PREPARATION AND PROPERTIES OF PT-RH-PD / CeO₂-ZrO₂-La₂O₃-Al₂O₃ FIBROUS CATALYST VIA ELECTROSPINNING

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In order to increase the specific surface area of Pt-Rh-Pd / Al₂O₃ automotive three-way catalyst and improve its low-temperature reduction performance, Ce, Zr, and La were added to the Pt-Rh-Pd / Al₂O₃ catalyst to prepare the fibrous Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ catalyst via an electrospinning technique. The fibrous catalysts were characterized by XRD, FT-IR, SEM-EDS, H₂-TPR and BET analysis. The catalytic effect of the catalyst on automobile exhaust was also studied. Results revealed that the surface of catalysts is mainly mesoporous. Ce, Zr and La can remarkably increase the specific surface area of the Pt-Rh-Pd / Al₂O₃ catalyst. The specific surface area of the catalyst prepared with Pt Rh Pd molar ratio of 0.75:0.01:1 is 301.5816 m² g⁻¹, and the average diameter of which is 790 nm. In addition, the reaction temperature of the catalyst is approximately 220 °C, which shows good low-temperature reduction performance. Moreover, the Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ catalyst has a catalytic conversion efficiency for NOx of 90.0% in automobile exhaust, a catalytic conversion efficiency for CO of 88.8%, and a catalytic conversion efficiency for SO₂ of 75%.

Keywords: electrospinning; fiber; three-way catalyst; composite metal oxide; rare earth element.

INTRODUCTION

With the rapid growth of the number of automobiles in the world, hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NOₓ) in automobile exhausts have increasingly polluted the air of cities.1,3 Automotive exhaust purification catalyst is essential for controlling exhaust pollution.5,7 Automotive exhaust purification catalyst carrier is generally composed of rare earth oxygen storage material and Al₂O₃ with high specific surface area, strong heat resistance and aging resistance.6,11 As is well known, high-performance rare earth oxygen storage material is a key component of automobile exhaust purification catalyst,12-14 which determines the catalytic performance and life of catalyst. As a consequence, improving the oxygen storage performance, specific surface area and thermal stability of the carrier are the main directions for the development of high-performance automotive exhaust purification catalyst.

Since the 1980s, CeO₂-ZrO₂-Al₂O₃ carrier has shown excellent oxygen storage performance in automotive exhaust purification catalyst.15 CeO₂-ZrO₂-Al₂O₃ carrier remarkably improves the dispersion of active components on the surface of the carrier and catalytic activity.16,17 In addition, CeO₂-ZrO₂-Al₂O₃ carrier can enhance the anti-poisoning ability of automobile exhaust evolution catalysts.18 It is beneficial to promote the water vapor conversion and steam reforming reactions and improve the catalytic conversion efficiency of the catalyst.19 However, CeO₂-ZrO₂-Al₂O₃ carrier is easy to sinter at high temperature, which causes its specific surface area to drop sharply and results in a significant decrease in its oxygen storage / release performance. Moreover, CeO₂-ZrO₂-Al₂O₃ carrier cannot fully adapt to the high temperature working state of automobile exhaust purification catalyst. It was found that the incorporation of Pr, Y, Nd plasma could obviously promote the high temperature stability of CeO₂-ZrO₂-Al₂O₃ support and strengthen the sintering resistance of the catalyst.20 The performance of the carrier affects not only the dispersion of precious metals, but also the high temperature stability of the catalyst.21 Therefore, the preparation of carrier with high temperature stability and high oxygen storage capacity has become one of the important means to improve the catalytic effect of three-way catalysts. The precious metals such as Pt, Pd and Rh are the mainly active components of the three-way catalyst.22 Reducing the amount of precious metals while enhancing the low-temperature catalytic activity and high-temperature thermal stability of the catalyst are the main goals of the catalyst development. In recent years, electrospinning technology can easily and effectively prepare nano to sub-micron fibers, which has been widely applied in catalyst research.23-25 The polymer prepared by electrospinning has a relatively controllable chemical environment and structure on the surface, which can be used to prepare nanoparticle catalysts with extremely high dispersion and large specific surface area.26 The fiber catalyst prepared via electrospinning can effectively solve the problems of difficult aggregation, shedding and deactivation of catalytically active particles.27 The impregnation method is a common method for preparing automobile exhaust purification catalysts. However, the catalyst prepared by the impregnation method exists problems of poor catalytic performance at low temperature and metal particles’ sintering at high temperature, which seriously diminishes the catalytic activity and shortens the life of catalysts.

In this study, Ce, Zr, and La were added to the Pt-Rh-Pd / Al₂O₃ catalyst to prepare the fibrous Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ catalyst via an electrospinning technique. The fibrous catalysts were characterized by XRD, FT-IR, SEM-EDS, H₂-TPR and BET analysis to study their microstructural and compositional evolution. This work provides a simple route to improve the catalytic performance for CO and NOₓ in automobile exhaust.

EXPERIMENT

AlCl₃, ZrCl₄, CeCl₃ and LaCl₃ were dissolved in the mixed solution of 30 mL CH₃Cl and 0.95 mL C₆H₁₂O with the Ce Zr La and Al molar ratio of 1:1:0.06:2, while the mass fraction of AlCl₃ is 1.94 wt.%. The solution was subsequently dried at 80 °C for 2 h to obtain white powder named CeCl₃-ZrCl₄-LaCl₃-AlCl₃. The white powder, as well as PVP, were then dissolved in the mixed solvent of 9 mL C₆H₁₂OH and 4 mL DMF, in which the content of mass fraction was 4 wt.%. Finally, Pt Rh and Pd molar ratios of
0.75:0.01:1, 0.75:0.23:1 and 0.75:0.34:1 were respectively dissolved in the mixed solution to prepare Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ precursor solution. The precursor solution of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ was loaded by a 10 mL syringe with a stainless-steel needle whose diameter was 0.8 mm. Several parameters related to electrospinning are listed in Table 1. Process scheme of preparing Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst by electrospinning is showed in Figure 1.

Table 1. Electrosprining parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinning voltage</td>
<td>17 ± 0.5 (kV)</td>
</tr>
<tr>
<td>Spinning distance</td>
<td>17 ± 0.5 (cm)</td>
</tr>
<tr>
<td>Advancing speed</td>
<td>0.003 ± 0.0005 (mm s⁻¹)</td>
</tr>
</tbody>
</table>

X-ray diffraction (XRD) patterns were collected using a Rigaku DX-2500 diffractometer with Cu Kα radiation (0.15406 nm) in the range of 10°-90° with a step size of 0.02°. Fourier transform infrared spectrometer (FT-IR) patterns were measured employing a Vertex 70 Fourier infrared spectrometer. The BET specific surface area (Brunauer Emmett Teller, BET) for determining the specific surface area, catalyst pore volume, catalyst pore size and distribution of the catalyst were tested employing ASAP 2020 specific surface area and mesoporous / microporous analyzer. Scanning Electron Microscope (SEM) images were observed applying a Hitachi HITA CHI S-3400N scanning electron microscope. H₂ temperature-programmed reduction (H₂-TPR) studies were carried out using a Chem-Star program temperature reduction instrument to observe the reduction characteristics of the catalysts. Prior to the experiment, the sample was pretreated in N₂ (25 mL min⁻¹) at 450 °C for 1 h.

The catalytic activity of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst was evaluated in a Dongfeng LZ6430BQBE car with a self-assembled catalytic device. As displayed in Figure 2, Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst was wrapped on the surface of ceramic rods and fixed in the self-assembled catalytic device with metal meshes. The smoke and dust samplers were used to collect automobile exhaust. Both a portable infrared CO analyzer and a gas chromatography mass spectrometer were used to detect the components and contents of the exhaust. The catalytic conversion efficiency was calculated by the following formula in which A represented contaminant content before catalyst installation and B represent contaminant content after catalyst installation.

\[
\text{Catalytic conversion} = \frac{A - B}{A} \times 100\% \tag{1}
\]

RESULTS AND DISCUSSION

Composition and structure of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst

Figure 3 presents the XRD spectrum of a Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst. From Figure 3, it can be found that characteristic diffraction peaks corresponding to the Al₂O₃ crystal structure appear at 2θ of 41.28°, 47.49°, 68.78° and 83.32°. The diffraction peak width is narrow, and the peak value is high, which indicate that the crystallization of Al₂O₃ crystals is excellent. Characteristic diffraction peaks with 2θ of 24.58°, 32.45°, 48.62°, 48.70°, 57.64° and 62.15° correspond respectively to the crystal planes of (111), (200), (220), (311), (222) and (400) cubic phases appearing on the spectrum, which are consistent with the CeO₂-ZrO₂ solid solution fluorite structure. The peak at 2θ of 52.45° reveals that the catalyst has a small amount of La₂O₃ crystal structure. Characteristic diffraction peaks with 2θ of 24.58°, 32.45°, 48.62°, 48.70°, 57.64° and 62.15° correspond respectively to the crystal planes of (111), (200), (220), (311), (222) and (400) cubic phases appearing on the spectrum, which are consistent with the CeO₂-ZrO₂ solid solution fluorite structure. The peak at 2θ of 52.45° reveals that the catalyst has a small amount of La₂O₃ crystal structure. CeO₂-ZrO₂-La₂O₃ not only plays the role of oxygen storage, but Zr⁴⁺ in CeO₂-ZrO₂-La₂O₃ also improves the dispersion among the catalyst carrier particles and the thermal stability of the active components, thus ensuring the catalytic performance. The presence of CeO₂ and La₂O₃ can occupy the active sites on the support surface and inhibit
the formation of α-Al₂O₃, thereby maintaining the high dispersion of the active components and increasing the specific surface area of the catalyst.

Figure 4 shows the FT-IR spectra of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst after pre-oxidation at 80 °C (a) and carbonization at 1100 °C (b). As shown in Figure 4(a), typical absorption peaks that appear at 2920 cm⁻¹ and 1466 cm⁻¹ are mainly caused by the stretching vibration and bending vibration of the C-H bond in PVP. The absorption peak at 3357 cm⁻¹ is attributed to H-OH stretching in PVP. The absorption peak at 1642 cm⁻¹ is attributed to the C≡C stretching vibration in PVP. The absorption peak at 1294 cm⁻¹ is generated by the C-O stretching vibration in C₆H₁₄O. From Figure 4(b), it is found that when the catalysts experienced carbonizing at 1100 °C for 1 h, all of the absorption peaks presented above finally disappeared, mainly in respect that PVP and the solvent (C₆H₁₂OH, DMF) in the catalysts are thermally decomposed and volatilized during the heating process. It proves that Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst is decomposed to generate stable carbon fiber structure and metal oxide structure after pre-oxidation and carbonization.

Figure 5 shows the EDS diagram of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalysts. It can be seen from the figure that a large amount of particles evenly distribute on the catalyst surface. In order to determine the composition of particles on the surface of the catalyst, the surface particles are analyzed applying EDS. From Figure 5, it is found that the content of Pd species in the particles is large, which proves that the Pd species can finely adhere to the surface of the fiber. Table 2 shows the element mapping of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst. As displayed in Table 2, the main components of the fiber are Al, Ce and Zr, while Pt, Rh and La are not detected, which may be attributed to the low content of Pt, Rh and La. It proves that Pt, Rh and La species are highly dispersed on the support materials.

The texture properties of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst are shown in Table 3. N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst are shown in Figure 3. XRD spectrums of Pt-Rh-Pd / Al₂O₃ catalyst and Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ catalyst.
fibrous catalyst are shown in Figure 6. It is noticed from Table 1 that the pore diameter of the Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst ranges from 2.42 nm to 4.68 nm, indicating that the fiber mainly belongs to the mesoporous material. The catalyst prepared with Pt Rh and Pd molar ratio of 0.75:0.01:1 has a maximum specific surface area of 301.5816 m² g⁻¹. With the increase of Rh content, the specific surface area of the catalyst gradually decreases, while the pore diameter gradually increases. When the molar ratio of Pt Rh and Pd is 0.75:0.34:1, the pore diameter of the catalyst is 3.54 nm.

As displayed in Figure 6, the specific surface area of the Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst decrease with the increase of Rh content, while the pore size of the catalyst gradually increases mainly due to the agglomeration between mesopores, which leads to the obvious increase of the pore size.

Surface morphology of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fiber

Figure 7 shows the SEM images and diameter distribution histograms of Pt-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst. As displayed in Figures 7(a) and (b), the average diameter of the fiber filaments prepared with a PtCl₄ mass fraction of 0.35% is 800 nm. However, the electrospinning of inorganic metal oxide fibers is often accompanied by the solidification of the spinning solution at the needle, which causes the needle to become blocked and exacerbate the spinning instability. In addition, from Figures 7(c) and (d), the increase in the amount of Pt⁺ strengthens the conductivity of the solution, which makes the fiber further stretched and refined by the electric field force. As seen in Figures 7(e) and (f), when the mass fraction of PtCl₄ increases to 0.65%, the fiber is greatly influenced by the electric field during the spinning process, which remarkably aggravates the spinning instability and leads to a large number of fiber fractures.

Table 2. Element mapping of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalyst

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight percentage (%)</th>
<th>Atomic percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>42.07</td>
<td>61.84</td>
</tr>
<tr>
<td>O</td>
<td>28.11</td>
<td>31.01</td>
</tr>
<tr>
<td>Ce</td>
<td>12.08</td>
<td>1.52</td>
</tr>
<tr>
<td>Zr</td>
<td>10.78</td>
<td>2.09</td>
</tr>
<tr>
<td>Al</td>
<td>4.71</td>
<td>3.08</td>
</tr>
<tr>
<td>Pd</td>
<td>2.00</td>
<td>0.33</td>
</tr>
<tr>
<td>Cl</td>
<td>0.25</td>
<td>0.12</td>
</tr>
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</table>

Table 3. Texture properties of catalysts prepared with different Rh contents

<table>
<thead>
<tr>
<th>Samples</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Rh-Pd / Al₂O₃ catalyst</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt Rh Pd molar ratio of 0.75:0.01:1</td>
<td>230</td>
<td>0.14</td>
<td>2.4</td>
</tr>
<tr>
<td>Pt Rh Pd molar ratio of 0.75:0.23:1</td>
<td>149</td>
<td>0.10</td>
<td>2.5</td>
</tr>
<tr>
<td>Pt Rh Pd molar ratio of 0.75:0.34:1</td>
<td>57</td>
<td>0.07</td>
<td>4.7</td>
</tr>
<tr>
<td>Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ catalyst</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt Rh Pd molar ratio of 0.75:0.01:1</td>
<td>302</td>
<td>0.18</td>
<td>2.4</td>
</tr>
<tr>
<td>Pt Rh Pd molar ratio of 0.75:0.23:1</td>
<td>246</td>
<td>0.15</td>
<td>2.4</td>
</tr>
<tr>
<td>Pt Rh Pd molar ratio of 0.75:0.34:1</td>
<td>199</td>
<td>0.18</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Figure 6. N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ fibrous catalysts.
CeO$_2$-ZrO$_2$-La$_2$O$_3$-Al$_2$O$_3$ catalyst has three typical reduction peaks. The reduction peak is asymmetric and broad, indicating that various reducible species in fibrous catalyst are present. The addition of catalytically active components Pt, Rh and Pd move the reduction peak of the catalyst toward the low-temperature peak. The reduction peak at 220 °C for the catalyst is sharp, perhaps because Ce, Zr and La refine the size distribution of catalytic particles, which indicates that the catalyst has better low-temperature reduction performance. Compared with Pt-Rh-Pd / Al$_2$O$_3$ fibrous catalyst carrier from Figure 9(b) without the addition of Ce, Zr and La, the reduction rate has been greatly increased, reducing the reduction peak of the catalyst from 400 °C to 220 °C. In addition, the reduction peak area of the catalyst is large. Apparently, the catalytic particles formed on CeO$_2$-ZrO$_2$-La$_2$O$_3$-Al$_2$O$_3$ are stabilized by the support surface, indicating that Pt-Rh-Pd / CeO$_2$-ZrO$_2$-La$_2$O$_3$-Al$_2$O$_3$ catalyst has good thermal stability, which can maintain the original oxygen storage performance of the catalyst without being sintering at high temperatures.$^{18,21}$

Pt-Rh-Pd / CeO$_2$-ZrO$_2$-La$_2$O$_3$-Al$_2$O$_3$ catalytic performance

Table 4 shows the catalytic performance of Pt-Rh-Pd / CeO$_2$-ZrO$_2$-La$_2$O$_3$-Al$_2$O$_3$ catalyst and Pt-Rh-Pd / Al$_2$O$_3$ catalyst. It can be obtained from Table 4 that the CO content in the vehicle exhaust without catalyst is 116 mg m$^{-3}$ and the NO$_x$ content is 14 mg m$^{-3}$. The tail gas contains 8 mg m$^{-3}$ of SO$_2$, mainly due to the small amount of S contained in the 92 # gasoline used in the test vehicle. During the travel of the car, the SO$_2$ generated by the combustion of organic compounds containing S is emitted.

The self-assembled catalytic device where the content of Pd was 0.00056 mol and the molar ratio of Pt, Rh and Pd was 0.75:0.01:1 was installed on the car to analyze the components of the exhaust gas. It is found that the NO$_x$ content after the installation of the catalyst is 1.4 mg m$^{-3}$. Adding Ce, Zr and La can effectively improve the catalytic performance of Pt-Rh-Pd / CeO$_2$-ZrO$_2$-La$_2$O$_3$-Al$_2$O$_3$ catalyst, and its catalytic efficiency for CO in automobile exhaust is 88.8%. The data shows that Ce, Zr and La can obviously improve the catalytic effect of Pt-Rh-Pd / CeO$_2$-ZrO$_2$-La$_2$O$_3$-Al$_2$O$_3$ catalyst, promote the oxygen storage performance of the catalyst and enhance the Pt-Rh-Pd / CeO$_2$-ZrO$_2$-La$_2$O$_3$-Al$_2$O$_3$ catalyst oxidative ability to CO.

CONCLUSIONS

Pt-Rh-Pd / CeO$_2$-ZrO$_2$-La$_2$O$_3$-Al$_2$O$_3$ fibrous catalyst for purifying automobile exhaust was prepared by electrospinning. The composition,
Structure and surface morphology of the samples were studied by SEM-EDS, XRD FT-IR and BET analysis. In addition, the reduction performance of the catalyst was tested by H₂-TPR. The catalytic effect of catalyst on automobile exhaust was also investigated. From the experimental results, the following conclusions could be drawn:

- **Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃** catalyst is mainly mesoporous, and Ce, Zr, La can effectively increase the specific surface area of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ catalyst. Meanwhile, the increase of Rh content will reduce the specific surface area of the catalyst and exacerbate the pore agglomeration on the
catalyst surface, which causes the pore size of the catalyst to increase.

- The Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ catalyst has a good surface morphology. Increasing the mass fraction of RhCl₃ will increase the fiber diameter and the spinning instability, resulting in fiber agglomeration and breakage.
- Ce, Zr and La can effectively improve the reduction ability of Pt-Rh-Pd / CeO₂-ZrO₂-La₂O₃-Al₂O₃ catalyst.

ACKNOWLEDGEMENTS

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