Au Nanoparticles Supported on Iron-Based Oxides for Soot Oxidation: Physicochemical Properties Before and After the Reaction

Chao Hu,* Zhenzhen Chen, Chao Wei, Xiaokang Wan, Wenzhi Li, and Qizhao Lin

ABSTRACT: The catalytic performance of Au nanoparticles (NPs) supported on different transition-metal oxides for soot oxidation was studied in this paper. The changes in the morphology, phase structure, and physicochemical properties of Au-supported iron-based oxides before and after the reaction with soot particles were observed by high-resolution transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and temperature-programmed reduction. It was found that the catalytic activity of Fe3O4, Fe2O3, Co3O4, and NiO for soot oxidation was significantly improved after loading Au NPs. Especially, under the action of Au/Fe2O3 and Au/Fe3O4, the oxidation of soot was close to 20% below 420 °C, and their T10 values were 73 and 50 °C, respectively. When Au/Fe2O3 and Au/Fe3O4 reacted with soot, the size of the catalysts increased, and the active oxygen and Fe 2p components decreased. Au promoted the reduction of iron ions to a lower temperature, which was beneficial to improving the oxidation performance of iron-based oxides.

1. INTRODUCTION

Soot particles emitted from diesel engines can cause severe environmental and health problems.1 For the elimination of soot particles, one of the most efficient after-treatment technologies is the use of a diesel particulate filter (DPF), in which particles are trapped.2 However, soot deposition in DPF gradually increases the exhaust gas back pressure, resulting in a lower efficiency of the engine.3 The loaded DPF needs to be regenerated by the combustion of soot deposits from the filter. The spontaneous combustion temperature of diesel soot is above 600 °C, while the temperature of the diesel exhaust gas is typically at 180−400 °C.4 Thus, oxidative catalysts combined with the DPF to decrease the combustion temperature of soot is believed to be a feasible method in reducing soot emission.

The key to reducing the soot oxidation temperature is to find a suitable catalytic system. Recently, a series of catalysts such as noble metals, alkaline-metal oxides, transition-metal oxides, and perovskite oxides have shown good performances for soot oxidation.5 Among the noble metals, Au catalysts have gained increasing attention because of their good catalytic activities in numerous reactions including the oxidation of volatile organic compounds, CO, and soot particles. In the catalytic combustion of methane, catalysts such as Au NPs loaded on La−Mn perovskites with a three-dimensional structure and Au−Pd loaded on Co3O4 show high performances, and the light-off temperature of methane can be achieved at 218 °C.6,7 As for the catalytic oxidation of CO, supported Au NPs have been shown to be useful catalysts from the report of their high low-temperature oxidation activities by Hutchings’ and Haruta’s groups.8,9 There have been a great number of studies on supported gold catalysts for CO oxidation. Recently, Zhang prepared a series of Au/LaPO4 catalysts with good activity and stability and achieved complete CO conversion at 25 °C.10

Moreover, the gold catalysts have a great preference on the catalytic combustion of soot particles. Craenenbroeck et al. studied the catalytic activity of Au−VOx/TiO2 and Au−VOx/ZrO2 on diesel soot particles and found that the ignition temperature of soot was 361 °C and the peak burning temperature was 419 °C.11 Au supported over ZnO is seen to be better than Ag/ZnO and CuO on soot particle oxidation, which is attributed to the stronger Coulombic force between Au3+ and soot.12 Wei and Zhao’s research group studied a series of catalysts with gold as the active component, including Au/Co3Zr2O2 and AuPt/Co3Zr2O2 alloy nanoparticles (NPs) and Au@Pt/Co3Zr2O2, Au@CeO2−δ/ZrO2, and Au@...
La₂O₃ core–shell-structured NPs. They observed that Au can significantly increase the active oxygen species on the surface of the catalyst and improve the catalytic activity. The catalytic activity of Au NPs is related to a variety of factors, including the particle shape and size, oxide support materials, preparation procedures, oxygen supply pathways, coordination between Au NPs and support, and so forth. Noble metals supported on oxides are typically deep oxidation catalysts. Strong metal–support interactions can exert dramatic influences on the catalytic performance of supported Au catalysts. The supports often play a key role in the process of catalytic reactions. There are reducible oxide and irreducible oxide supports. The difference in the reducibility of these oxide can affect the properties of catalysts. For example, Widmann observed that the catalytic activity for the oxidation of CO obeyed the sequence of Au/TiO₂ > Au/ZrO₂ > Au/ZnO > Au/Al₂O₃. In the catalytic oxidation of ethyl acetate and toluene, Carabineiro concluded that Au/NiO and Au/CuO performed better than Au/Fe₂O₃, Au/MgO, and Au/LaO. In the catalytic oxidation of toluene or propene, Liotta found that the catalytic activity decreased in the order of Au/CeO₂ > Au/7.5Ce/Al₂O₃ > Au/TiO₂ > Au/Al₂O₃.

The activity of the catalyst for soot particle oxidation is related to its activation of oxygen and the contact opportunity between the catalyst and soot particles. Au can promote the adsorption activation of oxygen molecules (O₂) and increase the number of active oxygen species (O₂⁻ and O₂²⁻) on the catalyst surface. Metal oxides are able to modify the catalytic property. One of the main catalytic functions of metal oxides in soot oxidation is to transfer the oxygen species from its surface to soot particles. The spillover of oxygen and the subsequent chemical adsorption of active oxygen are the two important steps in the soot oxidation mechanism. The role of the catalyst is to increase the transfer of active oxygen species to the surface of the soot, but it does not change the rate-determining step. Their catalytic reactions depend largely on the electronic state of the metal oxide. Moreover, transition-metal oxides display excellent redox properties due to the change in their valence state in the oxidation reactions. Metal ions can promote electrons to accumulate on the surface of the soot in a higher energy state, thereby enhancing the driving force to effectively transfer electrons from the soot to O₂. The oxygen spillover and the electron-transfer mechanisms complement each other in the oxidation reaction of soot with the catalyst.

High-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy are often used to investigate the changes in the soot morphology and reactivity. Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) is constantly used to study the chemically bonded species on the catalyst surfaces and the molecular interaction between the catalyst and adsorbates under reaction conditions. The aim of this work is to study the catalytic performances and the intrinsic activity of the transition-metal-oxide-supported gold catalysts for soot oxidation. A series of catalysts of Au/oxide (oxide = Fe₂O₃, Fe₃O₄, Co₃O₄, NiO, and CeO₂) were designed and successfully synthesized by the deposition–precipitation method. Especially, the structures, electronic properties, and reduction of catalysts Au/Fe₂O₃ and Au/Fe₃O₄ were investigated before and after the reaction with soot particles. The catalysts were investigated using HRTEM, XRD, X-ray photoelectron spectroscopy (XPS), and temperature-programmed hydrogen reduction (H₂-TPR). Using these properties of the catalysts, the nature of the interactions between iron-based oxides and Au NPs was also investigated.

2. RESULTS AND DISCUSSION

2.1. Catalytic Performances of Transition-Metal Oxides for Soot Oxidation. The catalytic performance of variable valence transition-metal oxides without Au NPs for soot oxidation is first studied, and the results are shown in Figure 1. The pure soot had almost no oxidation below 550 °C, and its initial oxidation temperature Tᵯ was 592 °C. The oxidation rate of the soot reached the highest at 600–700 °C, and the complete oxidation was achieved near 700 °C. The five transition-metal oxide catalysts studied in this paper, Fe₂O₃, Fe₃O₄, Co₃O₄, NiO, and CeO₂, can oxidize the soot particles at...
the temperature of 400–450 °C. 450–600 °C was the main temperature range of the catalytic oxidation of soot particles, which were almost completely oxidized before 600 °C. It can be seen that the transition-metal oxide can effectively reduce the oxidation temperature of soot particles, so that the complete conversion temperature can be reduced by at least 100 °C. Among them, Fe₂O₃ had the best ability to catalyze the oxidation of the soot, its initial oxidation temperature was 450 °C. The temperature corresponding to its maximum conversion rate was 492 °C, and the burnout temperature was 535 °C; the complete conversion temperature of the soot decreased by 150 °C. The order of the catalytic oxidation activity of these five variable valence transition-metal oxide catalysts to soot particles is: Fe₂O₃ > Co₃O₄ > Fe₃O₄ > NiO > CeO₂. Fe₂O₃ and Fe₃O₄ iron-based catalysts show good catalytic activity in soot oxidation.

The conversion rate of Fe₂O₃ and Fe₃O₄ for soot particle oxidation before 420 °C is close to 20%, but the conversion curve is smooth. For Fe₂O₃, the curve starts to steepen at 445 °C, and the burnout temperature was 535 °C; the complete conversion temperature of the soot decreased by 150 °C. The order of the catalytic oxidation activity of these five variable valence transition-metal oxide catalysts to soot particles is: Fe₂O₃ > Co₃O₄ > Fe₃O₄ > NiO > CeO₂. Fe₂O₃ and Fe₃O₄ iron-based catalysts show good catalytic activity in soot oxidation.

In order to characterize the catalytic activity of these catalysts on soot particles more directly and accurately, the characteristic temperatures $T_{10}$, $T_{50}$, $T_{90}$, and $T_m$ of the catalytic reaction are summarized, as shown in Table 1. By comparing the relationship between the characteristic temperatures of different catalysts, the catalytic activity can be easily judged, the lower the characteristic temperature, the stronger the catalytic activity. The $T_{10}$ of Fe₂O₃ and Fe₃O₄ are 87 and 100 °C, respectively.

### 2.2. Catalytic Performances of Au/Oxide for Soot Oxidation

The transition-metal oxide catalyst supported by Au NPs was prepared by the DP method. The catalyst and soot particles were mixed and ground to form a mixture, which was then subjected to thermogravimetric analysis. According to the soot quality change and the calculation formula of the soot conversion rate, the conversion efficiency of soot particles with different catalysts is obtained, as shown in Figure 2. According to the temperature value corresponding to the conversion efficiency, the conversion characteristic temperatures of soot particles oxidation are summarized in Table 2.

As can be seen from Figure 2, the Au-supported transition-metal oxide catalyst can further reduce the oxidation temperature of soot particles, but the effects of catalysts with different supports in reducing the oxidation temperature of soot particles are different. In general, the initial oxidation temperature of soot particles on Au/CeO₂, Au/Co₃O₄, Au/Fe₂O₃, Au/Fe₃O₄, and Au/NiO was 350–450 °C, and the main reaction temperature range was 400–600 °C; the soot particles basically burned out after 600 °C.

Comparing Figures 1 and 2, it can be found that the catalytic activity of the transition-metal oxide has changed after loading with Au NPs. For example, after the catalyst Co₃O₄ was loaded with Au NPs, its initial oxidation temperature of soot particles decreased from 420 to 354 °C, the burnout temperature decreased from 537 to 491 °C, and the characteristic temperature of the maximum combustion rate decreased from 487 to 395 °C. The catalytic activity of Co₃O₄ was improved after loading Au NPs. However, for the catalyst CeO₂, its catalytic activity decreased after Au NPs were supported. The initial oxidation temperature of soot increased from 413 to 430 °C, the burnout temperature increased from 586 to 616 °C, and the characteristic temperature of the maximum combustion rate decreased from 528 to 582 °C. For the catalysts Fe₂O₃, Fe₃O₄, and NiO after loading with Au NPs, their initial temperature, burnout temperature and maximum combustion rate characteristic temperature had all decreased, which means that Au NPs increased their catalytic oxidative activity of soot particles. The order of the activity capacity of Au-loaded transition-metal oxides for the catalytic oxidation of soot particles was: Au/Co₃O₄ > Au/Fe₂O₃ > Au/Fe₃O₄ > Au/NiO > Au/CeO₂. Au/Fe₂O₃ and Au/Fe₃O₄ show good catalytic oxidation activity after loading Au NPs.

Interestingly, catalysts Au/Fe₂O₃ and Au/Fe₃O₄ had a conversion efficiency of nearly 20% for soot particles before 400 °C, but the conversion curves were always relatively smooth. For Au/Fe₃O₄, the conversion curve began to steepen at 425 °C and the soot conversion rate gradually increased. For catalyst Au/Fe₂O₃, the conversion rate of soot particles began to increase slowly at 441 °C. The $T_{10}$ of Au/Fe₂O₃ and Au/Fe₃O₄ is 73 and 50 °C, respectively. For catalysts Au/Fe₂O₃ and Au/Fe₃O₄, the possibility of the catalytic oxidation of soot particles before 425 °C is very small. Therefore, we believe that the conversion efficiency of soot particles is nearly 20% mainly due to the physical reaction between the soot particles and iron-based catalyst, whose mechanism needs further experimental study.

### 2.3. Characterization of the Catalysts before and after the Reaction with Soot Particles

Characterizing of the structure and properties of the catalysts before and after the reaction with soot particles will help us to understand the physicochemical properties of the catalyst and the catalytic oxidation mechanism of soot particles more clearly.

Figure 3 shows the TEM images of Au/Fe₂O₃ before and after the reaction with soot particles. Before the reaction, Au NPs were small, spherical, and relatively dispersed, and Fe₂O₃ was large in size and forms a block structure. Au NPs were well attached to the surface of Fe₂O₃. The average diameter of Au NPs was 11.2 nm before the reaction and was 17.4 nm after the reaction. Their size distribution is shown in Figure 4. The increase in the size of Au NPs may be due to the slight sintering and aggregation after the reaction between the catalytic and soot particles at 400 °C. These small Au NPs agglomerated to form a larger particle, but they were not sintered to form a block structure.

Figure 5a,b shows the high-resolution electron microscopy images of catalyst Au/Fe₃O₄ before and after the reaction with...
soot particles, respectively. It can be calculated from the figure that the lattice spacing of Fe₃O₄ is 0.316 nm, which is consistent with the lattice spacing of Fe₃O₄ (220) of 0.30 nm. The lattice spacing of Au is 0.273 nm, which is close to 0.24 nm of Au (111). The crystal structure with a lattice spacing of 0.278 nm can be measured from the high-resolution electron microscope image of the catalyst after the reaction with soot particles, which is more consistent with the lattice spacing of Fe₂O₃ (104) of 0.27 nm.

The catalyst Au/Fe₃O₄ after the reaction with soot particles is studied by EDS analysis, as shown in Figure 6. It indicates the existence of Fe and Au in the catalyst. Cu from the TEM grid has the highest peak. Because the loading content of Au in the catalyst Au/Fe₃O₄ was low, the peak of Au is relatively small and the peak of Fe is relatively high. The peak corresponding to oxygen in the catalyst can also be seen from the figure.

Figure 7 shows the XRD spectra of the catalysts Au/Fe₂O₃ and Au/Fe₃O₄ before and after the reaction with soot particles. Au/Fe₂O₃ and Au/Fe₃O₄ showed characteristic diffraction peaks of α-Fe₂O₃ at 2θ = 24.1, 33.2, 35, 41, 49, 54, and 62° (PDF 00-033-0664), and the characteristic diffraction peaks of Au (PDF 00-065-2870) appear at 2θ = 38, 44, and 77°. In addition, the characteristic diffraction peaks (PDF 00-019-0629) of γ-Fe₂O₃ (400) appearing at 2θ = 30 and 43.5° were observed in the XRD spectra of Au/Fe₃O₄ before and after the reaction with soot particles. In the XRD pattern of the Au/Fe₃O₄ catalyst, the characteristic diffraction peaks of α-Fe₂O₃ and γ-Fe₂O₃ simultaneously appeared, indicating the co-existence of the two phases because γ-Fe₂O₃ can be converted into α-Fe₂O₃ when heated over 300 °C in the air.

Before the soot oxidation reaction, the number of characteristic diffraction peaks of the catalysts was small and the peak width was large. This is due to the small nanometer size of the catalysts particles before the reaction, which leads to a large half-peak width. According to the Scherrer equation, the larger

| catalyst | characteristic temperature (°C) |
|----------|--------------------------------|
| Au/CeO₂  | 430 554 616 582 |
| Au/Co₃O₄ | 354 416 491 395 |
| Au/Fe₂O₃ | 73 463 520 474 |
| Au/Fe₃O₄ | 50 491 548 495 |
| Au/NiO   | 395 514 576 531 |

Figure 2. Catalytic performance of Au/Oxide (oxide = CeO₂, Co₃O₄, Fe₂O₃, Fe₃O₄, NiO, and CeO₂) on soot particles.

Table 2. Characteristic Temperature of Catalytic Oxidation of Au/Oxide with Soot Particles (Oxide = Co₃O₄, Fe₂O₃, Fe₃O₄, NiO, and CeO₂)

Figure 3. TEM images of Au/Fe₃O₄ before (a) and after (b) reaction with soot particles.
the average crystallite size of the catalyst, the smaller the half width of the diffraction peak. After the soot oxidation reaction, the half width of the characteristic diffraction peak of the catalyst becomes smaller, indicating that the size of the catalyst increases. As the temperature increases, the crystallite size of the catalyst becomes larger, which is consistent with the increase in the size of Au NPs measured in the TEM image.

In order to further analyze the changes in the oxidation—reduction properties of the catalysts before and after the reaction with soot particles, XPS tests were carried out on the catalysts Au/Fe$_2$O$_3$ and Au/Fe$_3$O$_4$ before and after the reaction. Due to the low content of Au NPs in the catalyst, XPS did not detect it. Fe 2p and O 1s photoelectron spectroscopy of the catalysts were mainly tested.
The Fe 2p energy spectrum of the catalysts before and after the reaction is shown in Figure 8. Au/Fe$_2$O$_3$ and Au/Fe$_3$O$_4$ have an obvious accompanying peak near 719 eV, indicating the presence of Fe$^{3+}$ on the catalyst surface. Both Fe 2p$_{3/2}$ (near 711 eV) and Fe 2p$_{1/2}$ (near 724 eV) belong to the characteristic peak of Fe$^{3+}$, and the position of the accompanying peak is 8 eV larger than the peak of Fe 2p$_{3/2}$. The peaks that occur near a binding energy (BE) of 709 eV are generally attributed to the ferric divalent Fe$^{2+}$ in the catalyst. As can be seen from the figure, the characteristic peak intensity of Fe$^{2+}$ is small, indicating that there is only a small part of ferric iron in the catalyst, and the iron mainly exists in the form of trivalent.

As can be seen from the XPS spectrum of Fe 2p, the characteristic peak intensity and area of the catalyst after the reaction were smaller than that before the reaction, indicating that the content of ferric iron on the surface of the catalyst decreased with the progress of the reaction, which would lead to the gradual decrease of the catalyst activity.

The O 1s energy spectra of the catalyst Au/Fe$_2$O$_3$ and Au/Fe$_3$O$_4$ before and after the reaction are shown in Figure 9. The BEs of O 1s are mainly located near 529.3, 531.0, and 532.3 eV. The peaks with BEs between 529.0 and 530.4 eV are mainly attributable to the lattice oxygen (O$_{\text{lat}}$; O$^{2-}$) on the catalyst surface. The peaks at 531.0−531.4 eV are attributed to the adsorbed oxygen (O$_{\text{ads}}$; O$_2^-$ and O$_3^-$) on the catalyst surface, while the peaks near 532.2−532.5 eV are the carbonate species or adsorbed water on the catalyst surface. In general, the molar ratio of O$_{\text{ads}}$ to O$_{\text{lat}}$ is used to measure the reactive oxygen content on the catalyst surface. The larger the ratio, the more active the oxygen components. Compared with the catalyst Au/Fe$_3$O$_4$, Au/Fe$_2$O$_3$ has a larger molar ratio of adsorbed oxygen to lattice oxygen. In the catalyst activity experiments, it has been proved that Au/Fe$_2$O$_3$ has a better catalytic effect on soot oxidation. In addition, after the reaction of Au/Fe$_2$O$_3$, carbonate species appeared on the surface, which may be due to the reaction of iron with carbon in the soot particles to form salts.

It can also be seen from the XPS spectrum of O 1s that the characteristic peak intensity and area of the catalyst are smaller than before the reaction, indicating that the active oxygen components on the surface of the catalyst gradually decreased after the reaction with soot particles.

The H$_2$-TPR profiles of the catalysts Au/Fe$_2$O$_3$ and Au/Fe$_3$O$_4$ before and after the reaction with soot particles are shown in Figure 10. Au/Fe$_2$O$_3$ and Au/Fe$_3$O$_4$ have obvious reduction peaks at 171 and 220 °C before they react with soot particles. According to the literature, the peak at low temperatures is mainly due to the reduction of cationic Au with different valence states. In addition, the preparation method makes it easier to form Au$^{3+}$ species instead of Au$^{0}$. The reduction peaks of bulk gold oxide have been reported to appear at about 195 °C. It can be seen from Figure 8 that the first peak is at 165−198 °C, indicating that the reaction between Au and iron oxide promoted its reduction. The reduction reaction in the range of 250−380 °C is related to the a-Fe$_2$O$_3$/Fe$_3$O$_4$/FeO multiple reduction process. The reduction peaks of the supports Fe$_2$O$_3$ and Fe$_3$O$_4$ are generally located near 440 °C. After loading Au NPs, the position of the reduction peak was advanced, indicating that Au promoted the
reduction of iron ions to a lower temperature, which was beneficial to improve the oxidation performance of iron-based oxides.

After the catalyst reacted with soot particles, the low-temperature reduction peaks become less intense, which suggests that the reaction between the catalyst and the soot decreased the amount of weakly bounded oxygen. The position of the second main reduction peak shifts backward and the area of the peak decreases, indicating that the oxidation components of iron oxides weakened after reacting with soot particles. For the catalyst Au/Fe3O4, its main reduction peak temperature shifts backward from 281 to 309 °C after reacting with soot. For Au/Fe2O3, the reduction peak shifts from 344 to 348 °C. Because the stepwise reduction of iron oxides is as follows: Fe2O3 → Fe3O4 → FeO, in this temperature range, the shift of the peak position after the reaction was mainly caused by the reduction of Fe^3+ and it was consistent with the XPS results.

3. CONCLUSIONS

A series of Au/Oxide catalysts were synthesized by the deposition–precipitation method, and their catalytic properties in soot oxidation processes were examined. These transition-metal oxides exhibit excellent soot oxidation activity, especially after loading Au NPs. The catalytic behavior of the catalysts Au/Fe2O3 and Au/Fe3O4 before and after the reaction with soot particles was empirically studied. TEM and XRD characterization performed over the Au/Fe2O3 catalyst revealed the presence of highly dispersed Au NPs with a size increase from 11 nm in the fresh sample to 17.5 nm in the spent one. Compared with Au/Fe3O4, Au/Fe2O3 had a better soot catalytic activity mainly due to the larger molar ratio of adsorbed oxygen to lattice oxygen and iron basically in the trivalent state. The H2-TPR measurement results showed that the strong metal–support interaction between Au NPs and the iron-based oxide could promote the reduction of iron ions and improve its soot oxidation performance. After Au/Fe2O3 and Au/Fe3O4 reacted with soot particles, the catalysts became more concentrated and the iron in the catalyst was converted from Fe^3+ to Fe^2+. The content of ferric iron and reactive oxygen components on the surface of the catalyst decreases gradually with the progress of the catalytic reaction, resulting in a decrease in catalyst activity.

4. EXPERIMENTAL SECTION

4.1. Catalyst Preparation. The catalysts of transition-metal oxides supported Au NPs were prepared by the deposition–precipitation method. This method can attach all active components to the metal oxide, increase the number of active components to the metal oxide, and improve its soot oxidation activity. After Au/Fe2O3 and Au/Fe3O4 before and after the reaction with soot particles were further observed by means of HRTEM, XRD, XPS, and TPR.

HRTEM was used to observe the changes in the morphology and structure of the catalyst before and after the reaction with soot particles, and the average particle size of the gold NPs was calculated. The instrument model used in the experiment was JEM-2011. Before the sample was tested using TEM, the catalyst powder was first dispersed in an acetone solution, followed by ultrasonic treatment for 10 min. Finally, the dispersed suspension was dropped on the ultra-thin copper network for test and analysis.

A high-power powder X-ray diffractometer was used to test and analyze the phase structure of the catalyst and compare the structural changes of the catalyst before and after the reaction with soot particles. The diffractometer used in the experiment was TTRAX-III type produced by Tokyo Rigaku Company. The target source used in the test was the Cu Ka target, the 2θ scanning angle of the catalyst sample was 20–80°, and the scanning rate was 4° min⁻¹.

XPS was used to test and analyze the surface element composition and the main valence state of the catalysts and to compare the change of the valence state of the catalyst before and after the reaction with soot particles. The optoelectronic spectrometer used in the experiment was the model PHI-1600 produced by Elmer Company using Al Kα (hv = 1486.6 eV) as the X-ray source with a voltage of 13 kV and a power of 400 W. A carbon C 1s peak (BE = 284.6 eV) was used to calibrate the X-ray source with a voltage of 13 kV and a power of 400 W. The target source used in the test was the Cu Ka target, the 2θ scanning angle of the catalyst sample was 20–80°, and the scanning rate was 4° min⁻¹.

Temperature-programmed reduction with H2 measurement (H2-TPR) was performed in a conventional flow apparatus. The sample (100 mg) was pretreated by calcination with N2 at 300 °C for 1 h and then cooled to room temperature. The gas flow of 10% H2/N2 (30 mL min⁻¹) passed the sample in the range of RT to 600 °C at a heating rate of 10 °C min⁻¹.

4.3. Catalyst Activity Evaluation. In order to ensure the consistency of the performance of soot samples, the carbon black Printex-U was used in these experiments to replace the soot particles, which is widely used as a model substance. The average particle size of soot particles was 25 nm, the volatile content was 5% at 950 °C, and the ash content was less than 0.02%. The catalysts (100 mg) were mixed with soot particles (20 mg) in an agate mortar to the close contact mode by using a spoon. The catalyst activity experiments were carried out on a thermogravimetric analyzer. The mixed samples of the catalyst and soot particles were placed on an aluminum crucible,
heating from room temperature to 800 °C at 10 °C/min. The sample carrier gas was air at a flow rate of 75.0 mL/min, and the equilibrium gas was nitrogen at a flow rate of 25.0 mL/min.

In this paper, the mass change of soot particles before and after the reaction was measured, and the conversion rate of soot particles was calculated, so as to evaluate the catalytic activity of the catalyst. The calculation formula of the conversion rate of soot particles is as follows

\[ \eta = \frac{[\text{Soot}]_B - [\text{Soot}]_E}{[\text{Soot}]_B} \times 100\% \]  

(1–1)

Among them, \([\text{Soot}]_B\) represents the quality of soot particles before reaction and \([\text{Soot}]_E\) represents the quality of soot particles after reaction. In this paper, \(T_{10}, T_{50}\), and \(T_{90}\) were used to represent the corresponding temperatures when the conversion rates of soot particles were 10, 50, and 90%, respectively. In addition, \(T_m\) was used to represent the characteristic temperature corresponding to the maximum conversion rate of soot particles. When the conversion rate is the same, the smaller the corresponding temperature value, the better the catalytic activity.

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**Notes**

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