Synthesis of Sulfur-Resistant TiO$_2$-CeO$_2$ Composite and Its Catalytic Performance in the Oxidation of a Soluble Organic Fraction from Diesel Exhaust

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Abstract: Sulfur poisoning is one of the most important factors deteriorating the purification efficiency of diesel exhaust after-treatment system, thus improving the sulfur resistibility of catalysts is imperative. Herein, ceria oxygen storage material was introduced into a sulfur-resistant titania by a co-precipitation method, and the sulfur resistibility and catalytic activity of prepared TiO$_2$-CeO$_2$ composite in the oxidation of diesel soluble organic fraction (SOF) were studied. Catalytic performance testing results show that the CeO$_2$ modification significantly improves the catalytic SOF purification efficiency of TiO$_2$-CeO$_2$ catalyst. SO$_2$ uptake and energy-dispersive X-ray (EDX) results suggest that the ceria doping does not debase the excellent sulfur resistibility of bare TiO$_2$, the prepared TiO$_2$-CeO$_2$ catalyst exhibits obviously better sulfur resistibility than the CeO$_2$ and commercial CeO$_2$-ZrO$_2$-Al$_2$O$_3$. X-ray powder diffraction (XRD) and Raman spectra indicate that cerium ions can enter into the TiO$_2$ lattice and not form complete CeO$_2$ crystals. X-ray photoelectron spectroscopy (XPS), H$_2$-temperature programmed reduction (H$_2$-TPR) and oxygen storage capacity (OSC) testing results imply that the addition of CeO$_2$ in TiO$_2$-CeO$_2$ catalyst can significantly enhance the surface oxygen concentration and oxygen storage capacity of TiO$_2$-CeO$_2$.

Keywords: cerium-doped titania; sulfur-tolerant materials; organic compounds purification; diesel oxidation catalyst; vehicle exhaust

1. Introduction

Diesel engines have been widely used in passenger cars and vans, due to excellent fuel efficiency and durability. However, diesel exhaust gases, such as carbon monoxide (CO), unburned hydrocarbons (HCs), nitrogen oxides (NOx), particulate matter (PM) and soluble organic fraction (SOF), are considered major sources of air pollutants [1–3]. Among these hazardous pollutants, SOF are the heavy liquid hydrocarbons (C > 16 [4,5], aromatics and oxygenated compounds [6]) adsorbed on soot, which mainly come from unburned fuel and lube oils [7,8]. The content of SOF is known to vary with engine operating conditions and can reach about 5–60% of the whole mass of the particulate matter [6,9–11]. Due to the fact that diesel SOF contains types of polycyclic aromatic hydrocarbons...
(PAHs) [12,13] which are recognized as strong carcinogens [14,15], purifying the SOF from diesel exhaust is an important and essential work.

Diesel oxidation catalyst (DOC) was employed to accelerate the oxidation and purification of diesel exhaust gases of CO, HC, and SOF. In recent decades, CeO$_2$-ZrO$_2$, Al$_2$O$_3$ and their mixed oxide-based catalysts were widely used as commercial DOC and displayed excellent catalytic CO and HC oxidation activity. Focusing on the purification of SOF, CeO$_2$-based oxygen storage materials (OSM) have been greatly impressed by considerable researchers due to the superior catalytic activity on hydrocarbons and SOF oxidation [16–18]. Meanwhile, controlled synthesized of nanostructured CeO$_2$-based catalysts and their catalytic performance in diesel soot oxidation are lucubrated [19,20]. However, CeO$_2$-based catalysts are easily poisoned by SO$_2$ [21–24]. And SO$_2$ is a subsistent in the diesel exhaust, since sulfur is present in almost all commercial diesel fuels [25–27], sulfur in fuels would be oxidized to SO$_2$ and then emitted from diesel engines [28,29]. Furthermore, sulfur poisoning resulting from sulfur species accumulation is more destructive, since even using ultra-low sulfur diesel (ULSD), cumulative exposure of a catalyst over its lifetime in a heavy-duty diesel may amount to kilograms of sulfur [30]. A large amount of sulfur species accumulation inevitably results in the blocking of channels of monolithic catalyst, and hence the strike of diesel exhaust after-treatment system. Thus, it is important and realistic for a diesel oxidation catalyst to improve the sulfur resistibility.

TiO$_2$ is known as an effective sulfur-resistant material [31–33], and our previous works [34–36] also prove that TiO$_2$-based diesel oxidation catalysts display excellent sulfur resistibility. However, TiO$_2$ is not active enough for catalytic diesel SOF combustion. Reports about the sulfur resistance catalyst for diesel SOF oxidation are still scarce. Considering all of this, in this work, CeO$_2$ was introduced in TiO$_2$ by a co-precipitation method, and its effects on sulfur resistibility and catalytic activity for diesel SOF combustion were investigated.

2. Results and Discussion

2.1. Sulfur Resistibility

The sulfur resistibility values of catalysts were measured by sulfur uptake testing. As shown in Figure 1, under SO$_2$ exposure, the weight of all samples increased with time; final weight increments tended to be flat after 1–3 h SO$_2$ exposure, except for CeO$_2$. After 4 h, chosen as representative exposure time of simulative 160,000 km vehicle aged catalyst, the final weight increments of TiO$_2$, TiO$_2$-CeO$_2$ and CeO$_2$ catalysts are 1.63 wt. %, 2.01 wt. % and 4.72 wt. %, respectively. The normalized sulfur uptake results are calculated by supposing 1 g of sample as standard, and the results are listed in Table 1. From the results it can be seen that the sulfur species accumulation is severe on CeO$_2$ catalyst but is slight on both TiO$_2$ and TiO$_2$-CeO$_2$ catalysts, which implies that the TiO$_2$-based catalysts (TiO$_2$ and TiO$_2$-CeO$_2$) present obviously better sulfur resistibility than the CeO$_2$ catalyst. Since the non-sulfating material of TiO$_2$ displays low SO$_2$ adsorption and hence relieves sulfate generation and exhibits superior sulfur resistibility [32,37]. Furthermore, the introduction of moderate amounts of ceria in TiO$_2$ has essentially no effect on the naturally excellent sulfur resistibility of TiO$_2$.

Table 1. Sulfur accumulation and normalized sulfur uptake of the TiO$_2$, TiO$_2$-CeO$_2$ and CeO$_2$ samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface Area a (m$^2$/g)</th>
<th>Sulfur Content (wt. %)</th>
<th>Normalized Sulfur Uptake c (µg/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>98</td>
<td>1.63</td>
<td>1.02</td>
</tr>
<tr>
<td>TiO$_2$-CeO$_2$</td>
<td>118</td>
<td>2.01</td>
<td>1.04</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>53</td>
<td>4.72</td>
<td>4.26</td>
</tr>
</tbody>
</table>

* Surface area was calculated by BET method from the N$_2$ adsorption-desorption results; * EDX results were obtained by detecting the simulative 160,000 km vehicle aged samples; * The normalized sulfur uptake = sulfur uptake/(100 × surface area) [37,38].
2.2. Catalytic Performance

Figure 2 shows the thermogravimetry-differential thermal analysis-differential thermogravimetry (TG-DTA-DTG) curves of the bulk lube without catalysts and the lube impregnated on catalysts; all of the DTA curves are the positive peaks indicating exothermic peaks, and all of the originally DTG negative peaks are inverted into positive peaks for a better readability of the graph. The combustion of lube without catalyst under air flow is shown in Figure 2a; the weight loss of bulk lube is tersely distinguished into two stages; about 90% of lube is deflagrated at 220–350 °C, and then the rest of 10% lubricating oil is consumed tardily after 350 °C. As shown in DTA curves of Figure 2a, a sharp and large exothermic peak is seen at about 325 °C which result from the rapid pyrolysis of bulk lube. Due to the decomposition of lube being an exothermic reaction, once ignition occurs, the heat continually increases and accumulates, and hence, most of lube is removed rapidly. The multiple peaks at 400–500 °C imply that the commercial lube contains multifarious hydrocarbons (lubricant additives) that are hard to decompose. Figure 2b plots the lubricant oxidation on CeO2 catalyst. About 93% of the lube is rapidly oxidized between 140 °C and 280 °C, and the rest of 7% of lube is fully burnt at 280–340 °C. The onset combustion temperature of $T_{10\%}$ is about 162 °C, the fastest weightlessness temperature of $T_m$ is about 186 °C and the final reaction temperature of $T_f$ is about 322 °C. Figure 2c shows the decomposition of lubricant with TiO2, the TG-DTG curves can be divided into four stages with different decomposition rates. About 16% of lube is decomposed at 205–266 °C, another 28% of the lube is burnt at 266–324 °C, about 49% of the lubricant is consumed at 324–396 °C and the rest of 7% of uninflammable lube is ignited between 396 °C and 420 °C. The onset combustion temperature of $T_{10\%}$ is about 249 °C, the final reaction temperature of $T_f$ is about 420 °C, and three obviously fast weightlessness peaks of lube combustion are observed at about 252, 289 and 363 °C. For the TiO2-CeO2 catalyzed lube...
combustion (Figure 2d), about 97% of the lubricating oil is rapidly combusted between 180 °C and 330 °C, and the rest of about 3% of lube is burnt out at 334–362 °C. The $T_{10\%}$, $T_m$ and $T_f$ is about 212, 261 and 362 °C, respectively.

Due to the fact that the weight loss of lube can be ascribed either to evaporation or to combustion, the activity of prepared catalyst is also identified by the integrated area of the exotherm. The normalized DTA peak areas are described in units of $\mu V \cdot ^\circ C/(mg lube)/(mg sample)$, and then different catalysts can be directly compared on a common basis [39,40]. The larger the value of normalized DTA exotherm peak area, the greater the fraction of lubricant combusted verses evaporated, and the better the catalytic performance [39–41]. The oxidation activity data of catalysts for lube combustion are listed in Table 2. CeO$_2$ catalyst exhibits an outstanding catalytic lube oxidation activity, which is consistent with our previous reports [40,41]. Although the introduction of TiO$_2$ slightly lowers the combustion temperature of lube, bare TiO$_2$ is not active enough for catalytic SOF oxidation. About 60% of lube is burnt at 350 °C in the lube/TiO$_2$ sample, while the value of lube without catalyst sample is about 90%. This is because the lube oxidation is an exothermic reaction; once ignition occurs, the heat continually increases and accumulates. Thus, the burn of lube without catalyst (containing more lube oil) is more violently than the lube/TiO$_2$. The TiO$_2$–CeO$_2$ catalyst obviously lowers the onset temperature of lube combustion and considerably promote the removing of lube resulting from combustion. Compared to TiO$_2$, the prepared TiO$_2$–CeO$_2$ catalyst presents obviously lower SOF removal temperature and larger exothermal peak area, which indicates that the TiO$_2$–CeO$_2$ catalyst presents better catalytic lube combustion activity.

![Figure 2](image-url) Simultaneous TG-DTA-DTG curves for simulating the catalytic performance for the combustion of SOF on (a) without catalyst; (b) CeO$_2$; (c) TiO$_2$ and (d) TiO$_2$–CeO$_2$ catalysts.
2.3. Catalyst Characterization

2.3.1. XRD and Raman Spectra

The XRD patterns of prepared catalysts are shown in Figure 3; both TiO\textsubscript{2} and TiO\textsubscript{2}-CeO\textsubscript{2} display only characteristic peaks which refer to the typical anatase structure of TiO\textsubscript{2}. The peaks of TiO\textsubscript{2} are sharper than those of TiO\textsubscript{2}-CeO\textsubscript{2}, which indicates that the addition of CeO\textsubscript{2} impedes the crystal growth and sintering and lower crystallinity of the TiO\textsubscript{2}-CeO\textsubscript{2} composite materials. In the case of TiO\textsubscript{2}-CeO\textsubscript{2}, the typical reflections of CeO\textsubscript{2} crystals at 28.7°, 33.2°, 47.7°, 56.6° and 77.1° are not observed, and the positions of typical anatase structure of TiO\textsubscript{2} shift obviously to smaller angles, which suggest that a complete CeO\textsubscript{2} crystal is not formed in the TiO\textsubscript{2}-CeO\textsubscript{2} catalyst, which is consistent with the XRD result.

To further confirm the above conjecture, Raman spectra were employed. As can be seen in Figure 4, CeO\textsubscript{2} presents a strong peak at about 464 cm\textsuperscript{-1}, which can be associated with the cubic CeO\textsubscript{2} [42]. TiO\textsubscript{2} and TiO\textsubscript{2}-CeO\textsubscript{2} catalysts show five visible peaks at 145, 196, 397, 517 and 639 cm\textsuperscript{-1}, which are the A\textsubscript{1g} + 2B\textsubscript{1g} + 3E\textsubscript{g} Raman-active modes of TiO\textsubscript{2} anatase phase (the peak at 517 cm\textsuperscript{-1} is complex of A\textsubscript{1g} and B\textsubscript{1g}) [43]. for the TiO\textsubscript{2}-CeO\textsubscript{2} catalyst, the characteristic Raman peak of CeO\textsubscript{2} at 464 cm\textsuperscript{-1} is not observed. This result further confirmed that a CeO\textsubscript{2} crystal is not formed in the TiO\textsubscript{2}-CeO\textsubscript{2} catalyst, which is consistent with the XRD result.

<table>
<thead>
<tr>
<th>Samples</th>
<th>T\textsubscript{WF} (°C)</th>
<th>T\textsubscript{m} (°C)</th>
<th>T\textsubscript{f} (°C)</th>
<th>Exothermal Peak Area (µV\textsuperscript{-2}C/mg Lube)</th>
<th>Exothermal Peak Area (µV\textsuperscript{-2}C/(mg Lube)/(mg Sample))</th>
</tr>
</thead>
<tbody>
<tr>
<td>lube</td>
<td>264</td>
<td>324</td>
<td>507</td>
<td>283.9</td>
<td>-</td>
</tr>
<tr>
<td>lube/CeO\textsubscript{2}</td>
<td>162</td>
<td>186</td>
<td>322</td>
<td>1068.1</td>
<td>119.5</td>
</tr>
<tr>
<td>lube/TiO\textsubscript{2}</td>
<td>249</td>
<td>261</td>
<td>362</td>
<td>901.6</td>
<td>102.6</td>
</tr>
<tr>
<td>lube/TiO\textsubscript{2}-CeO\textsubscript{2}</td>
<td>212</td>
<td>261</td>
<td>362</td>
<td>1029.5</td>
<td>115.5</td>
</tr>
</tbody>
</table>

\* Three obviously fast weightlessness peaks are observed over the lube/TiO\textsubscript{2} sample.

Figure 3. XRD patterns of the TiO\textsubscript{2} and TiO\textsubscript{2}-CeO\textsubscript{2} catalysts.

Figure 4. CeO\textsubscript{2} presents a strong peak at about 464 cm\textsuperscript{-1}, which can be associated with the cubic CeO\textsubscript{2} [42]. TiO\textsubscript{2} and TiO\textsubscript{2}-CeO\textsubscript{2} catalysts show five visible peaks at 145, 196, 397, 517 and 639 cm\textsuperscript{-1}, which are the A\textsubscript{1g} + 2B\textsubscript{1g} + 3E\textsubscript{g} Raman-active modes of TiO\textsubscript{2} anatase phase (the peak at 517 cm\textsuperscript{-1} is complex of A\textsubscript{1g} and B\textsubscript{1g}) [43]. for the TiO\textsubscript{2}-CeO\textsubscript{2} catalyst, the characteristic Raman peak of CeO\textsubscript{2} at 464 cm\textsuperscript{-1} is not observed. This result further confirmed that a CeO\textsubscript{2} crystal is not formed in the TiO\textsubscript{2}-CeO\textsubscript{2} catalyst, which is consistent with the XRD result.
2.3.2. Nitrogen Adsorption-Desorption

The nitrogen adsorption–desorption isotherms and pore size dispersion of TiO$_2$ and TiO$_2$-CeO$_2$ are shown in Figure 5; both TiO$_2$ and TiO$_2$-CeO$_2$ are mesoporous materials and show distinct H3 and H4 complex hysteresis loops indicating slit pore features; compared to TiO$_2$, the prepared TiO$_2$-CeO$_2$ displays obviously larger pore size; the textual features are listed in Table 3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface Area (m$^2$/g)</th>
<th>Pore Volume (cm$^3$/g)</th>
<th>Average Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>98</td>
<td>0.22</td>
<td>7.2</td>
</tr>
<tr>
<td>TiO$_2$-CeO$_2$</td>
<td>118</td>
<td>0.26</td>
<td>8.6</td>
</tr>
</tbody>
</table>
The surface areas of TiO₂ and TiO₂-CeO₂ catalysts are about 98 m²/g and 118 m²/g, respectively, which indicates that the introduction of CeO₂ slightly increases the surface area of TiO₂. The pore volume and average pore size of TiO₂ are about 0.22 cm³/g and 7.2 nm, respectively; the pore volume and average pore diameter of TiO₂-CeO₂ catalyst are 0.26 cm³/g and 8.6 nm, respectively. It can be seen that the addition of CeO₂ to TiO₂ increases its surface area, pore volume and average pore size; this is possibly due to the addition of CeO₂ which impedes crystal growth and sintering and lowers crystallinity of the TiO₂-CeO₂ composite materials, and this speculation is consistent with the XRD results (Figure 3). The larger surface area, pore volume and pore size can be advantages to the contacting, transmitting and diffusion of the lube molecules on the catalyst, and hence, be beneficial to the catalytic SOF oxidation activity.

2.3.3. XPS

Figure 6 shows the XPS spectra of O 1s region of the CeO₂, TiO₂ and TiO₂-CeO₂ catalysts, all samples show two XPS peaks, the peak at about 530.1 eV can be assigned to lattice oxygen, and the peak with a binding energy of 532.1 eV is characteristic of surface adsorbed oxygen [37,44]. Due to the superior oxygen storage capacity, the peak of surface adsorbed oxygen of CeO₂ is obviously stronger than the lattice oxygen; the surface adsorbed oxygen ratio is about 55%. For the TiO₂ catalyst, the surface adsorbed oxygen ratio is about 38%, and the addition of CeO₂ obviously increases the surface adsorbed oxygen ratio, where the value of TiO₂-CeO₂ is about 42%. Usually, surface adsorbed oxygen is more reactive than lattice oxygen due to its higher mobility [45,46], and our previous work also confirms that the adsorbed oxygen is more active than the lattice oxygen in the catalytic SOF oxidation reaction [40]. Thus, the addition of CeO₂ in TiO₂ enhances the amounts of surface adsorbed oxygen of TiO₂-CeO₂, which can be responsible for the improved catalytic activity of SOF oxidation.

Figure 6. XPS (O 1s) spectra of the CeO₂, TiO₂ and TiO₂-CeO₂ catalysts.

Additionally, the XPS (Ti2p) spectra of TiO₂ and TiO₂-CeO₂ catalysts are both located at 458.5 eV (2p3/2) and 464.2 eV (2p1/2), which are characteristic of TiO₂ species. Compared to bare CeO₂, the cerium peaks of TiO₂-CeO₂ are very weak and indiscernible, which indicates that the surface concentration of Ce in TiO₂-CeO₂ catalyst is very low; this phenomenon further confirms that Ce dopants are not gathering on the surface and are possibly entering into TiO₂ lattice, which is consistent with the XRD results (Figure 3).
2.3.4. H$_2$-TPR

The redox property of a catalyst is closely related to the catalytic performance. The redox behavior of the prepared catalysts is described by hydrogen temperature-programmed reduction (H$_2$-TPR) and shown in Figure 7.

![H$_2$-TPR profiles of the CeO$_2$, TiO$_2$ and TiO$_2$-CeO$_2$ catalysts.](image)

The TPR peak of individual TiO$_2$ shows a weak peak at about 500–700 °C which may be ascribed to the reduction of TiO$_2$, and this phenomenon has been observed by other researchers [47,48]. The CeO$_2$ obviously shows a two-step reduction, the multiple low-temperature reduction peak at about 300–600 °C can be assigned to the reduction of surface oxygen, and the peak after 700 °C is ascribed to the reduction of CeO$_2$ bulk oxygen [47]. For the TiO$_2$-CeO$_2$, the reduction peak at 300–700 °C can be ascribed to the reduction of TiO$_2$ and surface oxygen of CeO$_2$; interestingly, the reduction peak of bulk oxygen of CeO$_2$ after 700 °C is poorly identified, which indicates that the TiO$_2$-CeO$_2$ catalyst exhibits lots of surface oxygen, and this result is consistent with XPS result. Consequently, the prepared TiO$_2$-CeO$_2$ catalyst with lots of surface oxygen species presents superior catalytic activity, due to the surface oxygen is highly reactive [45,46].

2.3.5. OSC

The CeO$_2$-based catalyst presents excellent oxygen storage capacity (OSC) and exhibits superior catalytic SOF oxidation activity [16,41]. The OSC of prepared catalysts were tested by an oxygen pulse injection technique and the results are listed in Table 4.

![Table 4. The oxygen storage capacity (OSC) of TiO$_2$, TiO$_2$-CeO$_2$ and CeO$_2$-based catalysts.](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>OSC (µmol O$_2$/g Sample)</th>
<th>Normalized OSC (µmol O$_2$/g CeO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>2.9</td>
<td>-</td>
</tr>
<tr>
<td>TiO$_2$-CeO$_2$</td>
<td>101</td>
<td>524</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>73</td>
<td>73</td>
</tr>
<tr>
<td>Ce$<em>{0.35}$Zr$</em>{0.60}$Nd$_{0.05}$O$_2$</td>
<td>269 [49]</td>
<td>638</td>
</tr>
</tbody>
</table>

* The prepared TiO$_2$-CeO$_2$ catalyst in this work is Ce$_{0.1}$Ti$_{0.9}$O$_2$.

It can be seen that the OSC of TiO$_2$ is about 2.9 µmol/g, which is very slight and may be within the measurement uncertainties. While the addition of CeO$_2$ significantly increases the OSC of TiO$_2$-CeO$_2$ catalyst, the OSC is about 101 (µmol O$_2$)/(g sample), and the normalized OSC of TiO$_2$-CeO$_2$ catalyst is
about 524 (µmol O₂)/(g CeO₂). For the pure CeO₂ sample, the OSC is about 73 (µmol O₂)/(g sample). It should be mentioned that the static oxygen storage capacity testing for OSC of pure CeO₂ is an undervalued result, due to the oxygen mobility of bare CeO₂ being very low. Thus, a CeO₂-based oxygen storage materials in our previous work [49] is used as reference, the normalized OSC of Ce₀.₃₅Zr₀.₆₀Nd₀.₀₅O₂ is about 638 (µmol O₂)/(g CeO₂). It can be seen that the normalized OSC of prepared TiO₂-CeO₂ catalyst is almost as good as the CeO₂-based oxygen storage materials. Based on the results, it can be suggested that although Ce ions enter into the TiO₂ lattice, the OSC of CeO₂ in TiO₂ is not degraded, the TiO₂-CeO₂ still exhibits good OSC. The good OSC of TiO₂-CeO₂ is one of the reasons that TiO₂-CeO₂ catalyst presents excellent catalytic SOF oxidation activity, this is consistent with the catalytic performance results (Figure 2 and Table 2) and the reports [16,41].

3. Materials and Methods

3.1. Catalyst Preparation

The TiO₂-CeO₂ catalyst was prepared by a co-precipitation method. Desired TiOSO₄·2H₂O and Ce(NO₃)₃·9H₂O mixture solutions with the molar ratio of Ti:Ce = 9:1, which was the optimal ratio to expose the single TiO₂ crystal structure in our previous studies [35,36], were slowly added to NH₃·H₂O solutions under vigorous stirring. And then the precipitate was filtered and washed many times, after dried at 120 °C overnight and calcined for 3 h at 500 °C under airflow, the TiO₂-CeO₂ catalyst powder was obtained. The TiO₂ and CeO₂ catalysts were prepared by the same method.

The simulative 160,000 km vehicle aged sample was obtained by following reference [50] and our previous works [35,37]. Fresh catalyst was placed in a reactor and aged at 670 °C for 15 h and then at 250 °C for 15 h in the gases mixture at flow rate of 800 mL/min: 600 ppm C₃H₆, 1500 ppm CO, 200 ppm NO, 50 ppm SO₂, 5% O₂, 4% CO₂, 8% vapor and N₂ balance.

3.2. Catalyst Evaluation

The catalytic activity for SOF combustion of prepared catalysts were tested using TG-DTA method [16,39]. Due to the fact that the diesel SOF is comprised primarily of lube with a small amount of unburned fuel [51], commercial lubricating oil was often used to simulate the diesel SOF catalytic combustion [16,39].

For this test, the prepared powder catalyst was dried overnight at 120 °C to remove the effects of surface adsorbed water, and then impregnated with 5.0 wt. % commercial lube (Shell Helix HX7 5W-40, Shell Petrochemicals Company Limited, Jiaxing, China), the slurry of lube/catalyst mixture was stirred and mixed till a homogeneous state was obtained. About 10 mg of the lube/catalyst mixture powder was placed in the sample pan of TG-DTA unit (HCT-2, Beijing Henven Instruments, Beijing, China) and dried at 120 °C for 1 h to eliminate the effects of adsorbed substances (water, volatile matters etc.), and then heated to 550 °C with a temperature rate of 5 °C/min under airflow at 30 mL/min. The TG-DTA curves were recorded to determine the catalytic performance for SOF combustion of the prepared catalysts.

The test on lube without catalyst was carried out as a reference. About 10 mg of the lube was placed in the sample pan of TG-DTA unit and dried at 120 °C for 1 h, and then heated to 550 °C with a temperature rate of 5 °C/min under airflow at 30 mL/min.

3.3. Catalyst Characterization

Sulfur uptake was tested on a thermogravimetric analyzer (TGA) HCT-2 (Henven Instruments, Beijing, China). Consulting the references [38,52] and our previous works [37,53], about 15 mg of catalyst was placed in the sample crucible and pretreated under a 35 mL/min of N₂ flow for 5 h at 300 °C, and then the gas mixture of 43 mL/min SO₂(0.05 vol. %)-N₂ and 31 mL/min O₂(15.0 vol. %)-N₂ was introduced at 300 °C for 4 h, the weight increase as a function of time was recorded by the TGA.
The sulfur cumulant of catalysts after mimicking 160,000 km vehicle aging were analyzed by an energy-dispersive X-ray (EDX) spectroscopy (IE-250, Oxford Instruments, Oxford, UK).

X-ray powder diffraction (XRD) patterns were collected on a powder X-ray diffractometer (DX-1000, Dandong Fangyuan Instrument Ltd., Dandong, China) employing Cu Kα radiation (λ = 0.1542 nm).

Raman spectra were recorded by a LabRAM HR Laser Raman spectrometer (HORIBA Jobin Yvon Inc., Paris, France) with an excitation wavelength of 532 nm.

N₂ adsorption-desorption isotherms were measured on a QUADRASORB SI automated surface area and pore size analyzer (Quantachrome Instruments Ltd., Boynton Beach, FL, USA). The specific surface area and pore size were calculated by the Brunauer-Emmett-Teller (BET) method and Barret-Joyner-Halenda (BJH) method, respectively. Before adsorption measurements, the samples were degassed at 300 °C for 3 h under vacuum.

X-ray photoelectron spectroscopy (XPS) data were collected on a Kratos XSAM 800 spectrometer (Kratos Analytic Inc., Manchester, UK) with Al Kα radiation. The binding energy shifts of the samples were calibrated by fixing the C1s binding energy (BE 284.8 eV).

H₂-temperature programmed reduction (H₂-TPR) experiments were performed in a quartz tubular reactor. Samples were pretreated at 450 °C for 1 h under the N₂ flow (35 mL/min) and then cooled to room temperature; after that, the samples were heated from room temperature to 800 °C with a heating rate of 10 °C/min under the flow of H₂ (5.0 vol. %)-N₂ mixture. The hydrogen consumption as a function of reduction temperature was recorded by a thermal conductivity detector (TCD) cell.

The oxygen storage capacity (OSC) of the samples was measured by a pulse injection technique [54]. The sample was firstly reduced in a H₂ flow (30 mL/min) at 550 °C for 1 h; after cooling to 200 °C, an oxygen pulse was injected every 5 min to obtain a breakthrough curve, from which the OSC was calculated.

4. Conclusions

From the aforementioned results, it can be concluded that moderate amounts of ceria dopants in titania can obviously enhance the catalytic SOF oxidation activity of TiO₂-CeO₂ catalyst. Meanwhile, the prepared TiO₂-CeO₂ catalyst can maintain the naturally excellent sulfur resistibility of titania; the sulfur resistibility of TiO₂-CeO₂ is as well as the bare TiO₂. The prepared TiO₂-CeO₂ catalyst significantly enhances the sulfur tolerance of conventional CeO₂-based SOF oxidation catalysts and displays a good catalytic SOF oxidation activity. The TiO₂-CeO₂ catalyst exhibits a typical phase of anatase, and the cerium ions can enter into the TiO₂ unit cell, impede the crystal growth and sintering and lower crystallinity of the TiO₂-CeO₂ composite materials and, hence, improve the surface area, pore volume and pore size of TiO₂-CeO₂ catalyst. Moreover, the addition of CeO₂ in TiO₂ can significantly enhance the surface oxygen concentration and oxygen storage capacity of TiO₂-CeO₂; the normalized oxygen storage capacity of TiO₂-CeO₂ is almost as good as the CeO₂-based oxygen storage materials. The improvement of textual features and surface oxygen concentration of TiO₂-CeO₂ catalyst are the main reasons for the enhancement of catalytic SOF oxidation activity.

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