CeO_2/ZrO_2 mixed oxides supported on Al_2O_3 for improved low temperature TWC activity

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Introduction

CeO_2/ZrO_2 mixed oxides are widely used in Three-Way Catalysts (TWCs). The materials promote the intrinsic catalytic activity of the Platinum Group Metal (PGM) components as well as provide Oxygen Storage Capacity (OSC) to the system maintaining the air-to-fuel ratio in the exhaust streams close to the stoichiometric conditions; both functions significantly improve the TWC activity. To further enhance the OSC and the hydrothermal durability of the materials, other dopants, including alumina, are also incorporated into the CeO_2/ZrO_2 mixed oxides [1-3].

In this study, we found that depositing CeO_2/ZrO_2 mixed oxides onto preformed alumina supports could improve their OSC property substantially, especially at low temperatures. Various analytical techniques were applied to characterize the materials. Compared to conventional CeO_2/ZrO_2 mixed oxides with similar compositions, the new materials maintain higher surface area and better phase stability after high temperature exposure. In addition, the new materials can provide higher OSC at low temperatures. TWCs based on the alumina supported CeO_2/ZrO_2 mixed oxides exhibit noticeably improved low temperature activity.

Materials and Methods

The alumina supported CeO_2/ZrO_2 mixed oxide was prepared by co-precipitation of salts of cerium nitrate and zirconium oxynitrate onto γ-Al_2O_3 powder. The material was washed, dried, and finally calcined at 500°C to form the $Al_2O_3/CeO_2/ZrO_2$ mixed oxide. For comparison purpose, a conventional CeO_2/ZrO_2 mixed oxide was also synthesized following the same method but without the addition of γ-Al_2O_3. The resulting CeO_2/ZrO_2 mixed oxide was subsequently blended with γ-Al_2O_3 to form a mixture of (Al_2O_3+CeO_2/ZrO_2) that had an identical composition to the $Al_2O_3/CeO_2/ZrO_2$ mixed oxide. Both materials were characterized for their thermal stabilities and OSC properties. These materials were also evaluated as supports for Pd, either as individual components or in fully formulated TWCs.

Results and Discussion

The physical properties of the Al_2O_3 supported CeO_2/ZrO_2 mixed oxide and the blended (Al_2O_3+CeO_2/ZrO_2) mixture, both after being exposed to 1000°C in static air for 4 hours, are summarized in Table 1. The $Al_2O_3/CeO_2/ZrO_2$ mixed oxide has a higher BET surface area and maintains a single phase of CeZr solid solution, indicating it has superior thermal stability compared to the blended (Al_2O_3+CeO_2/ZrO_2) mixture. H_2-TPR was used to measure the OSC properties of the materials. The percentage of Ce that was reduced from Ce^{IV} to Ce^{III} at temperatures below 500°C is also listed in Table 1. The results show that the OSC measured on the Al_2O_3/ CeO_2/ZrO_2 mixed oxide is about double the amount of the OSC recorded for the blended material, implying significantly improved OSC properties for the new material.

Both materials were evaluated as Pd supports at a Pd loading of 1 wt.%. The Pd powder catalysts were aged at 1050°C for 36 hours under 5-minute lean / 5-minute rich cycling conditions prior to activity evaluation. The CO and HC light-off activities, represented by the temperatures when 50% conversion was achieved, are summarized in Table 2. The light-off temperature of the of $Al_2O_3/CeO_2/ZrO_2$ supported Pd catalyst is about 20°C lower compared to that of the (Al_2O_3+CeO_2/ZrO_2) supported catalyst. TEM analysis of the aged Pd catalysts shows that the CeO_2/ZrO_2 mixed oxide particles on the $Al_2O_3/CeO_2/ZrO_2$ sample are about one order of magnitude smaller than the CeO_2/ZrO_2 mixed oxides in the (Al_2O_3+CeO_2/ZrO_2) sample. In addition, the Pd particles on the $Al_2O_3/CeO_2/ZrO_2$ sample are much smaller and maintain higher dispersion after aging.

Fully formulated TWCs were coated on monolith substrates using both materials as the Pd supports. A common Rh component was also incorporated into the formulations. The TWCs were aged on a 4.6L gasoline engine under 4-mode cycling conditions for 100 hours with an average bed temperature of 925°C. Engine dynamometer testing was conducted on another 4.6L gasoline engine capable of changing the air-to-fuel ratio from 13.5 to 15.5 with a perturbation frequency of 1Hz and amplitude of 0.5. CO/NOx crossover and the corresponding HC conversions were measured at 400°C and 350°C, respectively, at a SV = 112,000 hr^{-1}. The results summarized in Table 2 show the TWC with the $Al_2O_3/CeO_2/ZrO_2$ mixed oxide has better CO/NOx crossover and HC conversions compared to the TWC with the (Al_2O_3+CeO_2/ZrO_2) mixture. The difference is more pronounced at 350°C, clearly demonstrating the advantage of $Al_2O_3/CeO_2/ZrO_2$ material for improving low temperature TWC performance.

Table 1 BET surface area (SA), XRD phase stability and percentage of Ce reduction at temperatures below 500°C on the materials after 1000°C/4h/air treatment

Materials	SA (m^2/g)	XRD	Ce^{IV} to Ce^{III} (% Ce)
$Al_2O_3/CeO_2/ZrO_2$	95	Single CeZr phase	48%
(Al_2O_3+CeO_2/ZrO_2)	83	Two CeZr phases	24%

Table 2 CO and C_3H_6 light-off activity on the Pd powder catalysts, and CO/NOx crossover and HC conversions on the fully formulated TWCs

Pd supports	Powder catalyst		PdRh TWC			
	T_{50} (°C)		400°C		350°C	
	CO	C_3H_6	CO/NOx	HC	CO/NOx	HC
$Al_2O_3/CeO_2/ZrO_2$	305	304	81%	84%	51%	55%
(Al_2O_3+CeO_2/ZrO_2)	321	322	70%	82%	9%	10%

Significance

Depositing CeO_2/ZrO_2 mixed oxides onto preformed alumina supports prevents the agglomeration and sintering of CeO_2/ZrO_2 particles, hence improving the thermal stability as well as the OSC properties of the materials. As Pd supports, the materials improve the CO/HC light-off activity. TWCs based on the materials exhibit significantly improved low temperature activity.

References

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