Study of catalyst performance for the soot oxidation reaction under H_2O condition

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Abstract: Recent increase in regulation of particulate matters has pressed for exploration of soot oxidation catalyst. Since gasoline vehicles oxidize PM under O_2 and H_2O conditions, we have studied catalysts that are suitable under gasoline conditions. In this study, we investigated the relationship between structure and activity of catalysts and suggested which catalyst shows good performance under H_2O condition. Catalysts with macroporous structure with dominant external surface area were suitable, and CeO_2 catalyst exhibited the best performance among prepared catalysts under H_2O condition from being able to produce strong oxidizing -OH radicals. The correlation between activity tests and characterizations were discussed

Keywords: Macroporous structure catalysts, CeO_2, -OH radical.

1. Introduction

Previous conventional studies for soot oxidation were often completed under O_2 and NOx condition, which is primarily present in diesel exhaust gas. However, unlike diesel, TWC-filtered gasoline exhaust gas contains less NOx, and most components of oxidation gas are O_2 and H_2O [1]. Thus, the role of H_2O in soot oxidation is crucial and needed to be considered for future studies regarding soot oxidation and related catalysts.

O_2 can be decomposed to active oxygen and supplied to soot on the catalysts [2]. H_2O generates -OH radical on the catalysts surface, which has strong oxidation ability [3]. The active oxygen and -OH radical oxidize the soot at low temperature. Thus, the catalyst used for Gasoline Particulate Filter (GPF) should have good O_2 and H_2O decomposition ability and have a structure which easily supply generated active oxygen and -OH radical to soot.

In this study, we compared the performance of catalysts with macroporous structure and mesoporous structure to find out the morphology effect on providing active oxygen and -OH radical to soot. Also, we made $CeZrO_2$ catalysts that are well known for having good oxygen storage capacity to find out the optimal ratio of cerium and zirconium under H_2O condition.

2. Experimental (or Theoretical)

The mesoporous $Ce_xZr_{1-x}O_2$(x = 0, 0.3, 0.5, 0.7, 1) catalysts were synthesized by coprecipitation method. Cerium nitrate hexahydrate and zirconyl chloride octahydrate were mixed together with cetyltrimethylammonium bromide in the aqueous solution. Subsequently, ammonium hydroxide was added to the solution, and then the slurry was aged at 80 ˚C for 5 days. Finally, the filtered slurry was calcined at 550 ˚C.

The macroporous $Ce_xZr_{1-x}O_2$(x = 0, 0.3, 0.5, 0.7, 1) catalysts were synthesized by crystal templating method. Cerium and zirconium precursor were obtained by mixing cerium nitrate hexahydrate and zirconyl chloride octahydrate into the ethylene glycol and methanol mixed solution. Subsequently, dried PMMA colloidal crystal templates were soaked in the precursor solutions. Finally, the filtered PMMA and precursor were dried in air and calcinated at 550 ˚C to remove PMMA.

The combustion test followed the TPO procedure. Soot and catalysts were mixed together with a mortar to achieve a tight contact between soot and catalysts. The soot-catalyst mixture is heated from room temperature to 700 ˚C (heating rate 5 ˚C/min) with O_2 (1% v/v) in He or O_2 (1% v/v) + H_2O (10% v/v) in H to modify dry and wet condition. The characterization analyses such as BET, SEM, etc. were followed to investigate the catalytic properties.

3. Results and discussion

The SEM images of soot, macroporous $Ce_{0.7}Zr_{0.3}O_2$ and mesoporous $Ce_{0.7}Zr_{0.3}O_2$ are presented in Fig.1. The size of soot particle is around 50 ~ 100 nm and the pore size of macroporous $Ce_{0.7}Zr_{0.3}O_2$ is around 200 ~ 300 nm. However, we couldn't find the pore size of mesoporous $Ce_{0.7}Zr_{0.3}O_2$. The BET result shows that the pore size of mesoporous $Ce_{0.7}Zr_{0.3}O_2$ is about 3.5nm and internal surface area is more dominant than external surface area. Also, soot particle size is bigger than its pore size, so internal surface area of the catalyst can't participate to the reaction. Therefore, macroporous structure catalysts are more suitable for soot oxidation because the external surface area is dominant.

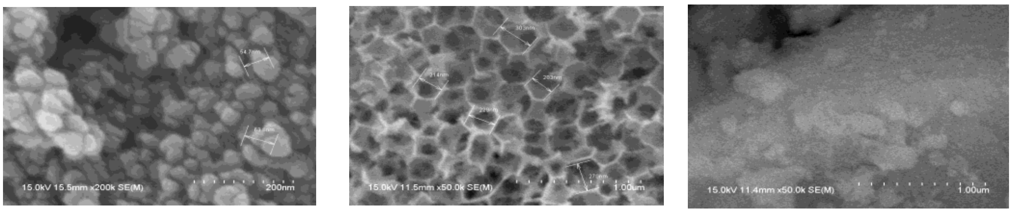

Figure 1. SEM image of (a) soot, (b) macroporous $Ce_{0.7}Zr_{0.3}O_2$ and (c) mesoporous $Ce_{0.7}Zr_{0.3}O_2$

The soot combustion temperature over macroporous $Ce_xZr_{1-x}O_2$ (x = 0, 0.3, 0.5, 0.7, 1) are shown in Fig. 2. The $Ce_{0.7}Zr_{0.3}O_2$ exhibited the best catalytic performance, and the combustion temperature of soot was about 435 ˚C under dry condition. However, the CeO_2 showed higher catalytic activity than other catalysts when water was introduced. It would be discussed at conference that characterizations of the catalysts and the reason of the activity test.

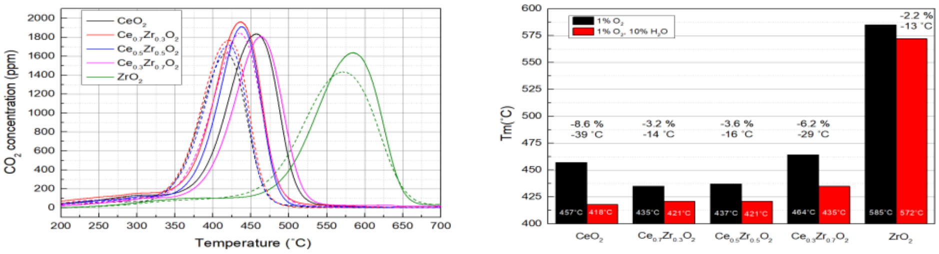

Table 2. Soot oxidation experiment result as tight contact with macroporous $Ce_xZr_{1-x}O_2$ (x = 0, 0.3, 0.5, 0.7, 1).
Experimental conditions: Soot:Catalyst = 1:10 wt:wt, ramp= 5˚C/min, 100ml/min,
Dry condition: 1 % O2 He balance, Wet condition: 1 % O2 10 % H2O, He balance

4. Conclusions

In this study, we compared the performance of catalysts with macroporous structure and mesoporous structure to find out the morphology effect on providing active oxygen and -OH radical to soot, and the macroporous catalyst indicated better performance. Furthermore, macroporous $Ce_{0.7}Zr_{0.3}O_2$ catalyst, which has great oxygen storage capacity, showed the best performance for soot oxidation in O_2 -condition among the prepared catalysts. However, under H_2O condition, CeO_2 showed the greatest improved performance.

References

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