Novel low temperature NO_x storage-reduction catalysts for diesel engine emissions

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Abstract: The promotional effect of Zr addition promoted the activity of $Pt/BaO/CeO_2$ catalyst for the NO_x storage reduction was investigated. The $Pt/BaO/Ce_{0.1}Zr_{0.9}O_2$ catalyst with the Ce/Zr molar ratio of 1:9 showed excellent NO_x removal activity along with good durability. The superior activity of the $Pt/BaO/Ce_{0.1}Zr_{0.9}O_2$ catalyst can be attributed to the greater amount of oxygen vacancies on the catalyst surface.

Keywords: NO_x storage reduction, Ce-Zr mixed oxides, low temperature

1. Introduction

The removal of NO_x emission from lean-burn engine exhaust has attracted much attention in environmental catalysis, and one of the most promising technologies is NO_x storage reduction (NSR)[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[1]. The NSR catalyst previous studied by us is $Pt/BaO/CeO_2$, which can effectively remove NO_x in the 200−400°C temperature range, performing relatively poorly at lower temperature due to both limited trapping and regeneration efficiencies[2]. NO_x emissions during engine cold start make up a significant portion of total NO_x emissions during test cycles, with the catalyst remaining below 200°C for a significant amount of time[3]. Therefore, in order to improve overall emissions performance, one feasible approach is to incorporate components with good low-temperature NO_x removal ability into the $Pt/BaO/CeO_2$ catalyst.

2. Experimental

The $CeZrO_x$ 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_2 and ZrO_2 were also prepared for comparison with the same method. Using the as-prepared oxide as supports, the 1wt.% Pt/8wt.% $BaO/CeZrO_x$ samples were synthesized by an impregnation method and then denoted as $Pt/BaO/CeO_2$, $Pt/BaO/Ce_{0.1}Zr_{0.9}O_2$, $Pt/BaO/Ce_{0.3}Zr_{0.7}O_2$, $Pt/BaO/Ce_{0.7}Zr_{0.3}O_2$, and $Pt/BaO/ZrO_2$, respectively. NSR cyclic measurements were conducted in alternating lean/rich atmospheres, while the lean feed contained 500 ppm NO and 8% O_2 and the rich feed contained 3% H_2, both in balance N_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_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_x conversion of NSR catalysts at different temperatures was summarized under alternating lean/rich condition in Figure 1. Apparently, the $Pt/BaO/Ce_{0.1}Zr_{0.9}O_2$ catalyst, with a Ce/Zr molar ratio of 1:9, showed the best NO_x removal efficiency. The NOx conversion over $Pt/BaO/Ce_{0.1}Zr_{0.9}O_2$ at low temperature was greatly improved was high as 100% in a wide temperature range from 150 to 400°C. At the same time, the $Pt/BaO/Ce_{0.1}Zr_{0.9}O_2$ went through 60 lean/rich cycles, and remained excellent performance. As shown in Table 1, $Pt/BaO/Ce_{0.1}Zr_{0.9}O_2$ contained the largest amounts of oxygen vacancies. The superior activity of the $Pt/BaO/Ce_{0.1}Zr_{0.9}O_2$ catalyst can be

attributed to the more oxygen vacancies which was conducive to the adsorption and storage of NO_x in the lean phase, especially the storage at the low temperature.

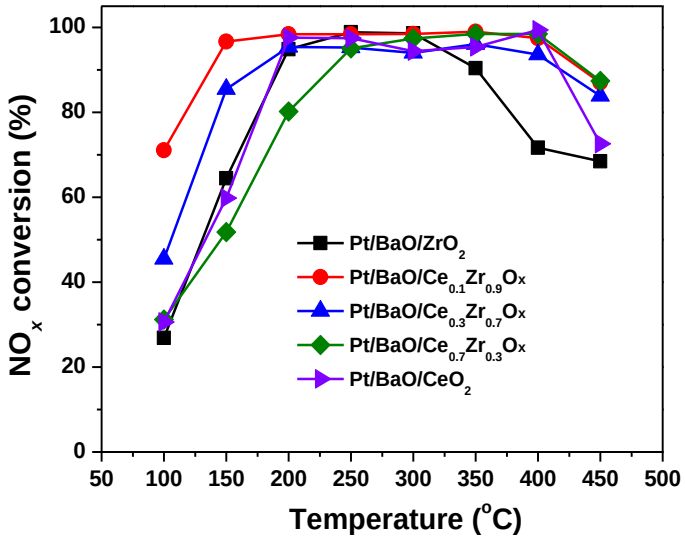

Figure 1. NO_x conversion of Pt/BaO/CeO_2, Pt/BaO/$Ce_{0.1}Zr_{0.9}O_2$, Pt/BaO/$Ce_{0.3}Zr_{0.7}O_2$, Pt/BaO/$Ce_{0.7}Zr_{0.3}O_2$, and Pt/BaO/ZrO_2, catalysts over 60 lean-rich cycles at different temperatures.

Table 1. The Ce^{3+} concentration of supports and catalysts.

Ce : Zr ratio	$CeZrO_x$	Pt/BaO/$CeZrO_x$	Pt/BaO/$CeZrO_x$-R[a]
ZrO_2	--	--	--
$Ce_{0.1}Zr_{0.9}O_2$	20.3	19.5	20.1
$Ce_{0.3}Zr_{0.7}O_2$	18.9	18.2	18.9
$Ce_{0.7}Zr_{0.3}O_2$	15.5	15.7	15.3
CeO_2	13.5	13.6	14.0

R[a]: catalysts were reduced by 3% H_2.

4. Conclusions

A novel NSR catalyst prepared by a hydrothermal method was used for NO_x storage reduction. The Pt/BaO/$Ce_{0.1}Zr_{0.9}O_2$ catalyst with a Ce:Zr molar ratio of 1:9 showed high NO_x removal efficiency and good durability. XPS results indicated that Zr addition increased the amount of oxygen vacancies, promoting NO_x storage at the low temperature.

References

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