

Novel Oxygen Storage Components Promoted Palladium Catalysts for Emission Control in Natural Gas Powered Engines

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Abstract: A three-way catalyst comprised novel oxygen storage components for emission control in natural gas powered engines was prepared. The addition of novel oxygen storage components to the Pd/ γ -Al₂O₃ catalysts resulted in improved activities of the fresh and aged catalyst by lowering the light-off temperature for methane in natural gas engines exhaust.

Keywords: Oxygen storage component (OSC), emission control for natural gas powered engines, palladium catalysts, light-off temperature.

Natural gas has received increased attention as an alternative fuel for motor vehicles because of its potential technical, economic, and environmental advantages¹. On the other hand, NO_x emission and CO as well as unburned CH₄ (a gas with much more severe greenhouse effect than CO₂) in natural gas powered engines need to be greatly reduced². But oxidizing methane at low temperature, such as at 350°C, is difficult because its light-off temperature is higher than that of other hydrocarbons³. The traditional three-way catalysts used for controlling emission from gasoline-powered vehicles are unable to oxidize all the hydrocarbons and reduce NO_x simultaneously in natural gas engine exhaust⁴.

In literature concerning methane oxidation, Pd/ γ -Al₂O₃ catalysts exhibited higher and longer-lasting hydrocarbon oxidation activity than Pt-Rh/alumina, Pt/alumina and Pd-Rh/alumina⁵. But its light-off temperature is still high (nearly 380°C). It has been reported that the use of CeO₂-ZrO₂ OSC as the support of catalysts for wilding the A/F windows⁶. In this paper, a series of Pd catalysts consisting novel oxygen storage components were prepared for removing CH₄, CO and NO_x simultaneously at low temperatures from natural gas engine exhaust.

First of all, a commercial γ -Al₂O₃ was used as the catalyst support. For improving the thermal stability of γ -Al₂O₃, the γ -Al₂O₃ was impregnated with an aqueous solution of La(NO₃)₃, and then dried for 2 h at 120°C, calcined at 800°C for 2 h, such stabilized γ -Al₂O₃ contained 4wt% La₂O₃. The oxygen storage component was prepared by using a coprecipitation method. The composition of OSC contained CeO₂-ZrO₂ (atom ratio

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1:1) with or without MnO_x as additives. The amount of MnO_x additives was 0 wt%, 5 wt%, 10 wt% and 15 wt%, respectively. The precipitate obtained was filtered off, dried at 120°C for 2 h and calcined at 600°C for 2 h.

The stabilized $\gamma\text{-Al}_2\text{O}_3$ and the novel oxygen storage component were impregnated separately with an aqueous solution of $\text{Pd}(\text{NO}_3)_2$, and then dried for 2 h at 120°C, calcined at 500°C for 2 h. The obtained powder was mixed with $\text{Sr}(\text{NO}_3)_2$ and $\text{ZrO}(\text{AC})_2$, and formed mixture which contained 3 wt% SrO and 4 wt% ZrO_2 with respect to the weight of the entire composition. And then some water was added into the mixture to ball milling. The resulting slurry was wash-coated onto a monolithic substrate (cordierite honeycomb) with 400 cells/in². The excess of the slurry in the cells was removed by an compressed air blow, and dried at 120°C for 2 h, calcined at 500°C for 2 h. The coating amount in the all catalysts was 140 g/L. The catalysts obtained were presented in **Table 1**.

The activity measurements were carried out in a conventional fixed-bed flow reactor. The gas hourly space velocity was $3.3 \times 10^4 \text{ h}^{-1}$, the model natural gas exhaust contains 500 ppm CH_4 , 700 ppm H_2 , 2% CO , 400 ppm NO_x , and about 10% H_2O . The amount of exhaust components was analyzed by a five components exhaust gas detector (Foshan FGA4000 analyzer). Results of the tests were listed in **Table 2**.

It can be seen from **Table 2** that with catalyst **1** containing no OSC, the light-off temperature of methane is high (360°C). And with catalyst **2** containing OSC but no MnO_x , the light-off temperature (340°C) did not change much. But for catalysts added novel OSC during the preparation, the light-off temperature decreased greatly, and when 5 wt% of MnO_x was added, it (catalyst **3**) exhibited the lowest light-off temperature for methane (280°C), and the NO_x and CO were removed perfectly. While increasing the amount of MnO_x to the catalyst, the light-off temperature of methane for catalyst **4** and **5**

Table 1 The components of the catalysts

Catalyst	Pd (wt%)	Al_2O_3 (wt%)	$\text{CeO}_2\text{-ZrO}_2\text{-MnO}_x$ (wt%)	SrO+ZrO_2 (wt%)
1	1	92	0	7
2	1	53	39(0wt%MnO _x)	7
3	1	53	39(5wt%MnO _x)	7
4	1	53	39(10wt%MnO _x)	7
5	1	53	39(15wt%MnO _x)	7

Table 2 The light-off temperature of fresh catalysts

Catalyst	T(°C)	X_{CH_4} (%)	X_{NO_x} (%)	X_{CO} (%)
1	360	50	100	100
2	340	50	100	100
3	280	50	100	100
4	290	50	100	100
5	310	50	100	100

increased to 290 °C and 310 °C respectively, it indicated that the activity reaches an maximum at a MnOx loading of about 5 wt%, and higher loadings lower the activity of catalysts for oxidation of methane.

Hydrothermal ageing was performed at 1000°C for 5 h, under 5 vol% H₂, 10 vol% H₂O and 85 vol% N₂. **Table 3** presents the result of the aged catalysts. From **Table 3**, it can be found that aging leads to lower activity and increase the light-off temperature for CH₄ with the catalysts **1, 2**, but with the catalysts **3, 4, 5**, comprising novel OSC, the light-off temperature for CH₄ only increased by 40-45°C, exhibiting higher activity and better thermal stability.

Table 3 The light-off temperature of aged catalysts

Catalyst	T(°C)	X _{CH4} (%)	X _{NOx} (%)	X _{CO} (%)
1	410	50	100	100
2	385	50	100	100
3	320	50	100	100
4	330	50	100	100
5	355	50	100	100

Acknowledgments

The authors would like to thank the National Natural Science Foundation of China (No: 20273043) and the Ministry of Education of China for providing financial support for this project.

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Received 24 November, 2003