

Highly active catalysts of iron-based materials with Au nanoparticles for soot oxidation

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Abstract: Gold nanoparticles supported on transition metal oxide catalysts have been prepared by deposition-precipitation. Their catalytic activity with or without Au doped has been tested for soot oxidation. Au improves the catalytic activity of transition metal oxide for the oxidation of soot particles. Under the catalysis of Au/Co₃O₄, the initial oxidation temperature of soot is 354 °C.

1 Introduction

Soot is an important part of particulate matter in the air, which not only reduces the air quality, but also endangers the health of the human body^[1]. Soot particles are mainly composed of amorphous carbon and PAHs, which are the main reason for toxicity^[2]. Vehicle exhaust emission is a major source of soot particles, moreover diesel engines account for a large proportion. At present, the most common technique for the treatment of exhaust pollution is adding a particulate filter (DPF) to capture and oxidize soot particles^[3-4]. DPF is the most widely used and effective after-treatment technique so far^[5-6]. However, this technology still has several disadvantages such as the deposition of soot particles in the filter tunnel to increase the exhaust back pressure, reducing diesel engine's performance^[7].

In recent years, it has been found that gold nanoparticles have high catalytic activity in the purification of hydrogen, elimination of nitric oxide, and oxidation of toluene and formaldehyde. Three-dimensional structure of La-Mn perovskite loads Au-Pd catalyst produced by Wang et al. can achieve the catalytic oxidation of methane at 382 °C^[8]. The contact between Au nanoparticles and CeO₂ nanocrystals affects the catalytic activity, and the attachment of Au on the surface of cubic crystals has higher CO oxidation activity than octahedron^[9]. Moreover, it has an excellent effect on the catalytic combustion of soot particles. Craenenbroeck et al. studied the catalytic activity of Au-VOx/TiO₂ with different vanadium loadings on soot particles of diesel engines. The ignition temperature of soot is 361 °C and the peak burning temperature is 419 °C^[10].

In this paper, the transition metal oxide doped noble metal Au nanoparticles were used to study their catalytic activity on soot particles, and the properties of oxidized soot particles were compared with and without Au nanoparticles.

2 Experimental

2.1 Catalyst preparation

In this paper, a deposition-precipitation method is used to prepare a transition metal oxide catalyst supporting gold nanoparticles. The method increases the active component due to attaching the active component to the metal oxide and distributes size of Au nanoparticles evenly.

Here is an example of preparing Au/Fe₂O₃: first, the gold chloride hydrate was dissolved in deionized water to prepare a HAuCl₄ aqueous solution with concentration of 10 g/L; weigh a certain quality of nano-Fe₂O₃ powder into HAuCl₄ aqueous solution. After ultrasonic dispersion for 7 minutes, the nano-Fe₂O₃ powder was placed for 10 minutes to dissolve in the prepared HAuCl₄ aqueous solution; a certain mass of urea (CO(NH₂)₂) was weighed and added into the mixture to form a suspension, the suspension was stirred by magnetic force for 3 h at 80 °C and stood for 13 h at room temperature; then put the sample into a drying chamber for 6 h at 80 °C; finally, the dried sample is placed in a tube furnace heated to 300 °C for 1 h. And then the sample is taken out and ground to obtain the iron oxide catalyst Au/Fe₂O₃ loaded with gold nanoparticles after natural cooling. In the same step, Fe₃O₄, Co₃O₄, NiO and CeO₂ were used as oxide-loaded Au nanoparticles to obtain Au/Fe₃O₄, Au/Co₃O₄, Au/NiO and Au/CeO₂ complex catalysts.

2.2 Catalyst activity tests

Carbon black Printex-U were used to replace the soot particles in the automobile exhaust in order to ensure the consistency of the performance of the soot samples. The average particle size was 25 nm, the content of volatile was 5% at 950 °C and the ash content was less than 0.02%. In the close contact model, the specific experimental steps

are: weigh 20 mg of soot particles and 100 mg of catalyst in a mass ratio of 1:5, mix them with each other, and then grind them thoroughly in a mortar for 15 minutes. Finally got the samples in close contact for thermal analysis experiments.

The experiment on evaluation of the catalytic activity for soot particles was carried out on a thermogravimetric analyzer whose model is TGA-Q500 V3.17 Build 265. The mixed sample of catalyst and soot particles was placed on the aluminum crucible and heated from room temperature to 800°C with the ramp rate of 10 °C/min.

In this paper, the conversion of soot particles was calculated by measuring the change of mass before and after the reaction with soot particles to evaluate the catalytic activity of the catalyst on soot particles. In this paper, T_{10} and T_{90} are used to express the corresponding temperatures of soot particle conversion at 10% and 90%, respectively. The smaller the value, the catalyst will have a better catalytic effect on soot particles when the conversion rate is same.

3 Results and discussion

3.1 Catalytic activity of transition metal oxides for soot oxidation.

The catalytic performance of the variable transition metal oxide catalyst for soot particles is shown in table 1. It can be known from the table that pure soot has almost no conversion below 550 °C, 592 °C is the initial oxidation temperature T_{10} , and the complete conversion is achieved near 700 °C. Five kinds of transition metal oxide catalysts have been studied in this paper such as Fe_2O_3 , Fe_3O_4 , Co_3O_4 , NiO and CeO_2 which make the soot particles start to transform at 400-450 °C, and 450-600 °C is the main temperature range for the oxidation reaction of soot particles. At last, soot particles are almost oxidized completely before 600 °C. It can be seen that the valence changing transition metal oxide can reduce the oxidation temperature of soot particles effectively and the complete conversion temperature is reduced by at least 100 °C. Fe_2O_3 is the best catalyst for soot oxidation and its initial oxidation temperature is 450 °C. The order of activity of these five variable-value transition metal oxide catalysts for catalytic oxidation of soot particles is: $\text{Fe}_2\text{O}_3 > \text{Co}_3\text{O}_4 > \text{Fe}_3\text{O}_4 > \text{NiO} > \text{CeO}_2$, Fe_2O_3 and Fe_3O_4 have good catalytic oxidation activity.

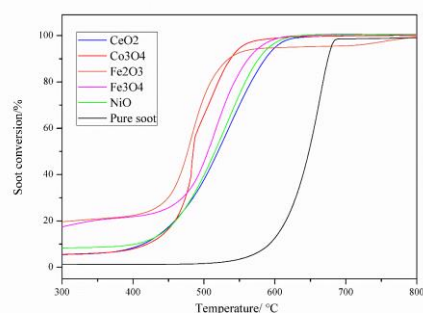


Fig.1. Catalytic performance of transition metal oxide catalyst for soot oxidation.

From Figure 1, we can find that the catalysts Fe_2O_3 and Fe_3O_4 have nearly 20% conversion efficiency for soot particles before 420 °C, but the conversion curve is relatively smooth before 420 °C. For $\text{Au}/\text{Fe}_2\text{O}_3$, the conversion curve starts to steep at 445 °C and the soot conversion rate increases gradually; the conversion rate of soot particles starts slowly at 471 °C for the catalyst $\text{Au}/\text{Fe}_3\text{O}_4$. Before 420 °C, the possibility of the conversion of soot particles is relatively small. The characteristic temperatures T_{10} and T_{90} of catalysts for soot particle reaction are summarized in table 1 according to the soot particle conversion rate curve shown in Figure 1 in order to characterize the catalytic activity of these five catalysts for soot particles more intuitively and accurately.

Table1. Characteristic temperature of catalytic reaction of soot particles with different catalysts

catalysts	characteristic temperature (°C)	
	T_{10}	T_{90}
CeO_2	413	586
Co_3O_4	420	537
Fe_2O_3	87	535
Fe_3O_4	100	562
NiO	402	577
Soot	592	674

4 Catalytic activity of Au/MOx for soot oxidation.

The conversion characteristic temperature of the soot is summarized and shown in Table 2. It can be seen from Fig. 2 that Au-loaded transition metal oxide catalyst can further reduce the oxidation temperature of the soot particles, but the effects of different supported catalysts for reducing the soot oxidation temperature are different. In general, the initial oxidation temperature of catalytic oxidation of soot particles by Au/CeO_2 , $\text{Au}/\text{Co}_3\text{O}_4$, $\text{Au}/\text{Fe}_2\text{O}_3$, $\text{Au}/\text{Fe}_3\text{O}_4$ and Au/NiO are 350-450 °C, and the main reaction temperature range is 400-600°C, the soot particles are burned out basically after 600°C.

Comparing Fig. 1 and Fig. 2, it can be found that the catalytic effect of the same transition metal oxide carrier changes after loading gold. For example, after the loading of Au, the initial oxidation temperature of Co_3O_4 catalyst decreases from 420 °C to 354 °C, and its burnout temperature decreased from 537 °C to 491 °C. The catalytic activity of Co_3O_4 was increased after loading Au. However, the catalytic activity of CeO_2 decreased after loading Au, the initial oxidation temperature of soot increased from 413 °C to 430 °C, the burnout temperature increased from 586 °C to 616 °C. For the catalysts Fe_2O_3 , Fe_3O_4 and NiO loaded with Au, the starting temperature, and burnout temperature of their catalytic oxidation of soot particles decreased, which means that Au improves their catalytic oxidation activity of soot particles. The order of activity of Au-doped transition metal oxides for catalytic oxidation of soot particles is: $\text{Au}/\text{Co}_3\text{O}_4 > \text{Au}/\text{Fe}_2\text{O}_3 >$

$\text{Au/Fe}_3\text{O}_4 > \text{Au/NiO} > \text{Au/CeO}_2$. $\text{Au/Fe}_2\text{O}_3$ and $\text{Au/Fe}_3\text{O}_4$ have good catalytic oxidation activity after the Au-based catalyst is loaded with Au.

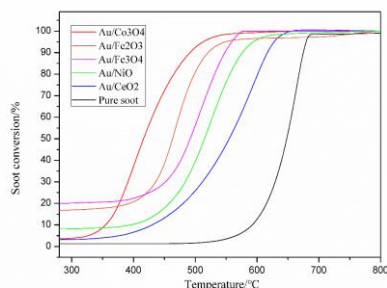


Fig.2. Conversion efficiency of catalytic oxidation of Au/MOx catalysts for soot particles

It can be seen from Fig. 2 that the catalysts $\text{Au/Fe}_2\text{O}_3$ and $\text{Au/Fe}_3\text{O}_4$ have nearly 20% conversion efficiency to soot particles before 400 °C, but the conversion curve has been relatively smooth. For $\text{Au/Fe}_2\text{O}_3$, the conversion rate curve starts to steepen and the soot conversion rate rises gradually. For catalysts $\text{Au/Fe}_2\text{O}_3$ and $\text{Au/Fe}_3\text{O}_4$, the possibility of catalytic oxidation of soot particles before 400 °C is very small, so we believe that nearly 20% conversion efficiency of soot particles is mainly due to the physical reaction between soot particles and iron-based catalysts, and the mechanism needs further experimental research.

Table2. Characteristic temperature of catalytic oxidation of Au/Oxide catalyst in close contact with soot (Oxide = Co_3O_4 , Fe_2O_3 , Fe_3O_4 , NiO, CeO_2)

catalysts	characteristic temperature (°C)	
	T ₁₀	T ₉₀
Au/ CeO_2	430	616
Au/ Co_3O_4	354	491
Au/ Fe_2O_3	73	520
Au/ Fe_3O_4	50	548
Au/NiO	395	576

5 Conclusion

Transition metal oxide catalyst without Au loading has good catalytic oxidation performance for soot particles.

Fe_2O_3 reduces the complete conversion temperature of soot particles by 139 °C, and the maximum burning rate corresponds to a characteristic temperature decrease by 170 °C. The catalytic initiation temperature and burnout temperature of the soot particles are further decreased after loading Au. Among these transition metal oxide, Co_3O_4 with Au nanoparticles has best catalytic activity, and its initial oxidation temperature is 354 °C. Gold nanoparticles increase the activity of the catalyst for the catalytic oxidation of soot particles.

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