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TOLUENE COMBUSTION OVER Pd-BASED MONOLITHIC CATALYSTS WITH A NOVEL $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ WASHCOAT

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Abstract

A novel $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ washcoat was prepared by impregnation, which acts as a host for the active Pd component to prepare a series of Pd-based monolithic catalysts for toluene combustion. The redox behavior and catalytic activity depend on the molar ratio of Ce to Zr.

Keywords: Toluene combustion, monolithic catalyst, washcoat, Pd

INTRODUCTION

Monolithic catalyst supports are widely applied to the purification of automotive exhaust gases, catalytic combustion of methane, and elimination of volatile organic compounds (VOCs) [1-3]. Nowadays, the monolithic support is usually coated by a $\gamma\text{-Al}_2\text{O}_3$ washcoat of high surface area. However, the $\gamma\text{-Al}_2\text{O}_3$ washcoat has some disadvantages, such as low thermal stability, the formation of spinel compounds at high temperature, formation of cracks, weakly cohesive ability [4, 5], etc. In view of the shortcomings of the traditional

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γ -Al₂O₃ washcoat, great efforts have been made on the development of new washcoat materials. On the other hand, it is well known that CeO₂-ZrO₂ mixed oxides are applied to a variety of catalytic reactions due to their excellent oxygen storage capacity (OSC), high thermal stability and promoted activity of precious metals on them loaded [6-8]. However, there are seldom reports on CeO₂-ZrO₂ mixed oxides used as a potential washcoat material. This prompts us to carry out an extensive and systematic investigation on this topic.

In the present paper, a novel Ce_xZr_{1-x}O₂ washcoat has been developed, which is used as the washcoat of the Pd-Ce_xZr_{1-x}O₂/substrate ($x=0, 0.2$ and 0.4) monolithic catalyst. The surface morphology, redox behavior and catalytic activity for toluene combustion were investigated.

EXPERIMENTAL

An aqueous solution containing Ce(NO₃)₃·6H₂O, Zr(NO₃)₄·5H₂O (Ce:Zr = $x:1-x$, molar ratio, $x = 0, 0.2$ and 0.4), and citric acid (citric acid: (Ce+Zr) = 1.5:1, molar ratio) was heated and stirred constantly at 80°C in a water bath. Appropriate amount of 95% ethanol, polyethylene glycol (average molecular weight = 10000), and an aqueous solution of H₂PdCl₄ were added as dispersant, binder, and active component, respectively. A cuboid monolith, obtained from a commercial cordierite monolith (2MgO·2Al₂O₃·5SiO₂, 200 cpsi = 31 cells/cm²), was used as substrate. The washcoating was carried out by dipping the cordierite monolith in the obtained solution. The washcoated monolith was blown out with air to remove the excessive solution. It was dried at room temperature overnight, and then at 130°C for 4 h in an oven, followed by calcination at 400°C for 1 h in a muffle furnace. The dipping and drying procedure was repeated once more. Finally, the catalysts were calcined at 400°C for 2 h. The nominal loadings of Pd and CeO₂-ZrO₂ mixed oxides were 0.1 wt.% and 6 wt.%, respectively. The monolithic catalyst obtained was designated as Pd-Ce_xZr_{1-x}O₂/substrate.

Scanning electron microscopy (SEM) was performed with a Hitachi S-4800 scanning electron microscope, operated at an accelerated voltage of 1.0 kV, the samples were sputtered with gold. In this work, the samples were subjected to ultrasound by immersing them in water inside a glass vessel and in an ultrasonic bath (KU-200 ultrasonic vibration cleaner, 40 kHz. and 220 W) for 60 min. The weight of the sample both before and after the ultrasonic treatment was measured. Brunauer-Emmett-Teller (BET) surface area was determined by N₂ adsorption at 77 K using a Quantachrome Autosorb-1 apparatus. Carbon monoxide temperature-programmed reduction (CO-TPR) measurements were carried out in a quartz microreactor, and about 100 mg of the sample was employed in each measurement. The sample was pretreated under flowing CO-Ar (5%-95%) with a total flow rate of 20 mL/min at room temperature. After that, the temperature was raised from room temperature to 850°C with a

heating rate of 10°C/min. The amount of CO₂ evolved during the reduction was monitored by a Balzers Omnistar 200 mass spectrometer at $m/e = 44$.

The as-prepared monolithic catalyst was cut into two cylinders (length = 40 mm, *i.d.* = 21 mm). The catalytic activity was measured in a fixed bed reactor. The concentration of toluene in air was 40000 mg·m⁻³, and the total flow rate was 0.3 m³·h⁻¹ corresponding to a gas hourly space velocity (GHSV) of 10800 h⁻¹. The concentration of toluene were analyzed by a GC-14C (Shimadzu) equipped with a FID detector.

RESULTS AND DISCUSSION

The surface morphology of the bare substrate and the Pd-Ce_xZr_{1-x}O₂/substrate ($x = 0, 0.2$ and 0.4) monolithic catalysts can be compared in the SEM micrographs as shown in Fig. 1. It is found that the surface morphology of the bare substrate (Fig. 1a) is irregular with various porosities, while the surface morphology of the monolithic catalysts (Fig. 1b-d) seems to repeat the substrate surface relief, indicating that the washcoat is actually fixed inside the pores of the monolithic substrate instead of only being attached to the external surface of the monolithic channel walls. Therefore, the interaction between the washcoat and the substrate may be very strong leading to good adhesion, and being very difficult to get removed, which will be further validated by an ultrasonic test. In addition, it appears that the surface morphology of all monolithic catalysts (Fig. 1b-d) at a magnification of 5000 times is similar and does not depend on the molar ratio of Ce to Zr in the catalysts.

In order to further verify the washcoat adherence, an ultrasonic test, which was employed as a severe method of testing adherence [1] was performed and the corresponding results are listed in Table 1. The weight losses of all the monolithic catalysts are less than 3.0%, indicating that the washcoat is well anchored onto the substrate and has a good vibration-shock resistance.

The BET surface areas of the substrate and the Pd-Ce_xZr_{1-x}O₂/substrate ($x = 0, 0.2$ and 0.4) monolithic catalysts are listed in Table 2. The substrate has a surface area of 0.46 m²/g, while the Pd-Ce_{0.4}Zr_{0.6}O₂/substrate monolithic catalyst has a surface area of 3.33 m²/g, which is the biggest of all the monolithic catalysts. Besides, the surface areas of the monolithic catalysts decrease from 3.33 m²/g to 2.20 m²/g with the decrease in x from 0.4 to 0.

Although CO was rarely used as reducing agent in the TPR characterization as compared to H₂, CO-TPR is one of the best probes to study the reducibility of both the PdO and the support and is helpful to identify the finely dispersed PdO. Accordingly, we have performed the CO-TPR experiment, and the results are shown in Fig. 2. It is found that the redox properties of the monolithic catalysts are strongly influenced by the molar ratio of Ce to Zr in the catalysts. The CO-TPR profile of the Pd-Ce_{0.4}Zr_{0.6}O₂/substrate ($x = 0.4$) monolithic catalyst

shows a weak reduction peak at 122°C, and two strong reduction peaks at 209 and 521°C, which correspond to the reduction of the finely dispersed PdO, large PdO particles [9] and surface Ce^{4+} species [10], respectively. The CO-TPR profile of the Pd-Ce_{0.2}Zr_{0.8}O₂/substrate ($x = 0.2$) monolithic catalyst shows two strong reduction peaks at 208 and 563°C associated with the reduction of the large PdO particles and surface Ce^{4+} species, respectively. Compared with the Pd-Ce_{0.4}Zr_{0.6}O₂/substrate monolithic catalyst, the weak reduction peak at 122°C disappears. The strong reduction peak at 209°C slightly shifts to a lower temperature, whereas the strong reduction peak at 521°C shifts to a higher temperature. At the same time, the reduction areas of the two strong reduction

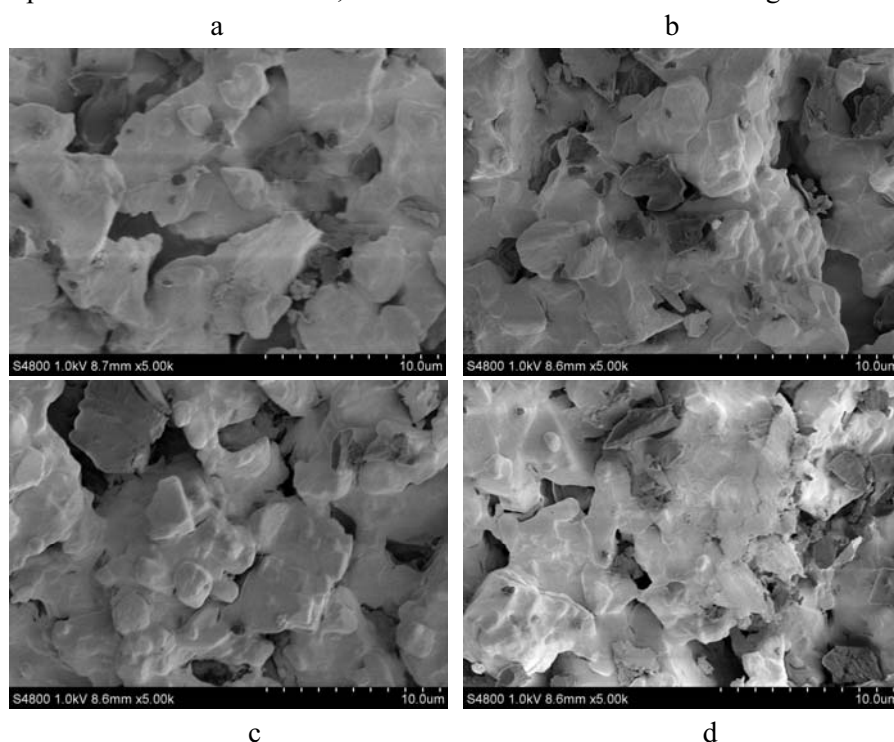


Fig. 1. SEM micrographs of the bare substrate and the Pd-Ce_xZr_{1-x}O₂/substrate ($x=0, 0.2$ and 0.4) monolithic catalysts. (a) bare substrate, (b) Pd-ZrO₂/substrate monolithic catalyst, (c) Pd-Ce_{0.2}Zr_{0.8}O₂/substrate monolithic catalyst, (d) Pd-Ce_{0.4}Zr_{0.6}O₂/substrate monolithic catalyst; (a)-(d) are top views of channels at a magnification of 5000

peaks decrease. The CO-TPR profile of the Pd-ZrO₂/substrate ($x = 0$) monolithic catalyst shows two strong reduction peaks at 195 and 662°C associated with the reduction of the large PdO particles and the oxygen species in zirconia. The strong reduction peak at 208°C shifts to a lower temperature,

and the area of the reduction peak decreases in comparison with the Pd-Ce_{0.2}Zr_{0.8}O₂/substrate monolithic catalyst. In summary, the areas of PdO (the finely dispersed PdO and large PdO particles) reduction peaks decrease with a decrease in x from 0.4 to 0. The amounts of the Zr component in the catalysts affect the redox properties of the monolithic catalysts.

Table 1

Weight losses of the Pd-Ce _{x} Zr_{1- x} O₂/substrate ($x=0, 0.2$ and 0.4) monolithic catalysts treated by ultrasonic vibration

Sample	ΔW (%)
Pd-Ce _{0.4} Zr _{0.6} O ₂ /substrate	0.9
Pd-Ce _{0.2} Zr _{0.8} O ₂ /substrate	1.1
Pd-ZrO ₂ /substrate	2.5

Table 2

BET surface areas of the substrate and the Pd-Ce _{x} Zr_{1- x} O₂/substrate ($x=0, 0.2$ and 0.4) monolithic catalysts

Sample	BET surface area (m ² /g)
Pd-Ce _{0.4} Zr _{0.6} O ₂ /substrate	3.33 ^a
Pd-Ce _{0.2} Zr _{0.8} O ₂ /substrate	3.28 ^a
Pd-ZrO ₂ /substrate	2.20 ^a
cordierite monolith	0.46

^aRelative to the total weight (monolith + washcoat)

The catalytic combustion of toluene over the Pd-Ce _{x} Zr_{1- x} O₂/substrate ($x=0, 0.2$ and 0.4) monolithic catalysts is shown in Fig. 3. During the catalytic combustion of toluene, the observed products were carbon dioxide and water, indicating that total combustion occurs in the reaction. As shown in Fig. 3, it is found that the catalytic activity of the catalysts depends on the molar ratio of Ce to Zr in the catalysts. The Pd-Ce_{0.4}Zr_{0.6}O₂/substrate monolithic catalyst exhibits the highest activity for toluene combustion, over which 95% toluene conversion is achieved at a temperature as low as 210°C. At the same time, the Pd-Ce _{x} Zr_{1- x} O₂/substrate catalysts with $x=0$ shows the lowest catalytic activity. In summary, the order of the catalytic activity in terms of x is $0.4 > 0.2 > 0$, which may be related with the decrease of the surface areas and the reduction areas of PdO with the decrease in x from 0.4 to 0. This is an indication that the molar

ratio of Ce to Zr in the catalysts plays an important role in the catalytic activity for toluene combustion. Therefore, a suitable molar ratio of Ce to Zr in $\text{Pd-Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{substrate}$ monolithic catalysts may be beneficial for PdO active species.

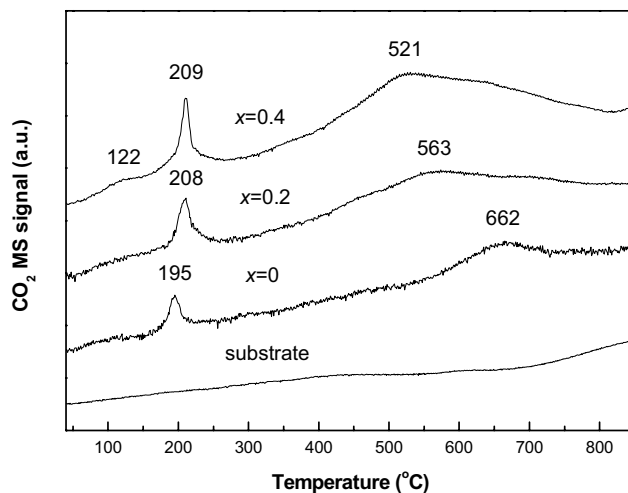


Fig. 2. CO-TPR profiles of the substrate and the $\text{Pd-Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{substrate}$ ($x = 0, 0.2$ and 0.4) monolithic catalysts

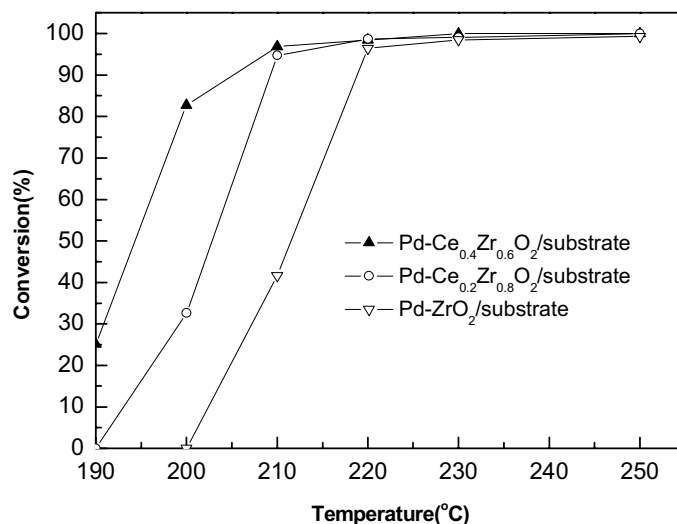


Fig. 3. Catalytic combustion of toluene over the $\text{Pd-Ce}_x\text{Zr}_{1-x}\text{O}_2/\text{substrate}$ ($x = 0, 0.2$ and 0.4) monolithic catalysts

CONCLUSION

The Pd-Ce_xZr_{1-x}O₂/substrate ($x=0, 0.2$ and 0.4) monolithic catalysts were prepared with Ce_xZr_{1-x}O₂ as a novel washcoat. The washcoat shows good vibration-shock resistance. The molar ratio of Ce to Zr in the catalysts affects the redox properties of the monolithic catalysts. The catalytic activity depends on x , and the order of the activity in terms of x is $0.4>0.2>0$.

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