

Preparation of Palladium only Three-way Catalyst Part 1: study on coating materials

ZHOU Zexing, WANG Xuezhong

Chinese Research Academy of Environmental Sciences

Anwai, Beijing , 100012 , P. R. China

Tel. +86-10-84915322; Fax: +86-10-84915923

Email: zhouzexing@sohu.com ; wangxuezhong@china.com

ABSTRACT:

Active Al_2O_3 / metal oxide additives, as coating materials of Pd only Three-Way Catalyst (Pd TWC), were prepared and characterized with BET, XRD and H_2 -TPR measurements. The thermal stability of active Al_2O_3 was enhanced by additives; the Ce-containing additives had oxygen storage capacity while La-containing samples didn't; Pd TWC prepared with two typical washcoats containing Al_2O_3 - CeO_2 / ZrO_2 and Al_2O_3 - La_2O_3 / BaO , respectively, showed excellent low temperature performances and three way reactivity; Addition of 30 ppm SO_2 to the feedstream decreased performances of Pd TWC, and the catalyst containing La_2O_3 / BaO was more likely to be poisoned.

Keywords: Palladium, Three-way catalyst, additives, SO_2 poison

INTRODUCTION

Precious metals Pt and Rh are main active components of three-way catalyst (TWC), which are widely used as a key aftertreatment technology of purifying automobile exhaust pollutants. Recently North America and Europe had employed more stringent regulations. To comply with these regulations, increasing the amount of precious metals in catalyst or using more effective catalytic technologies are demanded. However, Rh is scarce in the earth, and 90% of its annual production is consumed for making auto-catalysts^[1]. In recent years, Pd, which is more abundant and stable in supply, attracted attention for developing advanced Pd only TWC or Pd-based TWC to replace or partially replace Rh, and to meet the more stringent emission standards (i.e. LEV standard). It is reported that effective Pd only TWCs have been successfully developed^[2,3,4].

In China, a new emission control standard GB14761-1999 (equal to Euro I) was employed from Jan. 1st 2000, and TWC converters are required since then. And the regulation is coming more stringent, Euro II (from 2004) and Euro III (from 2010) will be employed. So it is essential to start researching and developing new catalyst technologies.

Though Pd catalyst has good low temperature activity and heat-resistant performance, there are still disadvantages. Specifically, significant improvement in NO_x conversion and anti-SO₂ poison effect under rich condition is required for TWC application. Improvement of PdTWC performance could be achieved by investigating coating technology and catalyst design. It is said that Pd catalyst performance could be enhanced by adding additives like rare earth oxides, alkali metal oxides, alkali earth metal oxides and transition metal oxides^[5,6,7,8].

The present study was performed to gain a better understanding of how additives affect the performance of Pd TWC, as the first report on study of Pd only TWC in our laboratory. In this purpose, the property of Al₂O₃ / metal oxide additives was studied; two typical honeycomb Pd TWC were prepared with washcoat containing Al₂O₃—CeO₂/ZrO₂ or Al₂O₃—La₂O₃/BaO; TWC performance and anti-SO₂ poison behavior were studied in a simulated gas stream using laboratory reactor.

EXPERIMENTAL

1. Preparation and characterization of Al₂O₃-additive materials

Al₂O₃ powder was impregnated with nitrate solution or aqueous nitric dissolution of typical oxides(Mg, Ca, Sr, Ba, La, Ce and Zr) to make single-oxide-additive samples. After

dried, the samples were calcined in an electric furnace at specified temperatures for 4 hours. Using the same technology, composite-oxide-additive samples of La/Ba or Ce/Zr in various ratio was prepared. These samples were characterized with BET, XRD and H₂-TPD measurements.

2.Catalyst preparation and evaluation

The catalysts were prepared by coating slurry, which was consisted of Al₂O₃-additives material, alumina sol, dispersing agent and water, to a ceramic monolith support (Corning Co. 400cs/in²). Catalyst size is 10 mm in diameter and 15 mm in length, loaded 1.0g/l of Pd, and calcined in an electric furnace at 900 for 4 hours.

The activity test was carried out in a conventional continuous-flow fixed bed reactor. Light-off performance was tested from 100 to 500 at a rate of 10 /min, and A/F ratio scanning performance (= 0.960-1.040) at 500 , in simulated gas stream. Inlet gas contained 3.0% CO, 1.0% H₂, 0.06% C₃H₈, 0.06% NO, 10% CO₂, 10% H₂O, 1.5-3.5% O₂, 0 or 0.003 %SO₂, nitrogen balance, and space velocity was 60,000 VHSV. Reactor inlet and outlet gas concentrations were determined using HC/CO/NO exhaust analyzer. Before test, the catalyst was pretreated with reaction gas steam at = 1.000 and 500 for one hour.

RESULTS AND DISCUSSION

1.Performances of Al₂O₃-additive samples

Figure 1 shows the specific surface area(S.S.A) of samples containing single-metal-oxide additives calcined at different temperature. The samples calcined at 1000 , except for CaO, still kept S.S.A of more than 45 m²/g. After calcined at 1200 , the S.S.A of all samples reduced obviously. These results suggest that additives could help Al₂O₃ in keeping high S.S.A at high temperature.

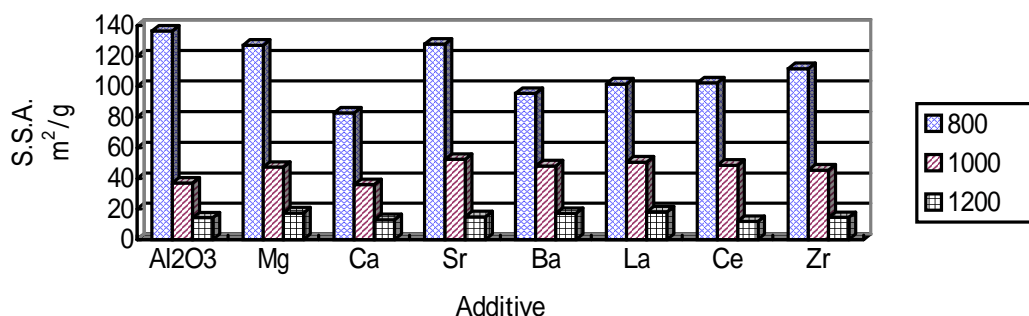


Fig.1 Specific surface area (S.S.A.) of Al₂O₃ -5% single metal oxide samples (calcination temperature: 800 , 1000 and 1200) .

Figure 2 shows the specific surface area of samples containing composite-metal-oxides additive with various composition ratio, calcined at 550 and 900 . All samples calcined at 900 kept high S.S.A. In addition, samples' S.S.A increase while increasing amount of the second additive (ZrO₂ or BaO).

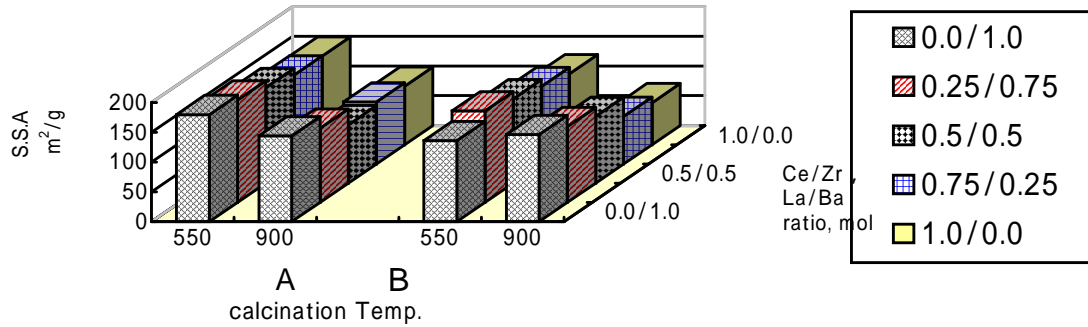


Fig.2 Specific surface area of Al₂O₃-CeO₂/ZrO₂ (A) and Al₂O₃-La₂O₃/BaO (B) composite oxide samples

(Total amount of CeO₂/ ZrO₂ or La₂O₃/BaO in sample: 16.7 % mol)

Table 1 shows XRD determination results of samples containing single-metal-oxide. Al₂O₃ appeared in the pure active Al₂O₃ when calcined at 1000 , but did not appeared in samples containing oxides until calcined at 1200 . XRD determination results also show that Al₂O₃ kept active Al₂O₃ in samples containing composite-metal-oxides.(Not presented in the paper)

Table 1 XRD determination results

Sample	Phase of sample calcined at			Comment
	800	1000	1200	
Al ₂ O ₃	*	, (few)	, ,	
Al ₂ O ₃ -3.5% (wt) BaO			, ,	less than in pure Al ₂ O ₃ , no BaO detected
Al ₂ O ₃ -3.5% (wt) La ₂ O ₃			, ,	less than in pure Al ₂ O ₃ , no La ₂ O ₃ detected
Al ₂ O ₃ -3.5% (wt) CeO ₂		, (few) , CeO ₂	, ' , , CeO ₂	less than in pure Al ₂ O ₃

* : , , , refers to phase state of Al₂O₃

2. OSC of samples containing composite-metal-oxides

Fig.3 shows the H₂-TPR profile on samples containing Ce oxide and La oxide.

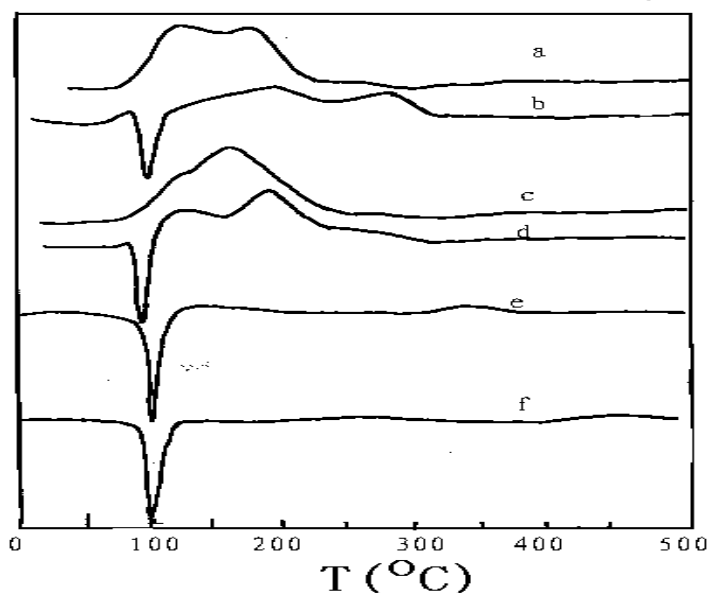


Fig.3 H₂-TPR profile on samples

a. Pd-Al₂O₃-CeO₂ 550 ; b. Pd-Al₂O₃-CeO₂ 900 ; c. Pd-Al₂O₃-CeO₂ / ZrO₂ 550 ;
d. Pd-Al₂O₃-CeO₂ / ZrO₂ 900 ; e. Pd-Al₂O₃- La₂O₃ 900 ; f. Pd-Al₂O₃- La₂O₃/BaO 900

Oxygen reduction peaks obviously appeared on the samples containing of CeO₂ and CeO₂/ZrO metal oxides, but not obviously appeared on samples containing of La₂O₃ and La₂O₃/BaO. It shows that the OSC of the first kind of samples is stronger than the second one. In addition ,OSC of Al₂O₃-CeO₂ sample decreased with increasing calcination temperature from 550 to 900 ,but OSC of sample calcined at 900 kept higher when ZrO₂ added. It shows that thermal stability of CeO₂ in high temperature condition was promoted with addition of ZrO₂. A strong and sharp minus peak appeared in the region of low temperature (90-100) on samples of b,d,e,f is attributed to desorption of H₂ adsorbed on Pd in samples. It suggests that total or parts of Pd in samples calcinated at 900 are in atomic state ,and total Pd in samples calcined at 550 are in oxide state.

3.Catalytic Activity

Light-off performance and Air/Fuel ratio scanning performance of two Pd only catalysts containing CeO₂-ZrO₂ and La₂O₃-BaO, respectively, are studied. Fig. 4 shows the experimental results on catalyst containing CeO₂-ZrO₂, and the profiles of catalyst containing La₂O₃-BaO are alike.

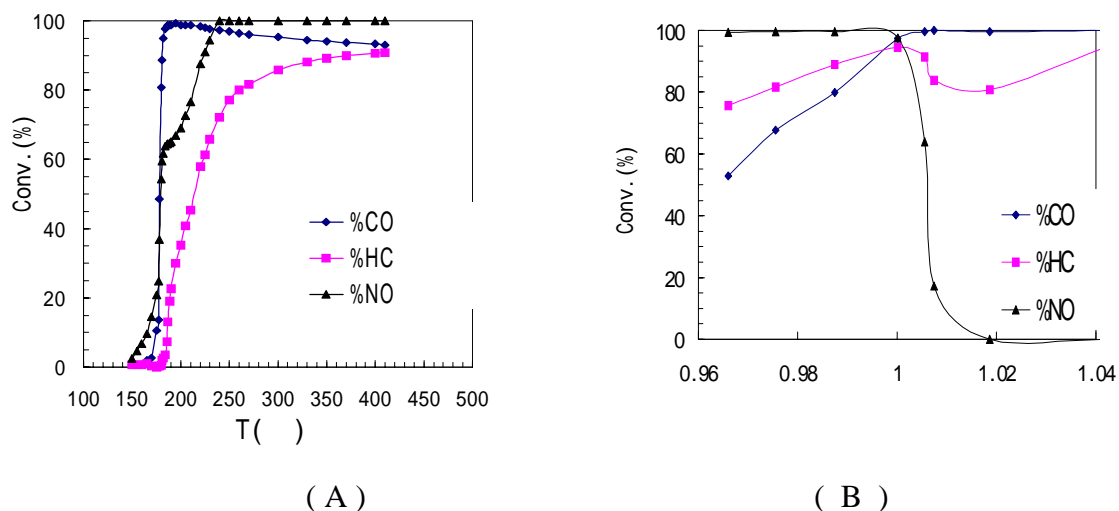


Fig. 4 catalytic performance on catalyst containing CeO₂-ZrO

(A. Light-off temperature; B. A/F ratio scanning)

It is found that the catalyst has a rather low light-off temperature of about 200 and a broad operation window of TWC. Data of Air/Fuel performance of two catalysts shows in table 2.

Table 2. Air/Fuel performance of two Pd catalysts

Catalyst		Crossover point conversion , %		Conversion at A/F=14.2,%		
additive	Pd-loading , g/l	CO-NOx	HC	CO	HC	NOx
Ce/Zr	1.0	97	94	63	80	100
La/Ba	1.0	95	93	56	94	100

All of two catalysts have high CO-NO_x and HC conversions at crossover point and high three-way conversion in rich condition (A/F = 14.2), except for HC conversion of catalyst containing of Ce-Zr.

The effect of SO₂ in gas stream on reaction activity is shown in table3.

Table 3 Effect of SO₂ on Light-off temperature performance

Catalyst		Light-off temp.,			Increase in light-off temp.,			SO ₂ ppm
Additive	Pd loading , g/L	CO	HC	NO _x	CO	HC	NO _x	
Ce/Zr	1.0	180	213	181	0	0	0	0
		296	365	304	+116	+152	+123	30
La/Ba	1.0	256	271	285	0	0	0	0
		299	312	/*	+43	+41	/	30

*Max conversion of NO_x is less than 50%

It was found that two catalysts have low Light-off temperatures of CO, HC, and NO_x without SO₂ in gas stream, and performance of the catalyst containing Ce/Zr is almost the same as conventional Pt/Rh TWC; In addition, the light-off temperature increases due to the addition of 30 ppm SO₂ to feedstream for two catalysts; The highest NO_x conversion on Pd catalyst containing La/Ba oxide was less than 50% due to strict SO₂ Poison.

CONCLUSION

In this work, Al₂O₃ / metal oxide additives, as key coating materials, were prepared and characterized with BET, XRD and H₂-TPR measurement. Then using typical washcoat slurry containing additives of Ce/Zr oxide or La/Ba oxide, two Pd TWC were prepared , and their performance was evaluated with simulated gas stream in laboratory.

The conclusions are as follow:

- 1) Utilization of additives (alkali earth metal oxides ,rare earth metal oxides and transition metal oxides)enhanced the thermal stability of active Al₂O₃;
- 2) ZrO₂ addition improved high temperature stability of CeO₂;
- 3) The Pd catalysts prepared with washcoat of Ce/Zr or La/Ba oxides have high CO, HC, NO_x conversion , broad Air/Fuel operation window and low light-off temperature;

- 4) Addition of 30 ppm SO₂ raised light-off temperatures of CO, HC and NO_x on two Pd catalysts, and, moreover, the catalyst containing La/Ba was more likely to be poisoned.

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