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Article

A new monolithic Pt-Pd-Rh motorcycle exhaust catalyst to meet future emission standards

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ABSTRACT

A new composite oxide material as support, $\text{CeO}_2\text{-ZrO}_2\text{-La}_2\text{O}_3\text{-PrO}_2\text{-Al}_2\text{O}_3$, was synthesized by a co-precipitation method. Pd-Rh, Pt-Rh, and Pt-Pd-Rh supported on monolithic carrier catalysts were obtained by an impregnation route. The textural, structural, and reductive properties of the catalysts were characterized by N_2 adsorption-desorption, temperature-programmed reduction, oxygen storage capacity measurements, and X-ray diffraction. The air-fuel-ratio (A/F), space velocity (SV), and temperature characteristics of the fresh and aged catalysts were investigated on a systematic basis. The results showed that among the three catalysts, Pt-Pd-Rh displayed the best performance. For an SV of 40000 h^{-1} in the case of fresh Pt-Pd-Rh, the light-off temperatures (T_{50}) for C_3H_8 , CO, and NO were 239, 187, and 191 °C, respectively, with corresponding ΔT ($T_{90} - T_{50}$) values of 21, 3, and 3 °C, respectively. After aging, the T_{50} for C_3H_8 , CO, and NO were 298, 203, and 223 °C, respectively, and the ΔT values were 22, 5, and 13 °C, respectively. Moreover, the window widths for the A/F in the case of fresh and aged Pt-Pd-Rh catalysts were wide. Overall, the excellent performance for the Pt-Pd-Rh catalyst makes it suitable as a motorcycle exhaust catalyst, which can meet future emission standards.

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1. Introduction

In 2010, the annual output and ownership of motorcycles in China were 25 million and 100 million units, accounting for more than 40% and 50% of those in the world [1], respectively, indicating that China has become the largest producer and consumer in the world for motorcycles. According to statistics, motorcycle exhaust emissions of hydrocarbons (HC), CO, and NO_x amounted to 7.48 million tons in China for the year 2011 [2]. What is more, in comparison with cars fueled by gasoline and diesel, the exhaust gases of motorcycles contain large proportions of small particles ($\sim 0.04\text{ }\mu\text{m}$) within the PM 2.5 frac-

tion, which are harmful to health. Therefore, it is imperative to reduce the emissions of the hazardous components in motorcycle exhaust gas [3,4]. On July 1, 2008, China began to implement the third stage of motorcycle emission standards [5], and the fourth stage, which is in the process of being drafted, will be stricter [6,7]. In addition, although electric fuel injection technology will be applied in motorcycles, there are still many technical challenges, such as major fluctuations in the air-fuel-ratio (A/F) and working conditions of high temperature and space velocity (SV) when compared with cars fueled by gasoline [8]. Therefore, it is critical to improve the performance of catalysts to meet future motorcycle emission standards.

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The support materials used in motorcycle exhaust gas catalysts typically consist of $\text{CeO}_2\text{-ZrO}_2$ oxides and Al_2O_3 . The $\text{CeO}_2\text{-ZrO}_2$ solid solution has good oxygen storage capability (OSC) and has merit in promoting a water gas shift reaction, but its resistance to aging and durability is relatively poor [9–11]. Al_2O_3 , however, possesses high specific surface area, large pore volume, and remarkable anti-aging performance [12,13]. According to Morikawa et al. [14], a modified Ce-Zr rare earth oxygen storage material (OSM) combined with Al_2O_3 exhibits good oxygen storage capability. Furthermore, Al_2O_3 has played an important role as a “diffusion barrier”, inhibiting the aggregation of Ce-Zr materials and precious metals during the sintering process. Transition and rare earth elements could be doped into ceria-based oxides to change their phase structure to improve oxygen transmission at low temperature and realize high thermal stability [15–17]. In addition, the active components of motorcycle exhaust gas catalysts are usually based on Pt, Pd, and Rh, specifically Pd itself or Pd-Rh, Pt-Rh, and Pt-Pd-Rh [18].

To exploit the key advantages of OSM and Al_2O_3 and further improve the performance of support materials by addition of rare earth elements, a new composite oxide, $\text{CeO}_2\text{-ZrO}_2\text{-La}_2\text{O}_3\text{-PrO}_2\text{-Al}_2\text{O}_3$, was synthesized by a co-precipitation method, and the Pd-Rh, Pt-Rh, and Pt-Pd-Rh supported on monolithic carrier catalysts were obtained by an impregnation route. Then the A/F, SV, and temperature characteristic of the catalysts before and after aging were investigated in a systematic manner. The results demonstrated that the new catalysts were suitable for motorcycle exhaust gas treatment, with the excellent performance characteristics meeting future emission standards.

2. Experimental

2.1. Preparation of catalysts

The composite oxide, $\text{CeO}_2\text{-ZrO}_2\text{-La}_2\text{O}_3\text{-PrO}_2\text{-Al}_2\text{O}_3$, was prepared by a co-precipitation method. An aqueous solution of $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Pr}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ was first mixed with $\text{ZrO}(\text{CO}_3)\cdot 6\text{H}_2\text{O}$ dissolved in concentrated HNO_3 . The resulting mixed solution was injected into a reactor. At the same time, a buffer solution of $\text{NH}_3\cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{CO}_3$ in excess was added to the reactor. The pH (pH = 9), reaction temperature, and stirring speed in the reactor were carefully controlled during the process. The obtained precursors were aged at 90 °C for 4 h, then filtered and washed with distilled water until no change in pH could be detected. The precipitates were dried at 70 °C, heated at 600 °C for 3 h, and then calcined at 900 °C for 5 h. The synthesized sample $\text{CeO}_2\text{-ZrO}_2\text{-La}_2\text{O}_3\text{-PrO}_2\text{-Al}_2\text{O}_3$ (mass ratio 30:10:5:5:50) was marked as CZLPA.

Pt, Pd, and Rh were loaded on CZLPA by an impregnation method using solutions of $\text{Pd}(\text{NO}_3)_2$, $\text{Pt}(\text{NO}_3)_4$, and RhCl_3 as the metal precursors, respectively. After drying, Pd/CZLPA, Pt/CZLPA, and Rh/CZLPA catalyst powders were obtained. The resulting catalyst powders, Pd/CZLPA and Rh/CZLPA, Pt/CZLPA and Rh/CZLPA, and Pd/CZLPA, Pt/CZLPA, and Rh/CZLPA, were mixed in specific proportions, respectively.

Then distilled water was added to each mixture, and homogeneous slurries were obtained by ball mill. The slurries were spread on a honeycomb cordierite (2.5 cm³, Corning, USA; coating amount 160 g/L). The fresh monolithic catalysts, Pd-Rh (Pd/Rh = 10/1), Pt-Rh (Pt/Rh = 10/1), and Pt-Pd-Rh (Pt/Pd/Rh = 3/7/1), were obtained after drying and calcining at 550 °C for 3 h and were labeled as Cat1f, Cat2f, and Cat3f, respectively. The amount of precious metal coating in each catalyst was 1.76 g/L. These fresh catalysts were next thermally aged at 1000 °C for 5 h in air and labeled as Cat1a, Cat2a, and Cat3a.

2.2. Characterization of catalysts

The textural properties of the catalysts were obtained by the N_2 adsorption-desorption method on a Quantachrome SI instrument. The specific surface area, pore volume, and pore size distribution of the catalyst powders were measured at –196 °C. Prior to each measurement, the catalyst powders were degassed at 300 °C for 3 h under vacuum.

Temperature-programmed reduction in H_2 ($\text{H}_2\text{-TPR}$) was carried out in a quartz tubular micro-reactor equipped with a thermal conductivity detector. Prior to analysis, the catalyst powders (100 mg) were pre-cleaned using N_2 (20 mL/min) with temperature cycling from room temperature to 450 °C, holding at this temperature for 50 min and then cooling to room temperature. Measurements were performed from room temperature to 600 °C in 5% $\text{H}_2\text{-95}\%$ N_2 (20 mL/min) at a heating rate of 8 °C/min.

OSC was performed in a purpose-built experimental device. Catalyst powders (200 mg) were reduced in pure H_2 (40 mL/min) as the temperature was raised from room temperature to 550 °C before measurement of OSC. Then the powders were maintained at this temperature for 60 min, cooled to 200 °C, and purged with pure He (20 mL/min). The OSC was measured by injecting discrete oxygen pulses into the sample bed until no further oxygen consumption was detected by TCD.

X-ray diffraction (XRD) patterns were recorded using a Rigaku D/max-rA diffractometer with $\text{Cu K}\alpha$ radiation (40 kV, 25 mA, $\lambda = 0.15406$ nm). The powders were scanned within the 2θ range of 10° to 80°. The crystalline phases were identified by comparing them with reference data from the International Centre for Diffraction Data (ICDD).

2.3. Performance evaluation of catalysts

The performance of the catalysts was evaluated in a multiple fixed-bed continuum flow micro-reactor with a gas mixture that simulated the exhaust from a motorcycle. First, the catalysts were pretreated under a reaction atmosphere at 550 °C for 1 h. Then activity was evaluated by cooling to the reaction temperature. The A/F characteristics were evaluated at 400 °C with an SV of 40000 h⁻¹; the SV properties were evaluated at 400 °C and the space velocity of 20000, 40000, and 60000 h⁻¹; the temperature characteristics were evaluated at an SV of 40000 h⁻¹. The composition of reaction gas was 0.045% C_3H_8 , 1.5% CO, 0.11% NO, 10% H_2O , 10% CO_2 , different levels of O_2 , and N_2 as balance. The contents of C_3H_8 , CO, and NO in the

stimulated gas before and after reaction were analyzed using an FGA-4100 five-component analyzer (Foshan Analysis Instrument Co., Ltd., China), and then the conversion for each composition was calculated.

3. Results and discussion

3.1. Textural properties of catalysts

Table 1 shows the textural parameters for fresh and aged catalysts. It can be seen that the textural properties of these catalysts are similar to each other. Compared with the fresh catalysts, the surface area and pore volume of aged catalysts decreased; also the average pore radius of aged catalysts increased, indicating the formation of bigger pores caused by sintering and collapse during the aging process [5,19]. The surface areas of the catalysts after aging are still about 70 m²/g, which is slightly higher than that of the literature [14,20], demonstrating that the catalysts prepared in this study have excellent age resistance and are suitable for the high-temperature environment of motorcycle exhausts.

Figure 1 shows the N₂ adsorption-desorption isotherms and the pore radius distribution of the catalysts. The aperture radii of the fresh catalysts were about 4–8 nm, and the shapes of the three isotherms are almost the same. They are typical of an irreversible type IV adsorption isotherm with a H₂ hysteresis loop, indicating that the pores of the samples are slit and ink-bottle-type mesopores. The larger the mesopores, the higher the pressure needed for capillary condensation to occur. Therefore, the extent of adsorption increases faster in the high-pressure regions, suggesting that the large pores are abundant [21,22], which is well suited to the high-speed environment of a motorcycle exhaust. After aging, the aperture radii are about 5–12 nm and the areas of hysteresis shrink, which further suggests the collapse of small pores after aging [19,23]. The hysteresis loops for Pd-Rh and Pt-Rh catalysts are closed at a relative pressure (p/p_0) of about 0.8, which is about 23% higher than fresh catalysts. By comparison, the hysteresis loops for the Pt-Pd-Rh catalyst are closed at $p/p_0 \approx 0.7$, which only increased by 7.7% compared with the fresh catalyst. This result demonstrated that the extent of collapse for Pt-Pd-Rh is significantly less than that for Pd-Rh and Pt-Rh; also, the durability at high temperature is enhanced for the Pt-Pd-Rh catalyst [23].

3.2. H₂-TPR study

Figure 2 displays H₂-TPR profiles of the fresh and aged cat-

Table 1

Textural parameters of the fresh and aged catalysts.

Sample	Surface area (m ² /g)	Pore volume (mL/g)	Average pore radius (nm)
Cat1f	131	0.36	5.46
Cat2f	123	0.36	5.76
Cat3f	130	0.36	5.58
Cat1a	74	0.31	8.32
Cat2a	69	0.32	9.15
Cat3a	75	0.34	9.04

Fig. 1. N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of the fresh and aged catalysts.

alysts. All the fresh and aged catalysts feature dominant broad peaks below 400 °C, which are attributed to the reduction of Pt, Pd, and Rh, and these reduction temperatures are lower than those reported in the literature [24–27], indicating that the catalysts possess superior reductive properties. The peak area responses for the aged catalysts are suppressed relative to the fresh ones, which is due to substantial agglomeration of noble metals and shrinkage of the specific surface area and pore volume. A consequence of this is that a portion of the precious metal species are entrapped, leading to a reduction in the reduced species such that the peak area responses are decreased

Fig. 2. H₂-TPR profiles of the fresh and aged catalysts.

[21,28]. The reduction in peak areas for the catalysts before and after aging follow the sequence Pt-Pd-Rh > Pd-Rh > Pt-Rh, indicating that Pt-Pd-Rh exhibits the best reducibility.

3.3. OSC measurements

The OSC of the catalysts before and after aging are shown in Fig. 3. The OSCs of aged samples are lower than that of fresh ones primarily because of the sintering of the support materials and agglomeration of the precious metals [14,27]. The OSC of Pt-Pd-Rh is the highest and that of Pt-Rh is the lowest, which may reflect the different combining capacities between the precious metals and the support materials, as well as differing synergistic effects among the noble metals [28]. This result indicated that the Pt-Pd-Rh catalyst is responsive to larger fluctuations in the A/F and the long-term high-temperature environment of the motorcycle exhaust.

3.4. XRD measurements

XRD patterns for the catalysts before and after aging are illustrated in Fig. 4. It can be seen that all the catalysts have a typical cubic $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ phase and an Fm-3m space group. In contrast to the standard spectrum of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, however, the characteristic diffraction peaks slightly shift to a lower 2θ degree, which is due to the doped rare earth elements, La ($\gamma_{\text{La}^{3+}} = 0.106$ nm) and Pr ($\gamma_{\text{Pr}^{3+}} = 0.101$ nm, $\gamma_{\text{Pr}^{4+}} = 0.09$ nm) with the larger atomic radius entering the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ ($\gamma_{\text{Ce}^{4+}} = 0.097$ nm, $\gamma_{\text{Zr}^{4+}} = 0.084$ nm) crystal lattice [17,22]. After aging, the diffraction peaks become sharper and more intense, and diffraction peaks for $\gamma\text{-Al}_2\text{O}_3$ are observed, indicating that high-temperature treatment leads to grain growth and an ordered arrangement of the cations. As shown in Fig. 4(b), the characteristic diffraction peaks for the catalysts shift slightly to higher 2θ degree after aging. This may be due to the following reasons: (1) the migration of larger radius La^{3+} and $\text{Pr}^{3+}/\text{Pr}^{4+}$ cations from the bulk to the surface of the crystal, and (2) the transformation of Ce^{3+} ($\gamma_{\text{Ce}^{3+}} = 0.114$ nm) to Ce^{4+} during the high-temperature calcination process, resulting in shrinkage of the cell [17,22,29,30].

The crystal size of the fresh and aged catalysts calculated according to the Scherrer equation is about 5.5–7.5 nm, which

Fig. 3. OSC of the fresh and aged catalysts.

Fig. 4. XRD patterns of the fresh and aged catalysts.

implies little change of crystal size before and after aging, indicating excellent thermal stability of the catalysts. This phenomenon may benefit from Al_2O_3 acting as a “diffusion barrier”, limiting the carrier materials’ contact with each other. Thus, Al_2O_3 inhibits agglomeration of carrier material particles and, to a certain extent, increases the thermal stability of the materials [14,31].

3.5. Air-fuel-ratio of catalysts

Figure 5 displays the A/F for the fresh and aged catalysts, which describes the relationships between the conversions of three kinds of fomites in the simulated motorcycle exhaust at the SV of 40000 h^{-1} and the A/F (S value). Figure 5(a) displays the properties of fresh catalysts. When $S < 1$, NO undergoes full transformation for all the fresh catalysts, and the conversion for CO is 80%. The performance of Pd-Rh and Pt-Pd-Rh for conversion of C_3H_8 is enhanced, which is due to Pd-Rh and Pt-Pd-Rh facilitating the steam reformation reaction of C_3H_8 [17,18,22]. When $S > 1$, there is complete conversion of CO, but the conversion of NO decreases significantly, and the window width of NO in the case of Pd-Rh is the narrowest, owing to the conversion of NO being affected by the concentration of O_2 . With high concentrations of O_2 , the reduction of NO may be suppressed. In addition, the conversion of C_3H_8 over Pt-Rh and Pt-Pd-Rh declines with increase of S , while the conversion of C_3H_8 over Pd-Rh is still complete. This may reflect the fact that the coupling reactions of C_3H_8 and NO with Pt-Rh and Pt-Pd-Rh

Fig. 5. Variations in the conversion of C₃H₈, CO, and NO in simulated motorcycle exhaust at the space velocity of 40000 h⁻¹ with air to fuel ratios (*S* value) over the fresh (a) and aged (b) catalysts and window widths for the fresh and aged catalysts based on 80% conversion of the three pollutants (c).

are more efficient than that with Pd-Rh. The aged catalyst properties can be seen in Fig. 5(b), in which the catalytic properties of the three pollutants declined. The main reasons for this are the collapse of keyholes, a decrease in the specific surface areas, sintering of precious metals, and a reduction in active sites during the high-temperature treatment process [19,27]. These results are consistent with the textural properties of the aged catalysts. Figure 5(c) summarizes the window widths of the fresh and aged catalysts based on 80% conversion of the three pollutants at an SV of 40000 h⁻¹. The window width for fresh catalysts follows the sequence Pt-Pd-Rh > Pd-Rh > Pt-Rh. After aging, the window widths for the catalysts decrease to different extents, the levels of decline being in the order Pt-Rh > Pd-Rh > Pt-Pd-Rh, indicating that the Pt-Pd-Rh catalyst possesses an excellent A/F property and good resistance to aging, which agrees with the TPR and OSC findings.

3.6. Space velocity of catalysts

Figure 6 reveals the window widths for fresh catalysts at the SV of 20000 and 60000 h⁻¹. In conjunction with Fig. 5(a) and 5(c), it can be seen that the windows become narrow when the SV increases. When the SV increases, the residence time for exhaust gas on the catalyst becomes shorter and mass transfer

is restricted so that reactants have less time to enter the catalyst channels and react. Among the three catalysts, the windows for Pt-Pd-Rh at the SV of 20000, 40000, and 60000 h⁻¹ are the widest, indicating that the Pt-Pd-Rh catalyst is well suited to the high-speed environment of motorcycle exhaust.

3.7. Temperature characteristics of the catalysts

Figure 7 shows the conversions for C₃H₈, CO, and NO at different temperatures for fresh and aged catalysts in simulated motorcycle exhaust at an SV of 40000 h⁻¹. The *T*₅₀ (conversion of 50% for specific reaction temperature), *T*₉₀ (conversion of 90% for specific reaction temperature), and Δ*T* (*T*₉₀ – *T*₅₀) are listed in Table 2. The conversions for C₃H₈, CO, and NO rise as the temperature increases, rapidly approaching complete conversion at high temperature. As a result of the high conversion of the saturated hydrocarbon over Pt, the *T*₅₀ and *T*₉₀ values for C₃H₈ for the Pt-Rh catalyst are the lowest among that of the three catalysts [24,32]. After aging, owing to the sintering of the support materials and agglomeration of precious metals, the surface activity sites decline and the catalytic properties decrease [32,33]. Consequently, the *T*₅₀, *T*₉₀, and Δ*T* of the catalysts are higher, especially for the Pt-Rh catalyst. The *T*₅₀ and *T*₉₀ for CO and NO are relatively lower, which can be ascribed to

Fig. 6. Variations of air to fuel ratio (*S* value) windows over the fresh catalysts at the space velocities of 20000 h⁻¹ (a) and 60000 h⁻¹ (b), and the window widths for the fresh catalysts at different space velocities based on 80% conversions of the three pollutants (c).

Fig. 7. C_3H_8 , CO, and NO conversions at different temperatures for the fresh (a) and aged (b) catalysts in simulated motorcycle exhaust at a space velocity of 40000 h^{-1} .

Table 2

Light-off temperatures (T_{50}), complete conversion temperatures (T_{90}), and ΔT values for C_3H_8 , CO, and NO over the fresh and aged catalysts in simulated motorcycle exhaust at a space velocity of 40000 h^{-1} .

Catalyst	C_3H_8			CO			NO		
	$T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$	$\Delta T/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$	$\Delta T/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$	$\Delta T/^{\circ}\text{C}$
Cat1f	240	265	25	176	178	2	183	188	5
Cat2f	190	220	30	178	180	2	178	181	2
Cat3f	239	260	21	187	190	3	191	194	3
Cat1a	300	330	30	206	215	9	209	215	6
Cat2a	298	346	48	227	231	4	231	239	8
Cat3a	298	320	22	203	208	5	223	236	13

the higher content of CO in the motorcycle exhaust compared with car fueled by gasoline. Once the CO ignites, the exhaust temperature rapidly increases, resulting in rapid and complete conversion of CO and NO. Moreover, the difference of T_{50} between CO and NO is not clear, demonstrating a high degree of coupling between the two molecules. Considering the T_{50} , T_{90} and ΔT data for the three pollutants before and after catalyst aging, the performance data for Pt-Pd-Rh is the most remarkable, particularly the results for the textural properties and the H_2 -TPR and OSC data.

4. Conclusions

A new composite oxide, CeO_2 - ZrO_2 - La_2O_3 - PrO_2 - Al_2O_3 , was synthesized by a co-precipitation method, and the supported monolith catalysts, Pd-Rh, Pt-Rh, and Pt-Pd-Rh, were obtained through an impregnation route. Of the three catalysts investigated, the Pt-Pd-Rh catalyst showed the best redox properties and the most effective oxygen storage capacity. Furthermore, the A/F, SV, and temperature characteristics for the Pt-Pd-Rh catalyst were the most superior. It is concluded that the new composite material is suitable as a motorcycle exhaust catalyst and can meet future environmental emission standards.

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Graphical Abstract

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A new monolithic Pt-Pd-Rh motorcycle exhaust catalyst to meet future emission standards

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A new composite oxide, CeO₂-ZrO₂-La₂O₃-PrO₂-Al₂O₃, was successfully synthesized by co-precipitation, and the supported monolith Pd-Rh, Pt-Rh, and Pt-Pd-Rh catalysts were obtained through an impregnation route. The Pt-Pd-Rh catalyst delivers outstanding performance and is suitable as a motorcycle exhaust gas catalyst that can meet future emission standards.

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一个新的满足未来排放标准的摩托车尾气净化催化剂

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摘要: 采用共沉淀法制备CeO₂-ZrO₂-La₂O₃-PrO₂-Al₂O₃复合氧化物载体材料, 以浸渍法制备了Pd-Rh, Pt-Rh和Pt-Pd-Rh型整体式催化剂。用N₂吸附-脱附、程序升温还原、储氧量和X射线衍射对其进行了表征, 并考察了老化前后催化剂的空燃比特性、空速特性和温度特性。结果表明, 在三种催化剂中, Pt-Pd-Rh型催化剂表现出更优异的性能。在40000 h⁻¹空速下, 新鲜Pt-Pd-Rh型催化剂对C₃H₈, CO和NO的起燃温度T₅₀分别为239, 187和191 °C, ΔT(T₉₀ - T₅₀)分别为21, 3和3 °C。老化后, C₃H₈, CO和NO的T₅₀分别为298, 203和223 °C, ΔT分别为22, 5和13 °C, 且老化前后空燃比窗口较宽, 适合于未来排放标准的摩托车尾气净化。

关键词: 摩托车尾气净化; 整体式催化剂; 铂-钯-铑; 空燃比特性; 空速特性; 温度特性

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1. 前言

2010年我国的摩托车年产量为2500万辆, 占世界总年产量的40%以上; 摩托车保有量为1亿辆, 占世界总保有量的50%以上^[1]. 中国已成为世界上最大的摩托车生

产大国和使用大国. 据统计, 2011年我国摩托车尾气中的碳氢化合物(HC)、CO和氮氧化合物(NO_x)的年排放量已达748万吨^[2]; 此外, 与汽油车和柴油车相比, 摩托车尾气中PM 2.5的尺度仅为0.04 μm, 危害大, 因此摩托车尾气净化程度的提高已刻不容缓^[3,4]. 2008年7月1日我

国开始全面实施摩托车第III阶段排放标准^[5], 未来摩托车第IV阶段排放标准正在起草过程中, 将更为严格^[6,7]. 此外, 与汽车相比, 未来的摩托车即使使用电子喷射技术控制空燃比, 依然面临着高温、高空速且空燃比波动较大等难题^[8]. 因此, 摩托车尾气要满足未来排放标准, 必须提高催化剂的性能.

摩托车尾气净化催化剂的载体材料一般由Ce-Zr储氧材料和Al₂O₃组成. 这是因为CeO₂与ZrO₂形成的固溶体具有良好的储氧性能和可促进水-气转化反应等优点, 但抗老化和耐久性能较差^[9–11], 而Al₂O₃具有高比表面积、大孔体积和高抗老化等优异性能^[12,13]. Morikawa等^[14]研究发现, 用Al₂O₃改性的Ce-Zr稀土储氧材料兼有储氧材料和Al₂O₃的共同优点, 同时Al₂O₃的加入起到了“扩散障碍”的作用, 抑制了Ce-Zr材料和贵金属的烧结团聚. 文献^[15–17]报道, 在含铈氧化物中掺杂其它过渡金属和稀土元素可改变其体相结构, 从而改善其在低温条件下氧的传输和高温热稳定性. 摩托车尾气净化催化剂的活性组分主要有Pt, Pd和Rh, 通常分为单Pd型、Pd-Rh型、Pt-Rh型以及Pt-Pd-Rh型催化剂^[18].

为了将储氧材料(OSM)与Al₂O₃的优异性能结合起来, 并能通过稀土元素的掺杂进一步提高载体材料的性能, 本文采用共沉淀法制备了新型复合氧化物CeO₂-ZrO₂-La₂O₃-PrO₂-Al₂O₃, 以其作为载体制备了Pd-Rh, Pt-Rh和Pt-Pd-Rh型整体式催化剂, 并结合摩托车尾气排放特征考察了老化前后催化剂的空燃比特性、空速特性和温度特性.

2. 实验部分

2.1. 催化剂的制备

采用共沉淀法制备CeO₂-ZrO₂-La₂O₃-PrO₂-Al₂O₃复合氧化物. 按一定化学计量比称取Ce(NO₃)₃·6H₂O, ZrO(CO₃)·6H₂O, La(NO₃)₃·6H₂O, Pr(NO₃)₃·6H₂O和Al(NO₃)₃·9H₂O, 其中ZrO(CO₃)·6H₂O用HNO₃溶解后加入其余硝酸盐的溶液配成浓度为10%的盐溶液. 以NH₃·H₂O和(NH₄)₂CO₃的混合溶液作沉淀剂进行滴定并保持pH = 9, 所得沉淀经90 °C陈化4 h, 过滤, 洗涤后, 于70 °C干燥, 600 °C预分解3 h, 900 °C焙烧5 h, 得到质量比为30:10:5:5:50的CeO₂-ZrO₂-La₂O₃-PrO₂-Al₂O₃载体材料, 记为CZLPA.

以CZLPA为载体, Pd(NO₃)₂, Pt(NO₃)₄和RhCl₃为贵金属前驱体, 采用等体积浸渍法制备催化剂. 首先将Pd(NO₃)₂, Pt(NO₃)₄和RhCl₃分别浸渍到CZLPA上, 经干

燥后得到Pd/CZLPA, Pt/CZLPA和Rh/CZLPA三种催化剂粉末. 然后分别将Pd/CZLPA和Rh/CZLPA催化剂粉末, Pt/CZLPA和Rh/CZLPA催化剂粉末, Pd/CZLPA, Pt/CZLPA和Rh/CZLPA催化剂粉末加入一定量蒸馏水进行球磨混合, 制成浆液, 取堇青石蜂窝基体(美国Corning公司)小样(2.5 cm³)进行涂覆, 涂覆量为160 g/L, 经空气吹扫, 干燥, 再于550 °C焙烧3 h, 得到新鲜的整体式Pd-Rh (Pd/Rh = 10/1)型、Pt-Rh (Pt/Rh = 10/1)型和Pt-Pd-Rh (Pt/Pd/Rh = 3/7/1)型催化剂, 分别记为Cat1f, Cat2f和Cat3f. 其中, 贵金属的涂覆量均为1.76 g/L.

将制得的新鲜整体式催化剂置于高温炉中, 在空气气氛下1000 °C热老化处理5 h, 得到老化的Pd-Rh型、Pt-Rh型和Pt-Pd-Rh型催化剂, 分别记为Cat1a, Cat2a和Cat3a.

2.2. 催化剂的表征

催化剂织构性能测定在美国康塔公司SI型比表面测定仪上进行. 首先将催化剂粉末样品于300 °C下抽真空预处理3 h, 然后以N₂为吸附质, 在-196 °C下进行N₂吸附-脱附实验, 计算样品的比表面积、孔体积和平均孔径.

H₂程序升温还原(H₂-TPR)测定在自组装微型流动反应装置上进行, 催化剂粉末样品用量为100 mg. 样品先在N₂气流(20 mL/min)中加热至450 °C, 并保持50 min, 然后降至室温, 切换到5% H₂-95% N₂混合气(20 mL/min), 再以8 °C/min的升温速率升到600 °C, TCD检测耗氢量.

储氧性能(OSC)测定在自组装的实验装置上进行, 催化剂粉末样品用量200 mg. 样品首先在40 mL/min的H₂气流下升温至550 °C, 并保持60 min进行活化, 再切换为He (20 mL/min), 自然降温至200 °C, 脉冲注入O₂, TCD检测.

X射线衍射(XRD)测定在日本理学电机D/max-rA型X射线衍射仪上进行, 采用Cu K_α (λ = 0.15406 nm)作为衍射源, 管电压40 kV, 管电流25 mA, 扫描范围2θ = 10°–80°, 晶相与国际衍射数据中心(ICDD)相比较来辨别.

2.3. 催化剂的评价

催化剂的评价在实验室自制的多路固定床连续流动微型反应器中进行, 各路气体分别用质量流量计控制进入混合器. 反应前, 催化剂在反应气氛下于550 °C预处理1 h, 然后降至反应温度进行活性评价. 其中, 空燃比特性于温度为400 °C, 空速为40000 h⁻¹条件下测定; 空速特性于温度为400 °C, 空速为20000, 40000和60000

h^{-1} 条件下测定; 温度特性在空速为 40000 h^{-1} 条件下降温测定。反应气为摩托车尾气模拟气, 组成为 $0.045\% \text{ C}_3\text{H}_8$, $1.5\% \text{ CO}$, $0.11\% \text{ NO}$, $10\% \text{ H}_2\text{O}$, $10\% \text{ CO}_2$ 和不同含量的 O_2 , 以 N_2 为平衡气。采用FGA-4100型汽车排气分析仪(佛分环保仪器检测设备有限公司)分析反应前后尾气中各组分的含量, 计算各组分的转化率。

3. 结果与讨论

3.1. 催化剂的织构性能

表1为新鲜和老化催化剂的织构参数。由表可见, 三种催化剂的织构性能相近。与新鲜催化剂相比, 老化后催化剂的比表面积和孔体积下降, 平均孔径增大, 表明老化后催化剂中的小孔因内聚力较大, 烧结坍塌融聚到一起而形成大孔^[5,19]。老化后催化剂的比表面积仍有 $70 \text{ m}^2/\text{g}$ 左右, 略高于文献值^[14,20], 说明以新型复合氧化物载体材料CZLPA负载的催化剂具有较好的抗高温老化能力, 适合摩托车尾气的高温环境。

图1为新鲜和老化催化剂的 N_2 吸附-脱附等温线和孔径分布。可以看出, 新鲜催化剂的孔径集中在 $4\text{--}8 \text{ nm}$, 各催化剂样品的吸脱附曲线均表现出典型的IV型等温线和 H_2 型滞后环, 说明样品的孔为狭缝型和墨水瓶型的介孔。介孔越大, 毛细管凝聚发生的压力越高, 所以高压区吸附量上升较快, 说明大孔较多^[21,22], 适合摩托车尾气的高空速环境。老化后, 孔径集中在 $5\text{--}12 \text{ nm}$, 向大孔方向移动, 而且回滞环面积有不同程度的收缩, 这进一步说明老化后小孔坍塌, 孔径变大^[19,23]。同时, Pd-Rh型和Pt-Rh型催化剂的回滞环均在相对压力(p/p_0)为 0.8 左右开始闭合, 比新鲜催化剂增大了 23% , 而Pt-Pd-Rh型催化剂的回滞环在 $p/p_0 = 0.7$ 左右开始闭合, 比新鲜催化剂仅增大了 7.7% , 说明Pt-Pd-Rh型催化剂小孔坍塌程度较小, 抗高温老化能力更优^[23]。

3.2. H_2 -TPR结果

图2为新鲜和老化催化剂的 H_2 -TPR谱。由图可见, 新鲜催化剂和老化催化剂的还原峰温均在 400°C 以下, 归属为贵金属Pd, Pt和Rh的还原峰^[24–27], 且相比于文献^[24–27]中以Ce基材料为载体的贵金属催化剂, 还原峰温向低温偏移, 说明本文制备的催化剂具有较好的还原性能。与新鲜催化剂相比, 老化后样品的还原峰面积有所下降。这是由于贵金属在载体表面发生团聚、烧结, 加之载体材料的比表面积和孔体积下降, 使得一部分贵金属物种被包裹掩埋, 造成可还原物种量减少所致^[21,28]。老化前后, 三种催化剂的还原峰面积大小为 $\text{Pt-Pd-Rh} >$

$\text{Pd-Rh} > \text{Pt-Rh}$, 可见Pt-Pd-Rh型催化剂还原性能较好。

3.3. OSC结果

图3为新鲜和老化催化剂的储氧量。由图可见, 与新鲜催化剂相比, 老化后三种催化剂的储氧量均有所下降, 主要是由于载体材料的烧结和贵金属的团聚所致^[14,27]。其中, 老化前后Pt-Pd-Rh型催化剂的储氧量最高, Pt-Rh型催化剂的最低。这可能是各贵金属元素与载体材料的结合能力和贵金属之间的协同作用不同的结果^[28]。由此可见本文制备的Pt-Pd-Rh型催化剂适合于空燃比波动较大且长期高温的摩托车尾气环境。

3.4. XRD结果

图4是新鲜和老化催化剂的XRD谱。可以看出, 新鲜和老化催化剂均为典型的立方结构 $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ 相, 空间群为Fm-3m。相对于Fm-3m结构的 $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ 标准谱, 谱峰向小角度偏移, 这可能是载体材料中掺杂的原子半径较大的稀土元素La ($\gamma_{\text{La}^{3+}} = 0.106 \text{ nm}$)和Pr ($\gamma_{\text{Pr}^{3+}} = 0.101 \text{ nm}$, $\gamma_{\text{Pr}^{4+}} = 0.09 \text{ nm}$)进入到 $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ 晶格($\gamma_{\text{Ce}^{4+}} = 0.097 \text{ nm}$, $\gamma_{\text{Zr}^{4+}} = 0.084 \text{ nm}$)的结果^[17,22]。老化后, 各催化剂的衍射峰变得强而尖锐, 并检测到 $\gamma\text{-Al}_2\text{O}_3$ 的衍射峰, 表明高温焙烧导致晶粒长大, 晶型趋于完整。另外, 老化后三种催化剂的衍射峰向大角度偏移, 这是由于半径较大的 La^{3+} , $\text{Pr}^{3+}/\text{Pr}^{4+}$ 由体相向表面迁移, 同时高温焙烧后 Ce^{3+} ($\gamma_{\text{Ce}^{3+}} = 0.114 \text{ nm}$)向 Ce^{4+} 转化, 造成晶胞收缩^[17,22,29,30]。

根据Scherrer公式计算得老化前后催化剂平均晶粒尺寸均在 $5.5\text{--}7.5 \text{ nm}$, 即老化后催化剂的平均晶粒尺寸变化不大, 说明催化剂的热稳定性能较好。这可能得益于 Al_2O_3 在材料中充当了“扩散障碍”的分散物质, 限制了载体材料之间的相互接触, 从而在一定程度上抑制了载体材料颗粒的团聚长大, 增加了材料的热稳定性^[14,31]。

3.5. 催化剂的空燃比特性

图5是新鲜和老化的催化剂在 40000 h^{-1} 空速条件下的空燃比特性, 即 C_3H_8 , CO和NO转化率与空燃比S的关系曲线。对于新鲜催化剂, 在富燃区($S < 1$), 三种催化剂均能使NO达到完全转化, 并使得CO转化率达到 80% 以上, 但Pd-Rh型和Pt-Pd-Rh型更有利于 C_3H_8 的转化, 这可能是由于富燃时Pd-Rh型和Pt-Pd-Rh型催化剂上更有利发生 C_3H_8 的蒸汽重整反应^[17,18,22]。在贫燃区($S > 1$), 随着S值的增大, 三种催化剂均能催化氧化CO达到完全转化, 而NO的转化率则急剧下降, 并且Pd-Rh型催化剂的NO窗口明显窄于其它两类催化剂。这是由于NO受 O_2 浓度的影响, 还原反应受到限制。同时, Pt-Rh和Pt-Pd-Rh型催

化剂上 C_3H_8 的转化率随着 S 值的增大有所下降,而Pd-Rh型催化剂上的 C_3H_8 仍然可以达到完全转化,这可能是由于Pt-Rh和Pt-Pd-Rh型催化剂上 C_3H_8 和NO的偶联反应更为明显.与新鲜催化剂比较,老化后的催化剂对三种污染物的转化能力均下降.主要原因是高温老化过程中,小孔坍塌,比表面积下降,贵金属烧结,活性位点减少,催化反应受限^[19,27].这与老化后催化剂的织构性能下降相一致.图5(c)汇总了三种催化剂在 40000 h^{-1} 空速下老化前后空燃比窗口的宽度.由图可见,新鲜催化剂的空燃比窗口宽度顺序为Pt-Pd-Rh > Pd-Rh > Pt-Rh;老化后,三种催化剂空燃比窗口宽度均有所下降,下降程度顺序为Pt-Rh > Pd-Rh > Pt-Pd-Rh.这表明Pt-Pd-Rh催化剂的空燃比性能及抗老化性能优异.这与TPR和OSC结果相一致.

3.6. 催化剂的空速特性

图6为新鲜催化剂在 20000 和 60000 h^{-1} 空速下的空燃比窗口.结合图5(a)和(c)可见,随着空速的增大,催化剂空燃比窗口不同程度变窄.这是由于空速增大,气体在催化剂上停留时间变短,传质受到限制,甚至反应物来不及进入催化剂孔道进行反应所致.可以发现,Pt-Pd-Rh型催化剂在 20000 , 40000 和 60000 h^{-1} 空速下的空燃比窗口最宽,空速特性最好,更适合于摩托车尾气的高空速环境.

3.7. 催化剂的温度特性

图7是新鲜和老化催化剂在 40000 h^{-1} 空速下模拟摩

托车尾气中 C_3H_8 , CO和NO转化率随温度的变化曲线.三种污染物对应的起燃温度 T_{50} (转化率达50%时的温度)、完全转化温度 T_{90} (转化率达90%时的温度)和 ΔT (T_{90} 与 T_{50} 的差值)列于表2.由图7可知,对于新鲜和老化催化剂,随着温度的升高, C_3H_8 , CO和NO的转化率升高,并可以迅速达到完全转化.其中,Pt-Rh型催化剂对 C_3H_8 的起燃温度和完全转化温度最低,这是因为贵金属Pt对饱和烃的转化较好^[24,32].老化后,各催化剂的 T_{50} , T_{90} 和 ΔT 都有所升高,而以Pt-Rh型催化剂最为明显.这主要是由于老化后,载体材料坍塌烧结,贵金属团聚,造成表面活性位数量下降,因而催化剂活性下降^[32,33].CO与NO的 T_{50} 和 T_{90} 都相对较低,这是因为摩托车尾气中CO含量相对汽车较高,一经起燃,CO反应热导致尾气温度骤升,所以很快就达到完全转化.此外,CO和NO的 T_{50} 相差较小,说明CO和NO二者耦合较好.综合老化前后三种污染物的 T_{50} , T_{90} 和 ΔT ,以Pt-Pd-Rh型催化剂的性能最优,与表征结果一致.

4. 结论

采用共沉淀法制备了新型复合氧化物材料 CeO_2 - ZrO_2 - La_2O_3 - PrO_2 - Al_2O_3 ,并以此为载体制备了Pd-Rh, Pt-Rh和Pt-Pd-Rh型催化剂.三种催化剂中,Pt-Pd-Rh型催化剂在老化前后还原性能和储氧量最优,空燃比特性、空速特性及温度特性最优,适合于未来摩托车尾气排放标准催化剂的需求.