New Effective Catalyst for Elemental Mercury Removal from Coal-Fired Flue Gas and the Mechanism Investigation

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Supporting Information

ABSTRACT: Mercury pollution from coal-fired power plants has drawn attention worldwide. To achieve efficient catalytic oxidation of Hg0 at both high and low temperatures, we prepared and tested novel IrO2 modified Ce−Zr solid solution catalysts under various conditions. It was found that the IrO2/Ce0.6Zr0.4O2 catalyst, which was prepared using the polyvinylpyrrolidone-assisted sol−gel method, displayed significantly higher catalytic activity for Hg0 oxidation. The mechanism of Hg0 removal over IrO2/Ce0.6Zr0.4O2 was studied using various methods, and the Hg0 oxidation reaction was found to follow two possible pathways. For the new chemisorption−regeneration mechanism proposed in this study, the adsorbed Hg0 was first oxidized with surface chemisorbed oxygen species to form HgO; the HgO could desorb from the surface of catalysts by itself or react with adsorbed HCl to be released in the form of gaseous HgCl2. O2 is indispensable for the chemisorption process, and the doping of IrO2 could facilitate the chemisorption process. In addition, the Deacon reaction mechanism was also feasible for Hg0 oxidation: this reaction would involve first oxidizing the adsorbed HCl to active Cl species, after which the Hg0 could react with Cl to form HgCl2. Additionally, doping IrO2 could significantly improve the Cl yield process. In summary, the novel IrO2 modified catalyst displayed excellent catalytic activity for elemental mercury oxidation, and the proposed reaction mechanisms were determined reasonably.

INTRODUCTION

Mercury is a heavy metal pollutant with high levels of toxicity, bioaccumulation, and persistence that has caused worldwide concern.1 The Minamata Convention on Mercury regarding mercury pollution was signed by many governments in 2013, which pressured major mercury emitters such as China and the United States to reduce mercury emissions.2,3 Coal-fired power plants are the primary sources of anthropogenic mercury pollution to the atmosphere because of high levels of coal consumption. Some researches proposed that mercury from coal-fired boilers contributed approximately 40% of the total mercury emissions in China.4,5 Mercury can exist in coal-fired flue gas in three different forms: elemental mercury (Hg0), gaseous oxidized mercury (Hg2+), and particulate-bound mercury (HgP). The distribution of these forms mainly depends on the chlorine content of the coal and the combustion conditions.6 Most oxidized and particulate-bound mercury can be easily removed from the exhaust with typical air-pollution-control devices (APCDs). However, Hg0 is highly volatile and insoluble and is the dominant mercury species that escapes into the atmosphere from coal-fired power plants. Therefore, the catalytic oxidation of Hg0 to Hg2+ (which can be dissolved in water and captured by WFGD under certain conditions) with HCl from flue gas is an economical and feasible method for achieving greater mercury removal efficiency with existing APCDs.6−10 For example, the catalysts involved in the process of selective catalytic reduction (SCR) of NOx, which usually occurs at 300−400 °C,11 have been investigated as potential Hg0 conversion catalysts when sufficient HCl is present in the flue gas.12,13 However, the presence of ammonia (NH3), which is used as an SCR reductant, can significantly inhibit Hg0 oxidation over conventional SCR catalysts.12,13 Therefore, it is reasonable to equip Hg0 oxidation catalysts at the tail section of the SCR unit, where the NH3 concentration is lower. In addition, the low-temperature SCR (approximately 150 °C) technique has become more popular in recent years and has a tendency for future industrial applications.14 Therefore, it is important to develop a new catalyst that could convert elemental mercury significantly at lower temperatures and thus be compatible with low-temperature SCR catalysts.

Many studies have proposed that the catalytic oxidation of Hg0 to Hg2+ over some catalysts with presence of HCl could be explained through the Deacon reaction pathway, in which HCl is converted to Cl2 or Cl atoms by oxygen.15−18 IrO2 has proven to be an active catalyst for the Deacon reaction, effectively converting HCl to Cl2.19,20 Thus, IrO2 is expected to be a promising catalyst component for Hg0 conversion in the...
presence of HCl. A solid solution of ceria (Ce) and zirconia (Zr) with cubic fluorite phase (Ce/Zr > 1:1) has been used as the catalyst carrier in recent studies because of its outstanding oxygen storage capacity and unique redox properties. In previous studies, catalysts for elemental mercury oxidation were developed from SCR catalysts, and Ce–Zr solid-solution-supported metal oxide catalysts exhibited significant catalytic activity for low-temperature-selective catalytic reduction of NOx from coal-fired flue gas. Other previous studies have reported that Ce–Zr supported catalysts display excellent catalytic oxidation ability for the ammonia slipping from SCR units, which would also mitigate the negative effects of NH3 on elemental mercury oxidation. Therefore, the Ce–Zr solid solution is a promising catalyst for Hg0 oxidation that would be compatible with SCR units at both high and low temperatures. Although Ir has been used as mercury-removal sorbent, the catalytic activity of the IrO2 modified Ce–Zr complex for mercury oxidation is still unclear. In addition, the interaction between IrO2 and the Ce–Zr supporter has not been studied previously. Mechanisms including the Mars–Maessen mechanism, the Eley–Rideal mechanism, and the Langmuir–Hinshelwood mechanism have been proposed for mercury oxidation over various catalysts. However, the mechanism of mercury removal over IrO2 modified catalyst is unclear. In particular, there is still no consensus regarding the role of Cl in the process of elemental mercury oxidation. Thus, we focus on the mechanism of mercury oxidation in this study.

Because Ir is a noble metal and is thus more expensive than most transition metals, the IrO2 content was set at a very low level (0.2%). To maintain catalytic performance despite the low Ir concentration, we used the sol–gel method with polyvinylpyrrolidone (PVP) to enhance the dispersion of IrO2 on the catalyst surface. We evaluated the efficiency of elemental mercury removal and adsorption behavior over various modified catalysts. In addition, we evaluated the possible catalytic mechanisms of elemental mercury using techniques such as H2 temperature-programmed reduction (TPR), Hg temperature-programmed desorption (TPD), and Cl2 yield. We focus our discussion on the effects of IrO2 and Cl in the oxidation process.

## EXPERIMENTAL SECTION

### Materials and Catalyst Preparation

The IrO2 doping catalysts were synthesized according to a method reported in literature. First, 0.2 g polyvinylpyrrolidone (Mw = 58 000) and quantitative iridium acetate were dissolved in 30 mL of ethanol, and the mixture was refluxed at 100 °C for 3 h. After this, the Ir colloid solution was added to Ce0.2Zr1.0O2 (see the Supporting Information), and the mixture was dried at 60 °C with electromagnetic stirring. Calcination was achieved by increasing the temperature from room temperature to 400 °C at a 1 °C/min ramping rate, after which the solution was heated at 400 °C for 5 h in air. The catalysts were labeled as IrO2/Ce0.2Zr1.0O2 (PVP). IrO2/Ce0.2Zr1.0O2 was prepared with the wet impregnation method. The Ir oxide content of Ce0.2Zr1.0O2 was set at 0.2 wt % for all catalysts.

### Catalyst Characterization

X-ray photoelectron spectroscopy (XPS) measurements were taken with an AXIS UltraDLD (Shimadzu–Kratos) spectrometer with Al Kα as the excitation source. The C 1s line at 284.8 eV was used as a reference for the binding-energy calibration. The H2 temperature program reduction curves were determined using a chemisorption analyzer (2920, AutoChem II, Micromeritics). The H2 flow rate was 50 cm3/min, and the temperature ramp rate was 10 °C/min.

### Catalytic Activity Measurement

The Hg0 adsorption and catalytic oxidation experiments over catalysts were performed in a fixed-bed quartz reactor; the experimental system is shown in Figure S1. The catalyst powder was placed in the reactor with quartz wool under atmospheric pressure, and the reactor was heated by a vertical electrical furnace. The feed gases were adjusted by mass-flow controllers and introduced into the reactor with a total flow rate of 500 mL/min. The gas with stable elemental mercury concentration from a Hg0 permeation tube flowed through the blank tube and the reactor tube. The mercury concentration was monitored by a Lumex 915+ or Tekran 3300 mercury analyzer. The Tekran 3300 systems were programmed to measure Hg2+ and Hg0 semicontinuously over a 2.5 min collection–analysis cycle. The reported Hg2+ fraction was calculated as the difference between sequentially measured Hg2+ and Hg0 concentrations.

For the Hg0 adsorption experiment, the Hg0 flow first passed through the blank tube to provide an original Hg0 signal. The Hg0 concentration for the adsorption experiment was ranged from 370 to 1500 ng/L for the different experiments. We used these high concentrations for two reasons. First, the Hg0 adsorption capacity of our catalysts is very high, so if a normal mercury concentration was used, it would take long time to reach equilibrium. High mercury concentration could shorten the adsorption time. Many previous studies have also used high mercury concentration. Second, high mercury concentration can minimize the relative error due to continuous data acquisition in the tests. For the results obtained from Tekran 3300 mercury analyzer, the mercury concentration was approximately 370 ng/L due to the test limit. After the Hg0 concentration had stabilized, the Hg0 concentration in the outlet was measured as [Hg0]1, and then the gas was switched to the reactor tube to begin Hg0 adsorption. For the Hg0 catalytic oxidation experiment with HCl and O2, the flow containing mercury was first passed through the catalysts to undergo adsorption. Next, HCl or other gases were added to the gas, and the Hg0 concentration in the outlet was measured as [Hg0]2, until the reaction attained equilibrium (stable for long time). The Hg0 oxidation efficiency (Eox) over the catalysts was quantified by the following equation:

$$E_{\text{ox}}(\%) = \frac{[\text{Hg0}]_1 - [\text{Hg0}]_2}{[\text{Hg0}]_1} \times 100\%$$

Hg-TPD was conducted using 30 mg of the catalyst in a quartz reactor. First, the Hg0 adsorption achieved by passing a gas mixture containing approximately 1090 ng/L Hg0 with O2/N2 or N2 as the balance gas through the reactor tube at 150 °C for 90 min with a total flow rate of 500 mL/min; next, the reactor tube was purged with N2 for 30 min. Desorption measurements were performed from 150 to 500 °C at a heating rate of 5 °C/min under a N2 atmosphere of 500 mL/min. An online mercury analyzer continuously recorded the desorbed concentration of Hg0.

Finally, the mechanism of Hg0 oxidation was evaluated using Deacon reaction evaluation units (with chlorine yield as the marker). The Cl2 concentration was monitored using a UV/vis spectrometer (BWTEK BRC642E). A photocell constructed to have an optical length of 80 cm.
RESULTS AND DISCUSSION

Catalytic Activity. The Figure 1 shows the catalytic oxidation efficiencies over catalysts under various conditions; preliminary tests showed that Ce0.6Zr0.4O2 supported catalysts displayed superior catalytic activity (Figure S2). The Hg0 oxidation efficiency over Ce0.6Zr0.4O2 was 22% when there was only 4% O2 in the gas at 150 °C. The mercury-removal efficiencies over IrO2 modified catalysts increased to approximately 41% and 44% in the presence of O2 for IrO2/Ce0.6Zr0.4O2 and IrO2/Ce0.6Zr0.4O2(PVP), respectively, which indicated that doping with only 0.2% IrO2 could significantly facilitate Hg0 conversion even without HCl. When HCl was introduced into the gas, mercury removal efficiencies were enhanced significantly over all three catalysts. For example, the mercury removal efficiency over IrO2/Ce0.6Zr0.4O2 increased from 41% to 90% in the presence of 3 ppm of HCl at 350 °C. The synthesis method also had an effect on the catalytic activity. The Hg0 oxidation efficiency over IrO2/Ce0.6Zr0.4O2(PVP) increased to approximately 97% at 150 °C. We propose that PVP might promote IrO2 dispersion over the catalyst, similar to results in other studies, and the catalytic activity was slightly enhanced in consequence.27 We also tested the effects of SO2 on Hg0 oxidation. Results showed that SO2 had a different influence on all three catalysts at high and low temperatures. We note that mercury concentrations decreased during addition of SO2 at both high and low temperatures (Figure S3). Some previous studies have proposed that SO2 could be transferred to SO3 over some catalysts and that SO3 could no longer be converted over the catalyst in the absence of O2. However, the breakthrough curve was very different in the presence of O3, the adsorption capacity was much larger with O2 present and the reaction took approximately 165 min to reach adsorption saturation. These results indicate that the adsorption process of Hg0 over the IrO2/Ce0.6Zr0.4O2 catalyst is likely a chemisorption process, and that O2 is indispensable for this process. The final detected concentration for Hg0 was approximately 60% of the initial level, which suggests that Hg0 can be oxidized over the IrO2 modified catalyst in the absence of HCl. This agrees with the results shown in Figure 1.

Halogen can strongly affect mercury removal. To clarify the effect of gaseous HCl, we also performed the Hg0 adsorption experiment over a IrO2/Ce0.6Zr0.4O2(PVP) catalyst pretreated with 10 ppm of HCl. The IrO2 modified catalyst was pretreated with 10 ppm of HCl and 4% O2 with N2 carrier at 350 °C for 4 h, after which it was purged with N2 for 1 h. Next, the Hg0 adsorption experiment was carried out, and the adsorption curve is shown in Figure 2. The result shows that the adsorption capacity of the catalyst was significantly improved by HCl treatment, and the removal efficiency of elemental mercury was higher than 99%, even after interacting with Hg0 for 300 min. To identify the interaction between HCl and O2 and evaluate the role of O2, we performed another Hg0 adsorption experiment over the catalyst. The catalyst was pretreated under 10 ppm of HCl without O2 for 4 h, after which it was purged with N2 for 1 h.

Figure 1. Catalytic oxidation of Hg0 over various catalysts and different condition at 350 and 150 °C. Reaction conditions: 500 ppm of SO2, O2; 4 vol % N2 as carrier; flow rate, 500 mL/min; catalyst weight, 30 mg. The space velocity (SV) was approximately 7.6 × 103 h−1.

Figure 2. Adsorption breakthrough curves of Hg0 over the IrO2/Ce0.6Zr0.4O2(PVP) catalysts under different conditions. Reaction conditions: 4 vol % O2; N2 as carrier; flow rate, 500 mL/min; catalyst weight, 30 mg. The space velocity was approximately 7.6 × 103 h−1.

IrO2/Ce0.6Zr0.4O2(PVP) was greater than 90% in the simulated coal-fired flue gas (including NO, NH3, SO2, H2O, O2, and N2) over a long experimental duration at both high and low temperatures(Figure S4 and S5). The results showed that catalysts had excellent durability for the complex components in the flue gas.

Adsorption Experiment. Adsorption generally plays a significant role in catalytic reactions. Therefore, to determine the catalytic mechanism of mercury oxidation over the IrO2 modified catalysts, we evaluated the adsorption of Hg0 under various conditions (Figure 2). First, Hg0 adsorption was performed over the IrO2/Ce0.6Zr0.4O2 catalyst in the absence of O2, and adsorption equilibrium was reached quickly within 30 min. After adsorption saturation was reached, the Hg0 concentration recovered to initial levels, such that Hg0 could no longer be converted over the catalyst in the absence of O2. However, the breakthrough curve was very different in the presence of O3, the adsorption capacity was much larger with O2 present and the reaction took approximately 165 min to reach adsorption saturation. These results indicate that the adsorption process of Hg0 over the IrO2/Ce0.6Zr0.4O2 catalyst is likely a chemisorption process, and that O2 is indispensable for this process. The final detected concentration for Hg0 was approximately 60% of the initial level, which suggests that Hg0 can be oxidized over the IrO2 modified catalyst in the absence of HCl. This agrees with the results shown in Figure 1.

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The resulting adsorption curve was similar to the curve from the treatment with HCl and O₂ showing that HCl can have an effect on mercury removal in the absence of O₂. Additionally, this result suggests that HCl and O₂ might not interact during the reaction.

Hg-TPD. After the mercury adsorption experiments, we used the Hg-TPD technique to identify the mercury captured on the IrO₂/Ce₀.₆Zr₀.₄O₂ catalysts, and the results are shown in Figure 3. After the catalyst adsorbed Hg⁰ in 4% O₂/N₂ atmosphere, two main desorption peaks are present at approximately 284 and 425 °C. According to some literature, two desorption peaks centered at approximately 110 and 260 °C can be observed over many catalysts during Hg-TPD experiment, and these correspond to the decomposition of weakly adsorptive species and strongly bound species, respectively. Because the adsorption experiment in this research was performed at 150 °C, it is reasonable that we cannot detect desorption peaks below 150 °C. The peak at 284 °C is close in value to the peak at approximately 260 °C shown by previous studies, so we suggest that it may reflect the desorption of strongly bound, physically adsorbed Hg⁰. The desorption peak at higher temperatures, then, likely corresponds to the decomposition of HgO. The fact that the peak area at 425 °C is much larger than the peak area at 284 °C indicates that the majority of the mercury species existed as HgO and chemisorption was the dominant mode of Hg⁰ adsorption on the IrO₂ modified catalyst. While, the intensities of the desorption peaks were much weaker over the catalyst that adsorbing Hg⁰ in a pure N₂ atmosphere. The desorption peak of HgO is still observed, possibly because Hg⁰ could still be chemically adsorbed and converted to HgO due to the outstanding oxygen storage capacity of the Ce₀.₆Zr₀.₄O₂ carrier.

To evaluate the effect of HCl on mercury adsorption, we pretreated the catalyst with HCl and O₂/N₂ atmosphere at 150 and 350 °C, respectively, before Hg⁰ adsorption, and the results are also given in Figure 3. A broad desorption shoulder is present from 250 °C over the catalyst pretreated with HCl under an 4% O₂/N₂ atmosphere at 150 °C. Meanwhile, a desorption peak is centered at 450 °C for the catalyst pretreated under HCl with 4% O₂ at 350 °C. The intensities of the mercury desorption peaks over the catalyst after HCl treatment were much weaker than the fresh catalysts, which meant the amount of mercury adsorbed over the catalyst became much less because of the HCl treatment. Some studies have shown that the thermal decomposition of HgCl₂ phase occurs at low temperatures ranging from 70 to 220 °C (with a maximum at 120 °C). Our results did not show any such desorption peaks over the HCl-pretreated catalysts, indicating that none of the HgCl₂ species existed over the surface of the HCl-pretreated catalysts, even after Hg⁰ adsorption. We also treated the catalyst with HCl in N₂ atmosphere at 350 °C before Hg⁰ adsorption. The resulting desorption profile was similar, and no obvious desorption peak was detected for the catalyst pretreated with HCl in N₂. This result suggests that HCl can affect the reaction in the absence of O₂, which supports the results shown in Figure 2.

The results in Figures 2 and 3 seem “contradictory.” Figure 2 shows that HCl treatment with or without O₂ can significantly improve the apparent adsorption capacity of Hg⁰ over the catalyst. In contrast, Figure 3 shows that the amount of desorption of adsorbed mercury over the HCl pretreated catalyst was much less than that from the amount from fresh catalyst. To explain these “contradictory” situation, we propose a new mechanism called the chemisorption—regeneration mechanism. First, elemental mercury is adsorbed to the surface of the catalyst, and the adsorbed Hg⁰ is oxidized with surface-chemisorbed oxygen species to form HgO (see reactions 2–3 below). The portion of formed HgO can desorb from the catalyst’s surface in the absence of HCl, which would regenerate active adsorption sites (reaction 4). Some studies have proposed that O₂ can be dissociated over IrO₂ catalyst (reaction 1), which could replenish the consumption of active oxygen. This could explain why elemental mercury could be oxidized in the presence of O₂ alone in Figure 1. When HCl exists in gas, it can adsorb to the catalyst surface and then react with formed HgO to HgCl₂ (reactions 5–7). HgCl₂ is much easier to be released as a gas from the surface of the catalyst. In this reaction pathway, HCl could affect the mercury adsorption property of the catalyst even in the absence of O₂. When the HCl treatment and Hg⁰ adsorption with O₂ were divided factitiously into two separate processes, as in the experiments shown in Figures 2 and 3, they demonstrated the chemisorption process for reactant and the regeneration process for the catalyst. When Hg⁰, O₂, and HCl coexisted in the experiment as shown in Figure 1 (and in real coal-fired flue gas), the chemisorption process and regeneration process by HCl could proceed simultaneously. The apparent experimental result was that Hg⁰ is converted into HgCl₂ continuously. The overall reaction could be considered to be catalytic oxidation, as in reaction 8.

![Figure 3. Temperature-programmed-desorption of Hg over the IrO₂/Ce₀.₆Zr₀.₄O₂ (PVP) catalysts under different conditions.](Image)

$$\begin{align*}
\text{O}_2(g) & \rightarrow 2\text{O} \quad (1) \\
\text{Hg}^{0}(g) & \rightarrow \text{Hg}^{0}(\text{ads}) \quad (2) \\
\text{Hg}^{0}(\text{ads}) + \text{O} & \rightarrow \text{HgO(ads)} \quad (3) \\
\text{HgO(ads)} & \rightarrow \text{HgO(g)} \quad (4) \\
\text{HCl(g)} & \rightarrow \text{HCl(ads)} \quad (5) \\
\text{HgO(ads)} + 2\text{HCl(ads)} & \rightarrow \text{HgCl}_2(\text{ads}) + \text{H}_2\text{O} \quad (6) \\
\text{HgCl}_2(\text{ads}) & \rightarrow \text{HgCl}_2(g) \quad (7) \\
\text{Hg(g)} + 2\text{HCl(g)} + \text{O}_2(g) & \rightarrow \text{HgCl}_2(g) + \text{H}_2\text{O(g)} \quad (8) \\
\end{align*}$$

**Verification of the Proposed Mechanism.** To verify the mechanism proposed above, we employed a Tekran mercury...
adsorption equilibrium was not yet reached, the Hg0 removal only shows the initial stage of the chemisorption process, when HgT was observed. This increase may have occurred because when HCl was added into the gas, a momentary increase of its outstanding oxygen storage capacity, which will be discussed later. After adsorption equilibrium was reached, HCl was introduced into the gas, and the results are shown in Figure 4b. When HCl was added into the gas, a momentary increase of HgT was observed. This increase may have occurred because the Hg0 formed over the catalyst reacted with HCl to form HgCl2, which then desorbed into the gas phase, as in reactions 5 and 6. Due to the desorption of oxidized mercury, the active sites on the surface of the catalyst were regenerated, and elemental mercury was adsorbed to the catalyst, which caused the decrease of Hg0 shown in Figure 4b.

Figure 4c shows the results of Hg0 adsorption over the catalyst in the absence of O2. After Hg0 adsorption equilibrium was reached, no oxidized mercury could be detected (Figure 4c). Next, O2 gas was introduced, and the concentration of Hg0 decreased significantly, likely because the chemisorption of Hg0 over the catalyst was improved by the replenishment of oxygen species. We also note that oxidized mercury was generated with the presence of O2 and the amount increased over time. Though large amounts of oxidized mercury were formed, the concentration of Hg2+ decreased until the concentration of Hg0 was stable. After that, the Hg0 increased more gradually, and more Hg2+ was generated. These results indicate that the oxidation of elemental mercury over the catalyst in the presence of O2 could proceed through reactions 2–4. Because Figure 4c only shows the initial stage of the chemisorption process, when adsorption equilibrium was not yet reached, the Hg0 removal efficiency was much higher. After reaching adsorption equilibrium, the removal efficiency would likely decrease to approximately 48% (corresponding to the results in Figures 1 and 4d). The catalytic oxidation of Hg0 with O2 and HCl was also monitored by the Tekran mercury analyzer, and the results are shown in Figure 4d. When approximately 370 ng/L Hg0 was passed through the catalyst at 350 °C in the presence of O2, approximately 175 ng/L Hg2+ could be detected in the gas after reaching equilibrium, which demonstrates that elemental mercury can be catalytically oxidized by O2 in the absence of HCl, like the result in Figure 1. This result also proves that the conversion of Hg0 could proceed through reactions 2–4. When HCl was introduced into the gas, a momentary significant increase of Hg2+ and Hg0 was observed. This could have been caused by the release of Hg2+ due to adding of HCl through reactions 5–6. As the oxidized mercury desorbed from the surface of the catalyst into gaseous form, the active sites on the catalyst were regenerated, which would accelerate the chemisorption of Hg0 (reactions 2–3), resulting in the decline of Hg0 concentration. Because the concentration of Hg0 decreased as HCl was added into the gas, the Hg2+ also decreased after the initial increase. After the reaction reached equilibrium, the Hg2+ began to increase again and finally recovered to its initial level. This indicates that mercury was balanced during the catalytic oxidation reaction.

H2-TPR. To investigate the redox ability of the catalysts, we tested the temperature program reduction (TPR) by hydrogen for the Ce0.6Zr0.4O2 and IrO2/Ce0.6Zr0.4O2 catalysts. The results are shown in Figure 5. The profile for the Ce0.6Zr0.4O2 catalyst has a broad reduction peak that begins at 300 °C and is centered at approximately 580 °C. We attribute this peak to the reduction of the Ce4+ in the Ce–Zr solid solution.37,38 A weak peak at 260 °C appears in the profile for the 0.2%IrO2/ZrO2 catalyst, which is ascribed to reduction of highly dispersed IrO2 species.39 Previous studies have shown that it is difficult to reduce ZrO2 by H2 at low temperatures, so the reduction peaks at approximately 530 °C over the profile of the 0.2%IrO2/ZrO2.
The catalyst could be caused by the interaction between IrO₂ and ZrO₂ support.\(^4\) A strong peak is present at approximately 190 °C for the IrO₂/Ce₀.₆Zr₀.₄O₂ catalyst, and this is not observed in the profiles of Ce₀.₆Zr₀.₄O₂ and IrO₂/ZrO₂. In general, peaks below 200 °C are probably caused by the reduction of crystalline IrO₂ species (large particles), and peaks above 250 °C are caused by the reduction of well-dispersed IrO₂ species.\(^3\) However, the peak centered at 190 °C over the IrO₂/Ce₀.₆Zr₀.₄O₂ cannot be attributed to the reduction of IrO₂ alone because the content of IrO₂ is only 0.2% and the H₂ consumption amount should be very low (similar to the small peak in the IrO₂/ZrO₂ profile). In addition, the large peak at 580 °C caused by reduction of Ce⁴⁺ in the profile for the IrO₂/Ce₀.₆Zr₀.₄O₂ catalyst vanished with the doping of 0.2% IrO₂. To identify the peak, we also show the H₂-TPR curve of IrO₂/CeO₂ in Figure S5, and a similar peak was detected at 210 °C. Therefore, it is reasonable to infer that the strong peak at low temperature (approximately 190 °C) could be explained by the interaction between IrO₂ and Ce–Zr support. Thus, Ir–Ce mixed oxide might exist in the IrO₂/Ce₀.₆Zr₀.₄O₂ catalyst, which resulted in an improved oxidation capacity at low temperatures. This would enhance reactions 2–4 over the catalysts and could explain why mercury oxidation in the presence of only O₂ was much more efficient with the addition of IrO₂.

**XPS Analysis.** To understand the chemical state of the elements on the catalyst surface, we present the XPS spectra of Zr, Ce, and O in Figure S7. Figure S7 shows the core level spectrum of Zr 3d at various binding energies: 182.9 eV for Zr 3d⁵/₂ and 184.7 eV for Zr 3d₃/₂. These peak values are typical of the Zr⁴⁺ in ZrO₂.\(^4\) Complicated Ce 3d XPS spectra for the Ce₀.₆Zr₀.₄O₂ and IrO₂/Ce₀.₆Zr₀.₄O₂ catalysts are given in Figure S7. The bands labeled u₁ and v₁ represent the 3d¹⁰⁴f¹ initial electronic state, corresponding to Ce⁴⁺ ions, and the peaks labeled as u₀, u₂, u₃, v₀, v₂, and v₃ represent the 3d¹⁰⁴f⁰ state of the Ce⁴⁺ ions.\(^1\) The ratio of Ce⁴⁺/(Ce³⁺+Ce⁴⁺) can be calculated from the area of these peaks,\(^2\) and the concentration of Ce⁴⁺ calculated for the Ce₀.₆Zr₀.₄O₂ catalyst was 33.53%. With the doping of 0.2% IrO₂, the percentage of Ce³⁺ ions increased to 40.19%. It has been proposed in many studies that the presence of Ce³⁺ species can create charge imbalance, vacancies, and unsaturated chemical bonds on the surface of the catalysts, which will lead to increased of chemisorbed oxygen on the surface and benefit the catalytic activity.\(^1\)\(^1\) Therefore, the O 1s spectra of various catalysts are also shown in Figure S7. The O 1s peaks can be divided into two peaks corresponding to the lattice oxygen at 529.3–530.0 eV and the chemisorbed oxygen at 531.3–532 eV.\(^1\)\(^1\) Surface chemisorbed oxygen has been reported to be the most active oxygen and plays an important role in oxidation reactions. The concentration of chemisorbed surface oxygen on the Ce₀.₆Zr₀.₄O₂ catalyst was 10.13%, and this percentage increased to 66.68% after IrO₂ doping, which supports the idea that the presence of IrO₂ could significantly improve catalytic activity. After Hg⁰ adsorption without O₂ over the IrO₂/Ce₀.₆Zr₀.₄O₂ catalyst, the percentage of chemisorbed oxygen decreased to 32.22%, suggesting that the adsorbed Hg⁰ was mainly oxidized by the chemisorbed oxygen species.

**The Role of IrO₂ and Another Possible Mechanism.** To determine the role of doping with IrO₂ during the Hg⁰ oxidation reaction, we show in Figure S6 the results of the Hg⁰ adsorption experiments over fresh Ce₀.₆Zr₀.₄O₂ and HCl-pretreated Ce₀.₆Zr₀.₄O₂ catalysts as well as the Hg⁰ adsorption breakthrough curves. The adsorption capacity of Hg⁰ over Ce₀.₆Zr₀.₄O₂ was very low, and adsorption equilibration was reached quickly. In contrast, the breakthrough curve over HCl-pretreated Ce₀.₆Zr₀.₄O₂ was very different, and the removal efficiency of elemental mercury was as high as 95% for over 400 min. This result is similar to the results in Figure 2, which showed that HCl treatment with or without O₂ could significantly improve the apparent adsorption capacity of Hg⁰ over the catalyst. Because the apparent adsorption capacity of Hg⁰ was improved by HCl treatment whether the catalyst was doped with IrO₂, we infer that doping IrO₂ has no obvious effects on reactions 5–7 (in which HCl functions) in the chemisorption–regeneration mechanism.

Although the H₂-TPR and XPS results indicate that doping with IrO₂ has a synergistic effect with the Ce–Zr carrier and can facilitate the oxidation capacity of the catalyst, the chemisorption process was improved over IrO₂ modified catalyst. However, this result cannot convincingly explain (because of the result in Figure S6) why the addition of 0.2% IrO₂ significantly improved the catalytic efficiency of Hg⁰ in the presence of HCl. As stated previously, the Deacon reaction has been proposed as a mechanism for Hg⁰ oxidation in the presence of HCl over many catalysts, and IrO₂ is an active component for the Deacon reaction. Although Cl₂ has been proven to be not essential for Hg⁰ oxidation, it can act as a marker of catalytic activity because Cl atoms on the catalysts can combine with each other to form Cl₂. Thus, Cl₂ yield over various catalysts was tested to evaluate the Deacon reaction as another possible mechanism. Figure 6 shows that one absorption peak centered at 330 nm is present observed after HCl and O₂ were passed through Ce₀.₆Zr₀.₄O₂ catalyst at 350 °C, and the peak can be assigned to Cl₂. With 0.2% IrO₂ doping, the intensity of the adsorption peak increased to over 0.04. Obviously, the preparation method could also affect the production of Cl₂, and the adsorption peak intensity increased to 0.084 over the PVP-promoted IrO₂/Ce₀.₆Zr₀.₄O₂ catalyst. The Cl₂ yield capacities decreased in the following sequence: IrO₂/Ce₀.₆Zr₀.₄O₂(PVP) > IrO₂/Ce₀.₆Zr₀.₄O₂ > Ce₀.₆Zr₀.₄O₂. This is the same with catalytic oxidation activity of Hg⁰ over these catalysts in the presence of HCl (Figure 1). Therefore, we infer that Hg⁰ can be oxidized through the Deacon reaction, in which Cl⁻ in catalyst or from adsorbed HCl was first oxidized by active oxygen species to atomic chlorine (reaction 9), after which the formed atomic chlorine atoms could combine to generate gaseous Cl₂ if no Hg⁰ was present in gas (reactions 10 and 11). When Hg⁰ existed in the gas and was adsorbed to the surface, the elemental mercury could react with Cl atoms to

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**Figure 5.** H₂-TPR curves of various catalysts.
form HgCl₂ (reaction 12). The overall reaction formula can also be expressed as reaction 8. The Cl₂ yield experiment was also carried out over the catalyst at 150 °C, and no obvious peak of Cl₂ was detected over the catalyst, which indicates that the Deacon reaction mechanism might only proceed at relatively high temperatures.

\[
\begin{align*}
2\text{HCl(ads)} + \text{O} &\rightarrow 2\text{Cl(ads)} + \text{H}_2\text{O} \\
\text{Cl(ads)} + \text{Cl(ads)} &\rightarrow \text{Cl}_2(\text{ads}) \\
\text{Cl}_2(\text{ads}) &\rightarrow \text{Cl}_2(\text{g}) \\
\text{Hg}(\text{ads}) + 2\text{Cl(ads)} &\rightarrow \text{HgCl}_2(\text{ads})
\end{align*}
\]

(9) (10) (11) (12)

According to the results above, there are two possible mechanisms for the catalytic oxidation of Hg⁰ over the IrO₂-modified catalysts (Figure 7). The first mechanism is the chemisorption–regeneration pathway in which Hg⁰ is first adsorbed and oxidized by surface chemisorbed oxygen to HgO. The TPR results and XPS spectra showed that doping of IrO₂ significantly enhanced the percentage of chemisorbed oxygen, such that the oxidation of Hg⁰ was enhanced in the presence of IrO₂. Some previous studies have also proposed that O₂ can be dissociated more easily on IrO₂, which could increase the replenishment of chemisorbed oxygen and result in superior chemisorption. The chemisorption process can proceed in the absence of chlorine (lacking both gaseous HCl and Cl⁻ on the surface), but O₂ was essential. Next, oxidized mercury could desorb from the surface in the form of HgO (or HgCl₂ in the presence of gaseous HCl). Thus, the active adsorption sites would be regenerated, and the adsorption of Hg⁰ could proceed continuously. In the second mechanism, the Deacon reaction, the adsorbed HCl is first oxidized by active oxygen species to active Cl species, and the resulting Cl atoms can combine with each other to form Cl₂ if no Hg⁰ is present in the gas. Our results show that doping with IrO₂ can significantly enhance the Cl yield from the reaction. When Hg⁰ is adsorbed to the surface of catalyst, it can react with Cl atoms to form HgCl₂, which can be released into the gas phase. The major difference between these two mechanisms is whether the adsorbed Hg⁰ or HCl is first oxidized by active species. Meanwhile, both of the two proposed oxidation processes could be promoted by doping with IrO₂.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05564.

Additional details on the preparation method of the Ce-Zr solid solution. Figures showing the experimental system, The catalytic oxidation of Hg⁰ over various catalysts under different condition at 350 °C; the catalytic oxidation of Hg⁰ over Ce₀.₆Zr₀.₄O₂ with different condition at 350 °C and 150 °C; the catalytic oxidation of Hg⁰ over IrO₂/Ce₀.₆Zr₀.₄O₂ (PVP) with simulated coal-fired flue gas at 350 and 150 °C; the adsorption curve over Ce₀.₆Zr₀.₄O₂; and the XPS spectra of Ce, O, and Zr in various catalysts. (PDF)

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**Notes**

The authors declare no competing financial interest.

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Figure 6. Cl₂ yield over various catalysts. Reaction conditions: 9000 ppm of HCl; O₂, 4 vol %; N₂ as carrier; flow rate, 40 mL/min; catalyst weight, 60 mg. The space velocity (SV) was approximately 3.04 × 10⁴ h⁻¹. The temperature was 350 °C.

Figure 7. Proposed mechanism of Hg⁰ oxidation.


