H2O/g | C 9H21O4V/g |
|--------------|----------------|------------------|------------|
| pure TiO2   | 44.00          | -                | -          |
| Ce0.1Ti     | 40.00          | 2.29             | -          |
| Ce0.2Ti     | 36.67          | 4.21             | -          |
| Ce0.5Ti     | 29.33          | 8.41             | -          |
| Ce1.0Ti     | 22.00          | 12.62            | -          |
| Ce0.5Ti-V   | 29.18          | 8.37             | 1.34       |

2.2. Catalyst Performance Test and Characterization

A laboratory-scale elemental mercury removal system was used in this study. The schematic of the setup is shown in Figure 2. The removal efficiency of Hg0 (η) and NO (η') could be calculated from the following equations:

\[ \eta = \frac{C_0 - C}{C_0} \times 100\% \]

\[ \eta' = \frac{C_0' - C'}{C_0'} \times 100\% \]

where \(C_0\) represents the inlet Hg0 concentration (\(\mu g\cdot m^{-3}\)), \(C\) represents the outlet Hg0 concentration (\(\mu g\cdot m^{-3}\)), \(C_0'\) represents the inlet NO concentration (\(\mu L\cdot L^{-1}\)), and \(C'\) represents the outlet NO concentration (\(\mu L\cdot L^{-1}\)). It is noteworthy that both adsorption and oxidation of Hg0 may happen over the catalyst. Therefore, reducing agents and a conversion system before Hg0 analyzer would be needed for calculating the oxidation efficiency and adsorption efficiency of the catalysts. However, neither the adsorbed Hg nor the gaseous Hg2+ could emit into the atmosphere, since the gaseous Hg2+ would be removed later (for example, in WFGD). In other words, only the Hg0 downstream of the catalyst should be considered as the mercury emission from the power plant in a practical situation. As a result, the removal efficiency of Hg0 defined by Equation (1) is used in this paper.

Figure 2. Schematic of the elemental mercury removal system.

The characterization tests of the samples were also conducted in order to study the physical and chemical properties of the catalysts. The main compositions, the crystalline structures, and the valence of selected elements were obtained by X-ray fluorescence (XRF), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), respectively.

3. Results and Discussion

3.1. The Effect of Reaction Temperature on Catalytic Performance

The Hg0 removal efficiency of four CeO2/TiO2 catalysts and one pure TiO2 catalyst were measured at various reaction temperatures with the aim of obtaining the optimal reaction temperature and the optimal CeO2 loading value. The reaction temperature ranged from 150 to 450 °C. The results are shown in Figure 3. It can be noted that the Hg0 removal efficiency of pure the TiO2 catalyst was much lower. The highest value was only about 25%, which is in consistent with the results of Kamata et al. [18]. In comparison, the Hg0 removal efficiency of the catalysts increased dramatically after the addition of cerium oxides. The efficiencies of all CeO2/TiO2 catalysts showed similar trends as the reaction temperature rose. From 150 to 350 °C, higher temperature led to better Hg0 removal performance of the catalysts. However, the efficiency started to decrease when the temperature was higher than 350 °C, which agrees well with some literature [12,19]. Nevertheless, the trend in Figure 3 seems to conflict with the result of our previous work, which is that the Hg0 removal efficiency declined monotonically as the reaction temperature increased [8]. That is understandable because only Hg0, O2, and N2 existed in the flue gas of reference [8], so physical adsorption was the dominant removal mechanism for elemental mercury. In comparison, the chemical reaction played a vital role in this study, since all flue gas components were considered in the simulated flue gas. As a result, the elemental mercury removal mechanism and the effect of reaction temperature on catalytic performance were changed. It also can be seen that different Ce loading values brought different performances. The Hg0 removal efficiency increased remarkably from pure TiO2 to Ce0.1Ti. More specifically, the value rose from 25.1% to 86.4% when the reaction temperature was 350 °C. With a further increase of CeO2 content, Ce0.2Ti provided
even better performance for elemental mercury removal. The value of $\eta$ remained over 80% in the temperature zone from 300 to 400 °C and reached 94.0% at 350 °C. The excellent efficiency should be mainly attributed to the redox reaction between cerium oxides and elemental mercury [20]. If the Ce loading value continued to increase, the Hg$^0$ removal efficiency began to decrease. The efficiencies of Ce0.5Ti and Ce1.0Ti are 79.6% and 77.8%, respectively. The reason may be that excessive cerium oxides covered too much surface of the catalyst, which blocked part of the elemental mercury from entering the catalyst [21].

![Figure 3](image_url)

**Figure 3.** The effect of reaction temperature on catalytic performance.

### 3.2. The Effects of Flue Gas Components on Catalysts Performance

#### 3.2.1. The Effect of O$_2$ on Catalytic Performance

The effect of O$_2$ concentration on the Hg$^0$ removal efficiency was studied at 350 °C. It can be clearly seen from Figure 4a that the efficiency of pure TiO$_2$ catalyst was much lower than that of other catalysts. The value of $\eta$ only increased from 18.6% to 25.4% as the O$_2$ concentration increased from 0% to 9%. For CeO$_2$/TiO$_2$ catalyst, although the efficiency rose obviously, $\eta$ was still less than 45% when the O$_2$ concentration was 0%. That indicates that O$_2$ in the simulated flue gas is one of the most important reactants for the oxidizing reaction of elemental mercury [22]. As the O$_2$ was introduced in the system, especially when the O$_2$ concentration was 6%, the Hg$^0$ removal efficiency of each CeO$_2$/TiO$_2$ catalyst was between 60% and 80%. If the O$_2$ concentration was further increased, the improvement of the catalytic performance was slight. Similarly to Section 3.1, Ce0.2Ti showed the highest Hg$^0$ removal efficiency among all samples. It is noteworthy that the value of $\eta$ in Figure 4a was lower than that in Figure 3 for each catalyst, even under the same working conditions (350 °C and 6% O$_2$). For example, the Hg$^0$ removal efficiencies of Ce0.1Ti in Figures 4a and 3 were respectively 68.8% and 86.4%. That is because that no other flue gas component except Hg$^0$, O$_2$, N$_2$, and HCl existed in the simulated flue gas in Section 3.2.1. The oxidizing reaction of elemental mercury was not as intense as that in Section 3.1. Hence, the value of $\eta$ was slightly lower.
3.2.2. The Effect of HCl on Catalytic Performance

Although the concentration of HCl is very low in the coal-fired boiler flue gas, it is still considered a decisive role in the oxidation of elemental mercury [23]. In order to study the effect of HCl concentration on the Hg$_0$ removal performance of the CeO$_2$/TiO$_2$ catalysts prepared by sol–gel, the Hg$_0$ removal efficiencies of all catalysts were measured under the condition of 350 °C and 6% O$_2$. The results, shown in Figure 4b, indicate that $\eta$ increased with the increase of HCl concentration. Low Hg$_0$ removal efficiency was found in pure TiO$_2$ catalyst. Besides, the value of $\eta$ was also relatively low for CeO$_2$/TiO$_2$ catalyst without the existence of HCl in the flue gas. However, the elemental mercury removal performance rose sharply as the HCl was introduced, even though the concentration of HCl

**Figure 4.** The effects of flue gas components on catalytic performance; (a) the effect of O$_2$; (b) the effect of HCl; (c) the effect of NO and NH$_3$; (d) the effect of the ratio of NH$_3$/NO; (e) the effect of SO$_2$. 

3.2.2. The Effect of HCl on Catalytic Performance

Although the concentration of HCl is very low in the coal-fired boiler flue gas, it is still considered a decisive role in the oxidation of elemental mercury [23]. In order to study the effect of HCl concentration on the Hg$_0$ removal performance of the CeO$_2$/TiO$_2$ catalysts prepared by sol–gel, the Hg$_0$ removal efficiencies of all catalysts were measured under the condition of 350 °C and 6% O$_2$. The results, shown in Figure 4b, indicate that $\eta$ increased with the increase of HCl concentration. Low Hg$_0$ removal efficiency was found in pure TiO$_2$ catalyst. Besides, the value of $\eta$ was also relatively low for CeO$_2$/TiO$_2$
catalysts without the existence of HCl in the flue gas. However, the elemental mercury removal performance rose sharply as the HCl was introduced, even though the concentration of HCl was only 15 μL·L⁻¹. That indicates that these catalysts could provide good Hg⁰ removal performance at a low HCl concentration, which means the CeO₂/TiO₂ catalysts prepared by sol–gel are promising for reducing the mercury emission from the boiler firing low-rank coal. The reason may be that the elemental mercury could be oxidized by CeO₂ in the catalysts, which has high chemical reactivity, instead of just relying solely on HCl in the simulated flue gas. Moreover, other flue gas components, such as NO, could also enhance the oxidation and removal of Hg⁰, which will be discussed in Section 3.2.3 [24]. Among all catalysts, Ce0.2Ti showed the highest Hg⁰ removal efficiency again.

3.2.3. The Effects of NO and NH₃ on Catalytic Performance

The effects of NO and NH₃ concentrations on the elemental mercury removal efficiency of the catalysts was investigated in this section. The ratio of NH₃ to NO was controlled at 1:1. From Figure 4c, it can be seen that the highest efficiency of pure TiO₂ catalyst was only 30.6%, which is much lower than that of other catalysts. For CeO₂/TiO₂ catalysts, relatively higher Hg⁰ removal efficiency was found when the concentrations of NO and NH₃ were 200 μL·L⁻¹ and 400 μL·L⁻¹. For instance, the value of η for Ce0.2Ti was about 96.3% under either set of working conditions. Actually, NO could react with O₂ in the flue gas and produce NO₂, which has strong oxidation that would improve the Hg⁰ removal performance of the catalysts [24]. As a result, the Hg⁰ removal efficiency increased when the concentrations of NO and NH₃ rose from 0 to 200 μL·L⁻¹. However, the value of η stopped rising, and even begin decreasing if more NO and NH₃ was introduced. That should be explained by the adverse effect of NH₃ on the oxidation of elemental mercury. The active site on the catalyst surface would be partly occupied because of the competitive adsorption between NH₃ and HCl, which would bring about an inhibitory effect on the oxidizing reaction between HCl and elemental mercury [25]. In addition, NH₃ could react with O₂ [26]. Considering the important role of O₂ in Hg⁰ oxidation process, high concentration HN₃ was definitely unfavorable for elemental mercury removal. In general, the efficiency of Ce0.2Ti is the highest. If the catalyst was placed in the middle or rare part of the SCR equipment, the concentrations of NO and NH₃ were moderate for elemental mercury removal, since the SCR reaction was carried out. Relatively high Hg⁰ removal efficiency was achieved.

3.2.4. The Effect of the Ratio of NH₃/NO on Catalytic Performance

The ratio of NH₃ to NO is one of the most vital parameters influencing the efficiency of NOₓ removal in a SCR system. According to Section 3.2.3, the concentration of NH₃ and NO could also influence the elemental mercury removal. Hence, it is necessary to study the effect of the NH₃/NO ratio on the Hg⁰ removal efficiency of the catalysts. The results are shown in Figure 4d. The range of NH₃/NO ratio during the test was from 0.8 to 1.2 with a constant NO concentration of 200 μL·L⁻¹. It can be observed that higher NH₃/NO ratio would cause a decline in Hg⁰ removal efficiency. The result is reasonable, since NH₃ could restrain the oxidation of elemental mercury, as mentioned in Section 3.2.3. Generally speaking, the initial NH₃ concentration is slightly higher than the initial NO concentration in order to ensure an ideal De-NOₓ performance. As can be seen from Figure 4d, the negative effect of high NH₃/NO ratio on Hg⁰ removal was relatively minor within the test range. Except for Ce1.0Ti, the Hg⁰ removal efficiencies of other catalysts decreased only by less than 10% as the NH₃/NO ratio changed from 1.0 to 1.2.

3.2.5. The Effect of SO₂ on Catalytic Performance

SO₂ is an important pollutant in the coal-fired boiler flue gas. The Hg⁰ removal efficiencies of the catalysts under various SO₂ concentration were shown in Figure 4e. The value of η shrink as more SO₂ was introduced into the simulated flue gas, whether for CeO₂/TiO₂ catalysts or pure TiO₂ catalyst. The Hg⁰ removal efficiency of Ce0.2Ti dropped from 78.7% to 58.3% when the concentration of SO₂ rose from 0 to 750 μL·L⁻¹. The influence of SO₂ on the elemental mercury removal from flue gas by a
catalyst is controversial in previous literature, which is closely related to the type of catalyst [27]. Some researchers believe that the competitive adsorption between SO\(_2\) and Hg\(^0\) would inhibit the oxidation and removal of elemental mercury when cerium oxides are added into the catalyst [12]. Besides, another reason for the adverse effect is that the functional group changed due to the introduction of SO\(_2\), which could result in an irreversible impact on the Hg\(^0\) removal efficiency of the catalyst [28]. The value of \(\eta\) stayed at a low level, even the concentration of SO\(_2\) fell back. This process can be described by the following reaction:

\[
2\text{Ce}^{4+} + \text{SO}_2 + 2[O] \rightarrow 2\text{Ce}^{3+} + \text{SO}_4^{2-} \tag{3}
\]

where [O] represents the reactive oxygen. On the other hand, some researchers pointed out the introduction of SO\(_2\) could promote the oxidation of elemental mercury to a certain extent [27]. The reaction between SO\(_2\) and the reactive oxygen would produce SO\(_3\), which has strong oxidation. Elemental mercury could be oxidized by SO\(_3\) and produce HgSO\(_4\). The reaction process can be presented as follows:

\[
\text{SO}_2 + [O] \rightarrow \text{SO}_3 \tag{4}
\]

\[
\text{Hg}^0 + \text{SO}_3 + [O] \rightarrow \text{HgSO}_4 \tag{5}
\]

According to the results in Figure 4e, the negative influence caused by Equation (3) overweighed the positive influence brought by Equations (4) and (5). Therefore, the Hg\(^0\) removal efficiency of the CeO\(_2\)/TiO\(_2\) catalyst prepared by sol–gel method would decrease as the SO\(_2\) concentration increased.

### 3.3. The Effect of Vanadium on Catalytic Performance

In this study, unlike the CeO\(_2\)/TiO\(_2\) catalysts, V\(_2\)O\(_5\)-CeO\(_2\)/TiO\(_2\) catalyst was also prepared by sol–gel method. Vanadium was added into Ce0.5Ti to obtain Ce0.5Ti-V, which contained 0.5wt% V\(_2\)O\(_5\). The effect of vanadium on the elemental mercury removal process over the catalyst was studied under various working conditions. The results can be found in Figure 5. In the temperature zone from 150 to 450 °C, the Hg\(^0\) removal efficiencies of Ce0.5Ti and Ce0.5Ti-V respectively ranged from 36.1% to 79.3% and 69.1% to 96.3%, as shown in Figure 5a. The Hg\(^0\) removal performance of catalyst increased obviously after the addition of vanadium. Specifically, the value of \(\eta\) was over 95% when the temperature was between 250 and 400 °C. Figure 5b shows the Hg\(^0\) removal efficiencies of the catalysts under various O\(_2\) concentrations. It can be noted that the trends of the two curves were similar as the O\(_2\) concentration increased. The Hg\(^0\) removal efficiency was higher in the presence of O\(_2\), but \(\eta\) went up slowly with the further increase of O\(_2\) concentration. In comparison, the elemental mercury removal performance of the catalyst improved after the addition of vanadium. According to the literature, vanadium oxides could perform similar functions as the cerium oxides in the process of elemental mercury removal [14]. Since vanadium is similar to cerium, which has many valence states (V\(^{5+}\) and V\(^{4+}\)), it can also promote the oxidation and removal of elemental mercury through the Mars–Maessen mechanism. V\(^{5+}\) could take part in the redox reaction as the oxidant because of its strong oxidation. Then, the production, V\(^{4+}\), could react with the oxygen in the flue gas and turn back to V\(^{5+}\) again. The process can be described as follows:

\[
\text{Hg}^0_{(\text{g})} \rightarrow \text{Hg}^0_{(\text{ads})} \tag{6}
\]

\[
\text{Hg}^0_{(\text{ads})} + \text{V}_2\text{O}_5 \rightarrow \text{HgO} + \text{V}_2\text{O}_4 \tag{7}
\]

\[
\text{V}_2\text{O}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{V}_2\text{O}_5 \tag{8}
\]
The effect of HCl concentration on the Hg⁰ removal efficiency is shown in Figure 5c. Higher concentration of HCl promoted the elemental mercury removal performances of both catalysts. Ce0.5Ti-V showed higher efficiency than Ce0.5Ti because vanadium oxides, just like cerium oxides, could provide abundant lattice oxygen, which is quite important for the oxidation of Hg⁰. The process could also be explained by Equations (6)–(8). When the ratio of NH₃ to NO was 1:1, the efficiency of Ce0.5Ti-V remained higher than 91% under various NO and NH₃ concentrations, as shown in Figure 5d. Similar results could be found in Figure 5e, which shows the effect of NH₃ to NO ratio on η of these two catalysts. The Hg⁰ removal efficiency of Ce0.5Ti-V still went down as the ratio of

**Figure 5.** Catalytic performance after the addition of vanadium; (a) the effect of temperature; (b) the effect of O₂; (c) the effect of HCl; (d) the effect of NO and NH₃; (e) the effect of the ratio of NH₃/NO; (f) the effect of SO₂.
NH$_3$ to NO increased. However, compared with Ce0.5Ti, the catalyst with the addition of vanadium showed much better resistance to higher NH$_3$ to NO ratio. The elemental mercury removal efficiency of Ce0.5Ti-V was still higher than 95% when the NH$_3$ to NO ratio was 1:2. Figure 5f shows the influence of SO$_2$ concentration on the Hg$^0$ removal efficiency. As mentioned in Section 3.2.5, $\eta$ would decline with the introduction of SO$_2$, since the functional groups on the catalyst’s surface would be affected. Nevertheless, it can be observed that the influence of SO$_2$ on the Hg$^0$ removal efficiency of Ce0.5Ti-V was negligible, which means Ce0.5Ti-V could provide excellent Hg$^0$ removal performance, even under high SO$_2$ concentration. The result is similar to the findings of Zhao et al. [14].

3.4. Simultaneous Removal of Hg$^0$ and NO

The novel CeO$_2$/TiO$_2$ catalysts in this study are not only used to remove the gaseous elemental mercury from flue gas, its ability to reduce the NO emission also needs to be taken into account. In this section, the simultaneous removal performances of Hg$^0$ and NO from simulated flue gas over pure TiO$_2$ catalyst and CeO$_2$/TiO$_2$ catalysts were investigated at various temperatures. The ratio of NH$_3$ to NO was 1:1, and the detailed working conditions are listed in Table 2. The results are presented in Figure 6. Similar to Hg$^0$ removal performance, pure TiO$_2$ catalyst showed much lower efficiency than other catalysts in terms of NO removal. The highest NO removal efficiency of pure TiO$_2$ was only about 26.4%. By observing the $\eta'$ of each CeO$_2$/TiO$_2$ catalyst, it can be found that NO removal efficiency showed a similar trend to Hg$^0$ removal efficiency. The value of $\eta'$ reached its highest peak at 300 or 350 °C. The slight difference was that the NO removal efficiency increased more significantly than Hg$^0$ removal efficiency as the temperature rose from 150 to 200 °C. In general, the value of $\eta'$ was slightly higher than that of $\eta$. When the reaction temperature was between 250 and 350 °C, the NO removal efficiencies of Ce0.1Ti, Ce0.2Ti, and Ce0.5Ti were above 85%. That indicates that the novel CeO$_2$/TiO$_2$ catalysts could provide excellent simultaneous removal performance of Hg$^0$ and NO, especially from 300 to 350 °C. It is worth noting that this temperature range matched well with the working zone of commercial SCR catalyst, which makes it possible to replace some of the traditional catalyst with the novel CeO$_2$/TiO$_2$ catalysts. After being oxidized over the novel catalyst, the mercury pollutants would eventually be eliminated by other APCDs, such as WFGD and PMCDs.

Actually, some studies have been focused on the NO removal performance of Ce catalyst due to the outstanding oxygen storage capacity and the existence of the Ce$^{3+}$/Ce$^{4+}$ pair [29,30]. Since Ce$^{4+}$ is a strong oxidant, it could react with NO, which is the dominant constituent of NO$_x$, to produce NO$_2$ and Ce$^{3+}$. The consumed Ce$^{4+}$ could be replenished by the reaction between Ce$^{3+}$ and O$_2$ in the flue gas. Then, the redox reaction between NO$_2$ and NH$_3$ occurs. This process could promote the NO removal in the SCR system [31]. The reaction equations are as follows:

$$\text{NO} + 2\text{CeO}_2 \rightarrow \text{NO}_2 + \text{Ce}_2\text{O}_3$$  \hspace{1cm} (9)

$$\text{Ce}_2\text{O}_3 + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CeO}_2$$  \hspace{1cm} (10)

$$6\text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}$$  \hspace{1cm} (11)

In order to confirm the oxidation of NO, the concentrations of NO and NO$_2$ were measured at the outlet after cutting off NH$_3$ from the simulated flue gas. The initial concentration of NO was 200 $\mu$L·L$^{-1}$ in each case. Part of NO was oxidized to NO$_2$ over the catalysts, as shown in Table 3. It is worth noting that NO$_2$ could enhance the elemental mercury oxidation and removal as the oxidant based on the analyses in Section 3.2.3. Considering the concentration of nitrogen oxides in flue gas is much higher than that of gaseous elemental mercury, Equation (9) has a synergistic effect on the Hg$^0$ removal over the CeO$_2$/TiO$_2$ catalysts.
TiO₂ was only about 26.4%. By observing the η' of each CeO₂/TiO₂ catalyst, it can be found that NO removal efficiency showed a similar trend to Hg₀ removal efficiency. The value of η' reached its highest peak at 300 or 350 °C. The slight difference was that the NO removal efficiency increased more significantly than Hg₀ removal efficiency as the temperature rose from 150 to 200 °C. In general, the value of η' was slightly higher than that of η. When the reaction temperature was between 250 and 350 °C, the NO removal efficiencies of Ce₀.1Ti, Ce₀.2Ti, and Ce₀.5Ti were above 85%. That indicates that the novel CeO₂/TiO₂ catalysts could provide excellent simultaneous removal performance of Hg₀ and NO, especially from 300 to 350 °C. It is worth noting that this temperature range matched well with the working zone of commercial SCR catalyst, which makes it possible to replace some of the traditional catalyst with the novel CeO₂/TiO₂ catalysts. After being oxidized over the novel catalyst, the mercury pollutants would eventually be eliminated by other APCDs, such as WFGD and PMCDs.

![Figure 6](image-url)

**Figure 6.** Simultaneous removal of Hg⁰ and NO over various catalysts. (a) Ce₁.₀Ti; (b) Ce₀.₅Ti; (c) Ce₀.₂Ti; (d) Ce₀.₁Ti; (e) pure TiO₂.

| Catalyst | Ce₁.₀Ti | Ce₀.₅Ti | Ce₀.₂Ti | Ce₀.₁Ti | Pure TiO₂ |
|----------|---------|---------|---------|---------|-----------|
| NO       | 175.3   | 184.0   | 190.8   | 194.7   | 198.3     |
| NO₂      | 25.9    | 16.1    | 9.7     | 5.0     | 1.5       |

3.5. Characterizations

3.5.1. Main Compositions of the Catalysts

In order to obtain the mechanisms of the elemental mercury removal process over the catalysts prepared by sol–gel, the micro-scale physical and chemical properties of the samples were characterized.
In this section, the contents of the elements and the oxides were measured by X-ray fluorescence (XRF). The mass fraction of each substance was listed in Table 4. It can be seen that pure TiO$_2$ catalyst almost contained no other impurities because the mass fraction of TiO$_2$ was 99.8%. From the data of the oxides in the table, it can be calculated that the mass ratios of CeO$_2$ to TiO$_2$ of Ce0.1Ti, Ce0.2Ti, Ce0.5Ti, Ce1.0Ti, and Ce0.5Ti-V were 9.45%, 20.5%, 49.8%, 97.8%, and 47.9%, respectively. The mass fraction of V$_2$O$_5$ in Ce0.5Ti-V was 0.483%. The results above show that the actual mass fractions of the main components in the catalyst samples are very close to the theoretical values, indicating that the sol–gel method can control the content of each component precisely, which is unrealizable for the wet impregnation method.

| Catalyst    | Ti/\% | O/\% | Ce/\% | V/\% | TiO$_2$/\% | CeO$_2$/\% | V$_2$O$_5$/\% |
|-------------|-------|------|-------|------|------------|-------------|--------------|
| pure TiO$_2$ | 76.2  | 23.6 | -     | -    | 99.8       | -           | -            |
| Ce0.1Ti     | 64.6  | 25.9 | 8.53  | -    | 90.2       | 8.52        | -            |
| Ce0.2Ti     | 56.0  | 26.4 | 15.9  | -    | 81.4       | 16.7        | -            |
| Ce0.5Ti     | 33.9  | 38.4 | 22.3  | -    | 63.1       | 31.4        | -            |
| Ce1.0Ti     | 21.2  | 41.9 | 28.7  | -    | 45.9       | 44.9        | -            |
| Ce0.5Ti-V   | 44.0  | 25.9 | 26.2  | 0.161| 65.0       | 31.1        | 0.483        |

3.5.2. Crystalline Structures of the Catalysts

In this section, X-ray diffraction (XRD) tests were conducted on each sample to explore the similarities and differences of crystalline structures of the main components in different catalysts. The highest curve in Figure 7 represents the Ce0.5Ti-V catalyst, only in which a tiny V$_2$O$_5$ peak could be found. The peaks of TiO$_2$, including anatase TiO$_2$ and rutile TiO$_2$, could be observed in each curve. However, the height of TiO$_2$ peak shrank as the content of TiO$_2$ decreased while the CeO$_2$ peak began to appear and increased gradually. It should be mentioned that CeO$_2$ would have existed uniformly on the catalyst when its content was low so that the diffraction peak of CeO$_2$ was invisible then [32]. The results in Figure 7 support this view because the CeO$_2$ peaks could only be found in Ce0.5Ti, Ce0.5Ti-V, and Ce1.0Ti. In particular, the peaks around 28.5° were the most significant ones.

![Figure 7. Crystalline structures of the catalysts.](image-url)

3.5.3. Valence of Selected Elements

X-ray photoelectron spectroscopy (XPS) tests were carried out for pure TiO$_2$ catalyst and CeO$_2$/TiO$_2$ catalysts. The O 1s XPS spectra of the samples before and after the elemental mercury test are shown.
in Figure 8. Previous studies have shown that the oxygen on the catalyst can be divided into two main forms: adsorbed oxygen and lattice oxygen [33]. Two peaks could be observed in the XPS results of O 1s. The binding energy of adsorbed oxygen (O\(\alpha\)) was between 530.8 and 531.3 eV, while the binding energy of lattice oxygen (O\(\beta\)) ranged from 529.4 to 529.8 eV. The fraction of each type of oxygen could be obtained by calculating the proportion of the integral area of each peak. The results are summarized in Table 5. It was found that the fraction of adsorbed oxygen went up as the Ce content increased. Since the adsorbed oxygen was directly involved in the elemental mercury oxidation process, the Hg\(^0\) removal efficiency of the catalyst increased after the addition of Ce. In addition, the proportion of adsorbed oxygen in the catalyst was lower than that in the fresh catalyst. Especially for pure TiO\(_2\) catalyst, the fraction of O\(\alpha\) dropped from 45.6% to 27.8%. The main reason is that, unlike other catalysts, Ce\(^{3+}\)/Ce\(^{4+}\) pair was absent in pure TiO\(_2\) catalyst, which could convert lattice oxygen into adsorbed oxygen.

Figure 8. Cont.
Figure 8. XPS results of O 1s.. (a) fresh Ce1.0Ti; (b) used Ce1.0Ti; (c) fresh Ce0.5Ti; (d) used Ce0.5Ti; (e) fresh Ce0.2Ti; (f) used Ce0.2Ti; (g) fresh Ce0.1Ti; (h) used Ce0.1Ti; (i) fresh pure TiO$_2$; (j) used pure TiO$_2$.

Table 5. The fraction of each type of oxygen.

| Catalyst   | Fraction/% |
|------------|------------|
|            | O$_\alpha$ | O$_\beta$ |
| Ce1.0Ti    | fresh      | 79.7      | 20.3      |
| Ce1.0Ti    | used       | 69.4      | 30.6      |
| Ce0.5Ti    | fresh      | 76.3      | 23.7      |
| Ce0.5Ti    | used       | 64.3      | 35.7      |
| Ce0.2Ti    | fresh      | 73.0      | 27.0      |
| Ce0.2Ti    | used       | 60.0      | 40.0      |
| Ce0.1Ti    | fresh      | 54.2      | 45.8      |
| Ce0.1Ti    | used       | 48.0      | 52.0      |
| pure TiO$_2$ | fresh    | 45.6      | 54.4      |
| pure TiO$_2$ | used     | 27.8      | 72.2      |

Ce0.5Ti and pure TiO$_2$ catalysts were selected to test the Hg XPS spectra after the elemental mercury removal experiment. The results are shown in Figure 9. The Hg-related peaks could hardly be seen in the curve of pure TiO$_2$, since its mercury removal efficiency was low, as mentioned in Section 3.1. The elemental mercury removal performance improved after the addition of Ce. Mercury XPS spectra can be divided into two peaks, one of which is located near 99.8 eV, and the other is located near 104.4 eV. The peak with lower binding energy represents Hg$^0$, while the peak with higher binding energy represents HgO [20]. It can be found that main peak of the mercury in Ce0.5Ti belonged to HgO, which indicates that chemical adsorption was the main mechanism of the Hg$^0$ removal over Ce0.5Ti.

In order to further study the Hg$^0$ removal mechanisms and to evaluate the effects of vanadium oxides on the valence of cerium in CeO$_2$/TiO$_2$ catalyst, Ce0.5Ti and Ce0.5Ti-V were chosen to conduct the XPS tests before and after the elemental mercury removal experiment. The results of Ce XPS spectra...
were shown in Figure 10. Among the eight cerium independent peaks, \(u_1\) peak and \(v_1\) peak belong to Ce\(_2\)O\(_3\), while the others belong to CeO\(_2\) [34,35]. The fraction of each type of cerium oxide can be found in Table 6; they were calculated through the same method used in the analyses of O 1s XPS spectra. The CeO\(_2\) fractions of catalysts were lower than that of fresh catalysts. The reason is that CeO\(_2\) provided part of lattice oxygen to attend the oxidation reaction of elemental mercury so that CeO\(_2\) turned into Ce\(_2\)O\(_3\). By comparing the results of the two catalysts, it can be noted that the impact of vanadium on the valence of cerium in the catalyst was slight.

![Figure 9. XPS results of Hg.](image)

![Figure 10. XPS results of Ce. (a) fresh Ce0.5Ti; (b) used Ce0.5Ti; (c) fresh Ce0.5Ti-V; (d) used Ce0.5Ti-V.](image)
Table 6. The fraction of each type of cerium.

| Catalyst          | Ce\(^{3+}\) | Ce\(^{4+}\) |
|-------------------|-------------|-------------|
| fresh Ce0.5Ti     | 26.10       | 73.90       |
| used Ce0.5Ti      | 34.35       | 65.65       |
| fresh Ce0.5Ti-V   | 25.35       | 74.65       |
| used Ce0.5Ti-V    | 34.09       | 65.91       |

3.6. Discussion on Mechanisms

The Ce/Ti catalysts synthesized by sol–gel presented outstanding elemental mercury and NO removal efficiency. The addition of V could further promote the performance of the catalysts. According to the above analyses, the mechanisms of the removal process were shown in Figure 11. Although gaseous Hg\(^0\) could turn into adsorbed Hg\(^0\) through physical adsorption, it was mainly removed by chemical reaction. Both Ce\(^{4+}\) and V\(^{5+}\) are strong oxidants and could offer part of the lattice oxygen to generate the reactive oxygen, which would take part in the oxidation process of Hg\(^0\) and NO. The consumed Ce\(^{4+}\) and V\(^{5+}\) could be replenished from the reaction between their lower valence forms and the oxygen in the flue gas. Then, Hg\(^0\) and NO would be oxidized into Hg\(^{2+}\) and NO\(_2\). It is noteworthy that NO\(_2\) could also promote the oxidation of Hg\(^0\). The NO\(_x\) emission could be removed by the redox reaction with NH\(_3\). For mercury emission, many compounds, such as HgO, HgCl\(_2\), Hg(NO\(_3\))\(_2\), and HgSO\(_4\), would be derived from the reaction between Hg\(^{2+}\) and flue gas components. Most of these compounds could eventually be controlled by WFGD or PMCD.

![Figure 11. Mechanisms of Hg\(^0\) and NO removal over the catalysts.](image)

4. Conclusions

In this study, a series of powdery CeO\(_2\)/TiO\(_2\) catalysts with various Ce contents, together with a pure TiO\(_2\) catalyst, were prepared by sol–gel method. The influences of reaction temperature and flue gas components on the elemental mercury removal efficiency were investigated. The simultaneous removal performance of NO and Hg\(^0\) and the effect of vanadium on the catalyst performance were also considered. Advanced characterization methods were employed to explore the mechanisms of NO and Hg\(^0\) removal of the novel catalysts. The following conclusions can be drawn:
(1) The Hg\textsuperscript{0} removal efficiency of CeO\textsubscript{2}/TiO\textsubscript{2} catalyst was much higher than that of pure TiO\textsubscript{2} catalyst. The optimal reaction temperature was 350 °C. Ce0.2Ti catalyst showed the best performance among all samples, since an excessive Ce loading value would cause the blockage of the catalyst.

(2) Both O\textsubscript{2} and HCl would benefit the removal of elemental mercury. However, higher NH\textsubscript{3}/NO ratio and SO\textsubscript{2} concentration could bring negative effects on the Hg\textsuperscript{0} removal process. When the NH\textsubscript{3}/NO ratio was set as 1:1, the Hg\textsuperscript{0} removal efficiency increased firstly and then decreased as the NO and NH\textsubscript{3} concentration rose from 0 to 600 μL·L\textsuperscript{-1}.

(3) The Hg\textsuperscript{0} removal efficiency increased remarkably after the addition of vanadium. Elemental mercury could be oxidized by V\textsuperscript{5+}, which is a strong oxidant. Besides, V\textsubscript{2}O\textsubscript{5}/CeO\textsubscript{2}/TiO\textsubscript{2} catalyst showed good resistance to NH\textsubscript{3} and SO\textsubscript{2}.

(4) Excellent simultaneous removal performance of NO and Hg\textsuperscript{0} could be obtained within the temperature window from 300 to 350 °C. The SCR process was reinforced, since NO could be oxidized into NO\textsubscript{2} by Ce\textsuperscript{4+}. NO\textsubscript{2} also has a synergistic effect on the Hg\textsuperscript{0} removal over the catalysts.

(5) The content of each component in the catalyst can be controlled accurately by the sol–gel method. Cerium oxides distributed evenly on the catalyst’s surface unless the Ce loading value was high enough. The proportion of adsorbed oxygen in the catalyst increased significantly after Ce was added. Chemical reaction, instead of physical adsorption, would be the dominant mechanism of Hg\textsuperscript{0} removal for the catalyst with high Ce content. Ce\textsuperscript{4+}/Ce\textsuperscript{3+} pair and V\textsuperscript{5+}/V\textsuperscript{4+} pair were of great importance in the removal mechanisms of NO and Hg\textsuperscript{0}.

Author Contributions: Conceptualization, Q.L.; methodology, Q.L. and M.C.; investigation, Q.L. and Y.H.; writing—original draft preparation, Q.L.; writing—review and editing, C.W. and D.C.; supervision, D.C.; project administration, D.C.; funding acquisition, C.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Basic Research Plan in Shaanxi Province of China (2019JM-067, 2020JQ-061) and the Chinese Postdoctoral Science Foundation (2019T120286).

Acknowledgments: The authors acknowledge financial support from the Natural Science Basic Research Plan in Shaanxi Province of China (2019JM-067, 2020JQ-061) and the China Postdoctoral Science Foundation (2019T120286).

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Tuzen, M.; Ulusozlu, O.D.; Karaman, I.; Soylak, M. Mercury(II) and methyl mercury speciation on Streptococcus pyogenes loaded Dowex Optipore SD-2. J. Hazard. Mater. 2009, 169, 345–350. [CrossRef] [PubMed]
2. Zhou, P.Y.; Zhang, A.C.; Zhang, D.; Feng, C.X.; Su, S.; Zhang, X.M.; Xiang, J.; Chen, G.Y.; Wang, Y. Efficient removal of Hg-0 from simulated flue gas by novel magnetic Ag\textsubscript{2}WO\textsubscript{4}/BiOI/CoFe\textsubscript{2}O\textsubscript{4} photocatalysts. Chem. Eng. J. 2019, 373, 780–791. [CrossRef]
3. Lv, Q.; Cai, M.; Wang, C.A.; He, Y.; Che, D.F. Investigation on elemental mercury removal by cerium modified semi-coke. J. Energy Inst. 2020, 93, 666–678. [CrossRef]
4. Global Mercury Assessment 2018. Available online: https://www.unenvironment.org/resources/publication/global-mercury-assessment-2018 (accessed on 4 March 2019).
5. Wang, P.Y.; Su, S.; Xiang, J.; You, H.W.; Cao, F.; Sun, L.S.; Hu, S.; Zhang, Y. Catalytic oxidation of Hg-0 by MnO\textsubscript{2}/CeO\textsubscript{2}/gamma-Al\textsubscript{2}O\textsubscript{3} catalyst at low temperatures. Chemosphere 2014, 101, 49–54. [CrossRef] [PubMed]
6. Xia, Y.J.; Liao, Z.Q.; Zheng, Y; Zhou, Z.J. Highly dispersed Mn–Ce binary metal oxides supported on carbon nanofibers for Hg\textsuperscript{0} removal from coal-fired flue gas. Appl. Sci. 2018, 8, 2501. [CrossRef]
7. Liu, H.W.; Diao, X.; Yu, B.; Shi, J.B.; Liu, Q.; Yin, Y.G.; Hu, L.G.; Yuan, C.G.; Jiang, G.B. Effect of air pollution control devices on mercury isotopic fractionation in coal-fired power plants. Chem. Geol. 2019, 517, 1–6. [CrossRef]
8. Lv, Q.; Cai, M.; Wang, C.A.; Zhang, Z.H.; Che, D.F. Investigation on elemental mercury removal and antideactivation performance of modified SCR catalysts. Asia-Pac. J. Chem. Eng. 2018, 13, 14. [CrossRef]
9. Xu, W.; Hussain, A.; Liu, Y.X. A review on modification methods of adsorbents for elemental mercury from flue gas. Chem. Eng. J. 2018, 346, 692–711. [CrossRef]
10. Reddy, B.M.; Khan, A.; Yamada, Y.; Kobayashi, T.; Loridant, S.; Volta, J.C. Structural characterization of CeO$_2$-TiO$_2$ and V$_2$O$_5$/CeO$_2$-TiO$_2$ catalysts by Raman and XPS techniques. J. Phys. Chem. B 2003, 107, 5162–5167. [CrossRef]

11. Xu, Y.H.; Chen, H.R.; Zeng, Z.X.; Lei, B. Investigation on mechanism of photocatalytic activity enhancement of nanometer cerium-doped TiO$_2$. Appl. Surf. Sci. 2006, 252, 8565–8570. [CrossRef]

12. Gao, X.; Jiang, Y.; Zhong, Y.; Luo, Z.Y.; Cen, K.F. The activity and characterization of CeO$_2$-TiO$_2$ catalysts prepared by the sol-gel method for selective catalytic reduction of NO with NH$_3$. J. Hazard. Mater. 2010, 174, 734–739. [CrossRef]

13. Liu, M.; Li, C.T.; Zeng, Q.; Du, X.Y.; Gao, L.; Li, S.H.; Zhai, Y.B. Study on removal of elemental mercury over MoO$_3$-CeO$_2$/cylindrical activated coke in the presence of SO$_2$ by Hg-temperature-programmed desorption. Chem. Eng. J. 2019, 371, 666–678. [CrossRef]

14. Zhao, L.; Li, C.; Li, S.; Wang, Y.; Zhang, J.; Wang, T.; Zeng, G. Simultaneous removal of elemental mercury and NO in simulated flue gas over V$_2$O$_5$/ZrO$_2$-CeO$_2$ catalyst. Appl. Catal. B-Environ. 2016, 198, 420–430. [CrossRef]

15. Zhao, L.; Li, C.; Zhang, J.; Zhang, X.; Zhan, F.; Ma, J.; Xie, Y.E.; Zeng, G. Promotional effect of CeO$_2$ modified support on V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst for elemental mercury oxidation in simulated coal-fired flue gas. Fuel 2015, 153, 361–369. [CrossRef]

16. Liu, Z.; Zhang, S.; Li, J.; Zhu, J.; Ma, L. Novel V$_2$O$_5$-CeO$_2$/TiO$_2$ catalyst with low vanadium loading for the selective catalytic reduction of NO$_x$ by NH$_3$. Appl. Catal. B-Environ. 2014, 158, 11–19. [CrossRef]

17. Gao, L.; Li, C.T.; Li, S.H.; Zhang, W.; Du, X.Y.; Huang, L.; Zhu, Y.C.; Zhai, Y.B.; Zeng, G.M. Superior performance and resistance to SO$_2$ and H$_2$O over CoO$_2$-modified MnO$_x$/bioassisted activated carbons for simultaneous Hg-$\text{O}$ and NO removal. Chem. Eng. J. 2019, 371, 781–795. [CrossRef]

18. Kamata, H.; Ueno, S.; Sato, N.; Naito, T. Mercury oxidation by hydrochloric acid over TiO$_2$ supported metal oxide catalysts in coal combustion flue gas. Fuel Process. Technol. 2009, 90, 947–951. [CrossRef]

19. Li, H.L.; Wu, C.Y.; Li, Y.; Zhang, J.Y. CeO$_2$-TiO$_2$ catalysts for catalytic oxidation of elemental mercury in low-rank coal combustion flue gas. Environ. Sci. Technol. 2011, 45, 7394–7400. [CrossRef]

20. He, C.; Shen, B.; Li, F. Effects of flue gas components on removal of elemental mercury over Ce-MnO(x)/Ti-PILCs. J. Hazard. Mater. 2016, 304, 10–17. [CrossRef]

21. He, C.; Shen, B.; Chi, G.; Li, F. Elemental mercury removal by CeO$_2$/TiO$_2$-PILCs under simulated coal-fired flue gas. Chem. Eng. J. 2016, 300, 1–8. [CrossRef]

22. Qiao, S.; Chen, J.; Li, J.; Qu, Z.; Liu, P.; Yan, N.; Jia, J. Adsorption and catalytic oxidation of gaseous elemental mercury in flue gas over MnO$_x$/alumina. Ind. Eng. Chem. Res. 2009, 48, 3317–3322. [CrossRef]

23. Kellie, S.; Cao, Y.; Duan, Y.F.; Li, L.C.; Chu, P.; Mehta, A.; Carty, R.; Riley, J.T.; Pan, W.P. Factors affecting mercury speciation in a 100-MW coal-fired boiler with low-NO$_x$ burners. Energy Fuels 2005, 19, 800–806. [CrossRef]

24. Olson, E.S.; Sharma, R.K.; Pavlish, J.H. On the analysis of mercuric nitrate in flue gas by GC-MS. Anal. Bioanal. Chem. 2002, 374, 1045–1049. [CrossRef]

25. Zhou, J.; Hou, W.; Qi, P.; Gao, X.; Luo, Z.; Cen, K. CeO$_2$-TiO$_2$ sorbents for the removal of elemental mercury from syngas. Environ. Sci. Technol. 2013, 47, 10056–10062. [CrossRef] [PubMed]

26. Eswaran, S.; Stenger, H.G. Understanding mercury conversion in selective catalytic reduction (SCR) catalysts. Energy Fuels 2005, 19, 2328–2334. [CrossRef]

27. Li, H.L.; Wu, C.Y.; Li, Y.; Li, L.Q.; Zhao, Y.C.; Zhang, J.Y. Impact of SO$_2$ on elemental mercury oxidation over CeO$_2$-TiO$_2$ catalyst. Chem. Eng. J. 2013, 219, 319–326. [CrossRef]

28. Kim, M.H.; Ham, S.-W.; Lee, J.-B. Oxidation of gaseous elemental mercury by hydrochloric acid over CuCl$_2$-TiO$_2$-based catalysts in SCR process. Appl. Catal. B-Environ. 2010, 99, 272–278. [CrossRef]

29. Ding, S.; Liu, F.; Shi, X.; He, H. Promotional effect of Nb additive on the activity and hydrothermal stability for the selective catalytic reduction of NO$_x$ with NH$_3$ over CeZrO$_2$ catalyst. Appl. Catal. B-Environ. 2016, 180, 766–774. [CrossRef]

30. Yang, B.; Shen, Y.; Shen, S.; Zhu, S. Regeneration of the deactivated TiO$_2$-ZrO$_2$-CeO$_2$/ATS catalyst for NH$_3$-SCR of NO$_x$ in glass furnace. J. Rare Earth. 2013, 31, 130–136. [CrossRef]

31. Koebel, M.; Madia, G.; Raimondi, F.; Wokaun, A. Enhanced reoxidation of vanadia by NO$_2$ in the fast SCR reaction. J. Catal. 2002, 209, 159–165. [CrossRef]
32. Mullins, D.R.; Overbury, S.H.; Huntley, D.R. Electron spectroscopy of single crystal and polycrystalline cerium oxide surfaces. *Surf. Sci.* **1998**, *409*, 307–319. [CrossRef]

33. Dupin, J.C.; Gonbeau, D.; Vinatier, P.; Levasseur, A. Systematic XPS studies of metal oxides, hydroxides and peroxides. *PCCP Phys. Chem. Chem. Phys.* **2000**, *2*, 1319–1324. [CrossRef]

34. Romeo, M.; Bak, K.; Elfallah, J.; Lenormand, F.; Hilaire, L. XPS study of the reduction of cerium dioxide. *Surf. Interface Anal.* **1993**, *20*, 508–512. [CrossRef]

35. Zou, Z.Q.; Meng, M.; Zha, Y.Q. Surfactant-Assisted Synthesis, Characterizations, and catalytic oxidation mechanisms of the mesoporous MnO$_x$-CeO$_2$ and Pd/MnO$_x$-CeO$_2$ catalysts used for CO and C$_3$H$_8$ oxidation. *J. Phys. Chem. C* **2010**, *114*, 468–477. [CrossRef]