Novel low temperature NO\textsubscript{x} storage-reduction catalysts for diesel engine emissions

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Abstract: The promotional effect of Zr addition promoted the activity of Pt/BaO/CeO\textsubscript{2} catalyst for the NO\textsubscript{x} storage reduction was investigated. The Pt/BaO/Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2} catalyst with the Ce/Zr molar ratio of 1:9 showed excellent NO\textsubscript{x} removal activity along with good durability. The superior activity of the Pt/BaO/Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2} catalyst can be attributed to the greater amount of oxygen vacancies on the catalyst surface.

Keywords: NO\textsubscript{x} storage reduction, Ce-Zr mixed oxides, low temperature

1. Introduction

The removal of NO\textsubscript{x} emission from lean-burn engine exhaust has attracted much attention in environmental catalysis, and one of the most promising technologies is NO\textsubscript{x} storage reduction (NSR)\textsuperscript{1}. NSR is an inherent transient operation in which the feed gases to the reactor are periodically switched between fuel-lean and fuel-rich gases\textsuperscript{1}. The NSR catalyst previous studied by us is Pt/BaO/CeO\textsubscript{2}, which can effectively remove NO\textsubscript{x} in the 200–400\textdegree C temperature range, performing relatively poorly at lower temperature due to both limited trapping and regeneration efficiencies\textsuperscript{2}. NO\textsubscript{x} emissions during engine cold start make up a significant portion of total NO\textsubscript{x} emissions during test cycles, with the catalyst remaining below 200\textdegree C for a significant amount of time\textsuperscript{3}. Therefore, in order to improve overall emissions performance, one feasible approach is to incorporate components with good low-temperature NO\textsubscript{x} removal ability into the Pt/BaO/CeO\textsubscript{2} catalyst.

2. Experimental

The CeZrO\textsubscript{2} nanomaterials were prepared by a hydrothermal method with different molar ratio of Ce to Zr (1:9, 3:7, 7:3). In addition, the CeO\textsubscript{2} and ZrO\textsubscript{2} were also prepared for comparison with the same method. Using the as-prepared oxide as supports, the 1wt.% Pt/8wt.% BaO/CeZrO\textsubscript{2} samples were synthesized by an impregnation method and then denoted as Pt/BaO/CeO\textsubscript{2}, Pt/BaO/Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2}, Pt/BaO/Ce\textsubscript{0.3}Zr\textsubscript{0.7}O\textsubscript{2}, Pt/BaO/Ce\textsubscript{0.7}Zr\textsubscript{0.3}O\textsubscript{2}, and Pt/BaO/ZrO\textsubscript{2}, respectively. NSR cyclic measurements were conducted in alternating lean/rich atmospheres, while the lean feed contained 500 ppm NO and 8% O\textsubscript{2} and the rich feed contained 3% H\textsubscript{2}, both in balance N\textsubscript{2}. The lean phase and rich were fixed at 90s and 6s respectively, and the lean-rich cycles was 60.

3. Results and discussion

The durations of lean and rich phases of a dynamic NO\textsubscript{x} storage and reduction cycle are important operating parameters that not only affect the performance of the NSR catalyst, but also influence the fuel efficiency. In this study, the experimental cycle-averaged NO\textsubscript{x} conversion of NSR catalysts at different temperatures was summarized under alternating lean/rich condition in Figure 1. Apparently, the Pt/BaO/Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2} catalyst, with a Ce/Zr molar ratio of 1:9, showed the best NO\textsubscript{x} removal efficiency. The NO\textsubscript{x} conversion over Pt/BaO/Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2} at low temperature was greatly improved was high as 100% in a wide temperature range from 150 to 400\textdegree C. At the same time, the Pt/BaO/Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2} went through 60 lean/rich cycles, and remained excellent performance. As shown in Table 1, Pt/BaO/Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2} contained the largest amounts of oxygen vacancies. The superior activity of the Pt/BaO/Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2} catalyst can be
attributed to the more oxygen vacancies which was conducive to the adsorption and storage of NO\textsubscript{x} in the lean phase, especially the storage at the low temperature.

![Graph showing NO\textsubscript{x} conversion vs. Temperature](image)

**Figure 1.** NO\textsubscript{x} conversion of Pt/BaO/CeO\textsubscript{2}, Pt/BaO/Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2}, Pt/BaO/Ce\textsubscript{0.3}Zr\textsubscript{0.7}O\textsubscript{2}, Pt/BaO/Ce\textsubscript{0.7}Zr\textsubscript{0.3}O\textsubscript{2}, and Pt/BaO/ZrO\textsubscript{2}, catalysts over 60 lean-rich cycles at different temperatures.

<table>
<thead>
<tr>
<th>Ce : Zr ratio</th>
<th>CeZrO\textsubscript{x}</th>
<th>Pt/BaO/CeZrO\textsubscript{x}</th>
<th>Pt/BaO/CeZrO\textsubscript{x} - R\textsuperscript{[a]}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO\textsubscript{2}</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2}</td>
<td>20.3</td>
<td>19.5</td>
<td>20.1</td>
</tr>
<tr>
<td>Ce\textsubscript{0.3}Zr\textsubscript{0.7}O\textsubscript{2}</td>
<td>18.9</td>
<td>18.2</td>
<td>18.9</td>
</tr>
<tr>
<td>Ce\textsubscript{0.7}Zr\textsubscript{0.3}O\textsubscript{2}</td>
<td>15.5</td>
<td>15.7</td>
<td>15.3</td>
</tr>
<tr>
<td>CeO\textsubscript{2}</td>
<td>13.5</td>
<td>13.6</td>
<td>14.0</td>
</tr>
</tbody>
</table>

\textsuperscript{[a]}: Catalysts were reduced by 3% H\textsubscript{2}.

4. Conclusions

A novel NSR catalyst prepared by a hydrothermal method was used for NO\textsubscript{x} storage reduction. The Pt/BaO/Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2} catalyst with a Ce:Zr molar ratio of 1:9 showed high NO\textsubscript{x} removal efficiency and good durability. XPS results indicated that Zr addition increased the amount of oxygen vacancies, promoting NO\textsubscript{x} storage at the low temperature.

**References**