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

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ABSTRACT:

Active Al₂O₃ / metal oxide additives, as coating materials of Pd only Three-Way Catalyst (Pd TWC), were prepared and characterized with BET, XRD and H₂-TPR measurements. The thermal stability of active Al₂O₃ was enhanced by additives; the Ce-containing additives had oxygen storage capacity while La-containing samples didn’t; Pd TWC prepared with two typic washcoats containing Al₂O₃-CeO₂/ZrO₂ and Al₂O₃-La₂O₃/BaO, respectively, showed excellent low temperature performances and three way reactivity; Addition of 30 ppm SO₂ to the feedstream decreased performances of Pd TWC, and the catalyst containing La₂O₃/BaO was more likely to be poisoned.

Keywords: Palladium, Three-way catalyst, additives, SO₂ 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 NOx 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 °C for 4 hours.

The activity test was carried out in a conventional continuous-flow fixed bed reactor. Light-off performance was tested from 100 °C to 500 °C at a rate of 10 °C/min, and A/F ratio scanning performance ( = 0.960-1.040 ) at 500 °C, 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 °C 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 °C, except for CaO, still kept S.S.A of more than 45 m²/g. After calcined at 1200 °C, 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 °C, 1000 °C and 1200 °C).
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).

![Graph showing specific surface area of different samples](image)

**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 in samples containing composite-metal-oxides.(Not presented in the paper)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase of sample calcined at</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800 °</td>
<td>1000 °</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>□</td>
<td>□, □ (few)</td>
</tr>
<tr>
<td>Al₂O₃-3.5% (wt) BaO</td>
<td>□</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃-3.5% (wt) La₂O₃</td>
<td>□</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃-3.5% (wt) CeO₂</td>
<td>□</td>
<td>□, □, □</td>
</tr>
</tbody>
</table>

* : □, □, □, □ refers to phase state of Al₂O₃.

Table 1 XRD determination results
2. OSC of samples containing composite-metal-oxides

Fig. 3 shows the H$_2$-TPR profile on samples containing Ce oxide and La oxide.

![Fig. 3 H$_2$-TPR profile on samples](image)

<table>
<thead>
<tr>
<th>Sample Configuration</th>
<th>Temperature ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-Al$_2$O$_3$-CeO$_2$</td>
<td>550</td>
</tr>
<tr>
<td>Pd-Al$_2$O$_3$-CeO$_2$</td>
<td>900</td>
</tr>
<tr>
<td>Pd-Al$_2$O$_3$-CeO$_2$/ZrO$_2$</td>
<td>550</td>
</tr>
<tr>
<td>Pd-Al$_2$O$_3$-CeO$_2$/ZrO$_2$</td>
<td>900</td>
</tr>
<tr>
<td>Pd-Al$_2$O$_3$-La$_2$O$_3$</td>
<td>900</td>
</tr>
<tr>
<td>Pd-Al$_2$O$_3$-La$_2$O$_3$/BaO</td>
<td>900</td>
</tr>
</tbody>
</table>

Oxygen reduction peaks obviously appeared on the samples containing CeO$_2$ and CeO$_2$/ZrO metal oxides, but not obviously appeared on samples containing of La$_2$O$_3$ and La$_2$O$_3$/BaO. It shows that the OSC of the first kind of samples is stronger than the second one. In addition, OSC of Al$_2$O$_3$-CeO$_2$ sample decreased with increasing calcination temperature from 550°C to 900°C, but OSC of sample calcined at 900°C kept higher when ZrO$_2$ added. It shows that thermal stability of CeO$_2$ in high temperature condition was promoted with addition of ZrO$_2$. A strong and sharp minus peak appeared in the region of low temperature (90-100°C) on samples of b,d,e,f is attributed to desorption of H$_2$ adsorbed on Pd in samples. It suggests that total or parts of Pd in samples calcinated at 900°C are in atomic state, and total Pd in samples calcined at 550°C are in oxide state.
3. Catalytic Activity

Light-off performance and Air/Fuel ratio scanning performance of two Pd only catalysts containing CeO$_2$-ZrO$_2$ and La$_2$O$_3$-BaO, respectively, are studied. Fig. 4 shows the experimental results on catalyst containing CeO$_2$-ZrO$_2$, and the profiles of catalyst containing La$_2$O$_3$-BaO are alike.

![Fig. 4 catalytic performance on catalyst containing CeO$_2$-ZrO$_2$.](image)

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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd-loading, g/l</th>
<th>Crossover point conversion, %</th>
<th>Conversion at A/F=14.2, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>La/Ba</td>
<td>1.0</td>
<td>95</td>
<td>63</td>
</tr>
<tr>
<td>Ce/Zr</td>
<td>1.0</td>
<td>94</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 2. Air/Fuel performance of two Pd catalysts
All of two catalysts have high CO-NOx 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 table 3.

**Table 3 Effect of SO2 on Light-off temperature performance**

<table>
<thead>
<tr>
<th>Additive</th>
<th>Pd loading , g/L</th>
<th>Light-off temp., ºC</th>
<th>Increase in light-off temp., ºC</th>
<th>SO2 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce/Zr</td>
<td>1.0</td>
<td>CO: 180, HC: 296, NOx: 213, 365, 304</td>
<td>CO: 0, HC: 0, NOx: +116, 152, 123</td>
<td>0, 30</td>
</tr>
<tr>
<td>La/Ba</td>
<td>1.0</td>
<td>CO: 256, HC: 312, NOx: 271, 312, 285</td>
<td>CO: 0, HC: +43, NOx: +41</td>
<td>0, 30</td>
</tr>
</tbody>
</table>

*Max conversion of NOx is less than 50%*

It was found that two catalysts have low Light-off temperatures of CO, HC, and NOx 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 NOx 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, NOx 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 NOₓ on two Pd catalysts, and, moreover, the catalyst containing La/Ba was more likely to be poisoned.

REFERENCES