Study of perovskite-type oxides and their supported Ag derivatives for catalytic oxidation of diesel soot

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Abstract: A series of perovskite-type oxides and derived Ag catalysts were prepared, and characterized by N₂-adsorption, X-ray diffraction and X-ray photoelectron spectroscopy. The influences of pretreatment and Ag loading on catalytic activity for diesel soot oxidation were also investigated. Prereduction resulted in a decrease in catalytic activity. An increase in activity with Ag addition was observed, especially with more than 5% Ag loading. This catalyst could be a promising candidate for the catalytic elimination of diesel soot.

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Keywords: perovskite-type catalysts; supported Ag catalyst; catalytic oxidation; diesel soot

1 INTRODUCTION

Emission control from diesel vehicles is a challenging issue. Although three-way catalytic converters for gasoline vehicles have been widely used commercially, their counterparts for diesel vehicles are not yet ready. Soot particles from diesel exhaust are characterized by their small size, more than 70% of which are smaller than 0.3 µm. Soot particulates can penetrate into the lungs and they can be a serious health hazard because of the presence of adsorbed hydrocarbons on their surfaces.¹

Soot emission from diesel engines can be reduced in various ways, such as by the application of new fuel additives, modifying the structure of diesel engines, and the installation of an exhaust-treatment system. Collection of soot particles in a monolithic filter in combination with simultaneous oxidation seems to be the best option to minimize contamination of the environment.² The following types of catalysts have been tested for the removal of diesel soot: (i) noble and base transition metals;^{3–5} (ii) oxides and other salts of base transition metals;^{4,6,7} and (iii) compounds of alkali metals.⁸ Application of noble metal catalysts (Pd, Pt, Rh) is not practical due to their high costs and their being prone to poisoning. Cu–K–V–Cl and Cu–K–Mo–Cl catalysts are thought to be the most active of these types. However, during the course of soot oxidation catalyzed by copper chlorides, C–Cl bonds might be formed, and in the presence of oxygen very toxic compounds such as chlorobenzenes and chlorophenols can be produced. For this reason, they

are less attractive for practical applications. Recently, perovskite-type oxides were also reported for the catalytic removal of diesel soot. Relatively good initial catalytic activities were found, but relatively little was understood about the factors influencing their catalytic performance.

Generally, perovskite-type oxide catalysts (general formula: ABO₃) are often used to explore the relationship between the chemical characteristics of the solid and catalytic behavior. Owing to their particular structure, it is possible to produce or suppress oxygen vacancies on the catalyst surface through partial replacement of A or B metallic ions in the lattice. These catalysts are well known for their good performance for the oxidation of CO and hydrocarbons, and were proposed as substitutes for noble metals in automotive exhaust catalysts.⁹

In this work, a series of perovskite-type oxides and Ag-doped catalysts were prepared by co-precipitation methods. The influences of pretreatment procedure and silver loading on catalytic behavior were studied in detail. It was hoped that the results might be useful for the development of catalytic filters of diesel soot.

2 EXPERIMENTAL

2.1 Catalyst preparation

Perovskite-type oxide La_{0.6}Ce_{0.4}Co_{1-x}M_xO₃ (M = Fe, Ni, Cu) catalysts were prepared by co-precipitation. La(NO₃)₃, Ce(NO₃)₃, Co(NO₃)₂, Fe(NO₃)₃, Ni(NO₃)₂, Cu(NO₃)₂ (all in AR grade purity), in

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calculated amounts, were mixed thoroughly, and the mixed solution was then titrated with sodium carbonate solution. The solution pH was maintained at 10. The precipitate was washed with de-ionized water, dried at 120 °C for 4 h, and then calcined at 900 °C for 2 h. Catalysts with a perovskite-type structure were thus obtained. Here-in-after $\text{La}_{0.6}\text{Ce}_{0.4}\text{Co}_{1-x}\text{M}_x\text{O}_3$ (M=Fe, Ni, Cu) catalysts will be indicated as CoM (M=Fe, Ni, Cu).

Ag-doped perovskite-type catalysts were prepared by impregnating each of the host catalysts with an aqueous solution containing a desired amount of AgNO_3 (AR grade), followed by drying at 120 °C for 2 h and calcining at 500 °C for 4 h in air. All catalyst compositions are expressed as weight percentages.

2.2 Evaluation of catalyst activity

Evaluation of catalyst activity was performed in a fixed-bed quartz reactor by feeding a gas mixture of O_2 (10%) and N_2 (90%) at $100\text{ cm}^3\text{ min}^{-1}$. The catalyst and the soot in a 10:1 weight ratio were well mixed by shaking in a bottle for more than 20 min. The contact between catalyst and soot after mixing was 'loose',^{10,11} which is closer to the practical case. Then, 0.22 g of this catalyst/soot mixture were then placed in a quartz-tube reactor. The temperature was raised at $3\text{ }^\circ\text{C min}^{-1}$ from 200 °C to 650 °C. The analysis of outlet mixtures was carried out by using an on-line gas chromatograph (SQ-206) equipped with a thermal conductivity detector. A column containing spherical carbon was used to separate CO and CO_2 . As the temperature increased more and more CO_2 was produced. With time, the concentration of CO_2 decreases as the soot burnt out and the conversion reached 100%. Activity is expressed as the temperatures, T_{50} and T_{90} (°C), at which the conversion of the initial diesel soot reaches 50 and 90% respectively in a temperature programmed oxidation reactor.

Catalysts were preoxidized by feeding O_2 at $50\text{ cm}^3\text{ min}^{-1}$ at 700 °C for 2 h, then cooled. With regard to prereduction of a perovskite-type oxide and its supported Ag derivatives, similar steps were adopted but H_2 was fed at 350 °C instead.

Diesel soot particulate was collected from the tail pipe of the Chinese-made model 195T diesel engine. The amount of adsorbed hydrocarbons was less than 1%. The carbon and hydrogen contents were determined by elemental analysis using CHN CORDER MT-5 equipment (Yanaco), and the results were 89.04% and 1.15% respectively.

2.3 Catalyst characterization

BET surface areas were measured by N_2 adsorption using a ST-03 system. X-ray diffraction (XRD) measurements were carried out on a Rigaku D/Max-Rc X-ray Diffractometer with Cu K_α radiation. Photoelectron spectra (XPS) were acquired with a VG Scientic ESCALAB 220i-XL spectrometer equipped with a hemispherical electron analyzer and Al K_α X-ray source. The powder samples were pressed

into small Inox cylinders and then mounted on a sample rod, placed in a pretreatment chamber and outgassed at 250 °C and 10^{-5} Torr for 2 h prior to being transferred to the analysis chamber. The base pressure in the ion-pumped analysis chamber was maintained below 5×10^{-9} Torr. A least-square routine of peak fitting was used for the analysis of XPS spectra. The relative concentrations of chemical elements were calculated by the usual quantification routine, including Wagner's energy dependence of attenuation length and a standard set of the VG Escalab elemental sensitivity factors. The C 1s peak was used as a reference.

3 RESULTS AND DISCUSSION

3.1 The influence of pretreatment on the activities of catalysts for diesel soot oxidation

The activities of catalysts with or without pretreatment were investigated, and the results are shown in Table 1. The temperatures T_{50} and T_{90} of soot oxidation without catalyst are centered at 570 °C and 605 °C, respectively. It can be seen from Table 1 that T_{50} and T_{90} decreased significantly in the presence of a perovskite catalyst. Catalytic oxidation of diesel soot can be carried out at a lower temperature than the thermal oxidation. The CO selectivity was almost zero. The catalyst CoNi has the highest activity, whereas the catalyst CoCu has the lowest activity. Törnåcrona¹² reported that for catalysts with rare-earth metals and transition metals as promoters, prereduction might alter the lattice oxygen contents and generate oxygen vacancies, which promote their catalytic activities. With the CoM (M=Fe, Ni, Cu) catalysts used in this study, prereduction leads to an apparent decrease in their catalytic activities, contrary to Törnåcrona's observation.

3.2 Catalytic activities of perovskite-type oxide supported Ag catalysts

Figure 1 shows the relationship between the activity of catalyst Ag/Co and the Ag loading. It is evident that activity is improved by adding 1% Ag, reaching a maximum at 5% Ag. The activity of the Ag/Co catalyst remained almost unchanged when the Ag loading increased from 5% to 15%. Therefore, for economic

Table 1. Influence of pretreatment on the activities of catalysts for diesel soot oxidation

Catalyst	Reaction temperature of soot conversion (°C)			
	without pretreatment		with prereduction	
	T_{50}	T_{90}	T_{50}	T_{90}
$\text{La}_{0.6}\text{Ce}_{0.4}\text{CoO}_3$	436	509	479	527
$\text{La}_{0.6}\text{Ce}_{0.4}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_3$	421	512	476	529
$\text{La}_{0.6}\text{Ce}_{0.4}\text{Cu}_{0.5}\text{Co}_{0.5}\text{O}_3$	454	524	484	535
$\text{La}_{0.6}\text{Ce}_{0.4}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_3$	433	520	478	525

Figure 1. Activities of various Ag/La_{0.6}Ce_{0.4}CoO₃ catalysts for soot oxidation at different reaction temperatures.

reasons, the optimal Ag loading of this kind of catalyst is 5%.

The activity of the CoM (M=Fe, Ni, Cu) catalyst is still relatively low, but is improved by adding Ag. The difference due to changing the nature of M is small. The results for the 5% Ag/CoM (M=Fe, Ni, Cu) catalysts are shown in Fig 2 and Table 2. The catalyst 5% Ag/Co has the highest activity. In addition, activity is significantly decreased by prereduction.

It can be seen from Table 3 that the activities of the 5% Ag/CoM (M=Fe, Ni, Cu) catalysts were also markedly decreased due to preoxidation at 700 °C. This suggests that the stability of a perovskite-type oxide supported Ag catalyst is relatively low.

3.3 Characterization of perovskite-type oxide supported Ag catalysts

From Table 4, we can see that BET surface area of a perovskite-type oxide and its supported Ag catalyst is very low. It is similar to the observation of Taguchi *et al.*¹³ Calcination at high temperatures is necessary to obtain a perovskite-type oxide catalyst, but such treatment often results in a dramatic decrease in the surface area.

Figure 3 shows the XRD patterns of the catalysts Co and 5% Ag/Co. Their diffraction peaks are similar to those of LaCoO₃, which is typical of a perovskite-type

Figure 2. Activities of 5% Ag/La_{0.6}Ce_{0.4}Co_{1-x}M_xO₃ (M=Fe, Ni, Cu) catalysts for soot oxidation at different reaction temperatures.

Table 2. Catalytic activities of perovskite-type oxide supported Ag catalysts

Catalyst	Reaction temperature of soot conversion (°C)	
	<i>T</i> ₅₀	<i>T</i> ₉₀
1% Ag/La _{0.6} Ce _{0.4} CoO ₃	420	502
5% Ag/La _{0.6} Ce _{0.4} CoO ₃	400	456
10% Ag/La _{0.6} Ce _{0.4} CoO ₃	398	452
15% Ag/La _{0.6} Ce _{0.4} CoO ₃	404	455
5% Ag/La _{0.6} Ce _{0.4} Fe _{0.5} Co _{0.5} O ₃	402	459
5% Ag/La _{0.6} Ce _{0.4} Ni _{0.5} Co _{0.5} O ₃	405	469
5% Ag/La _{0.6} Ce _{0.4} Cu _{0.5} Co _{0.5} O ₃	412	466
5% Ag/La _{0.6} Ce _{0.4} Ni _{0.5} Co _{0.5} O ₃ (prereduced)	493	544

Table 3. Influence of preoxidation on the activities of perovskite-type oxide supported Ag catalysts for diesel soot oxidation

Catalyst	Reaction temperature of soot conversion (°C) with preoxidation	
	<i>T</i> ₅₀	<i>T</i> ₉₀
5% Ag/La _{0.6} Ce _{0.4} CoO ₃	443	511
5% Ag/La _{0.6} Ce _{0.4} Ni _{0.5} Co _{0.5} O ₃	439	504
5% Ag/La _{0.6} Ce _{0.4} Cu _{0.5} Co _{0.5} O ₃	449	507
5% Ag/La _{0.6} Ce _{0.4} Fe _{0.5} Co _{0.5} O ₃	437	502

oxide structure. In addition, diffraction peaks ascribed to CeO₂ can be observed. There is no conclusive evidence for the existence of a crystalline phase for Ag⁰ or Ag₂O in the 5% Ag/Co catalyst, this means that Ag is highly dispersed.

Surface structures of the three catalysts CoNi, 5% Ag/CoNi and 5% Ag/CoNi (pre-reduced) were analyzed by XPS and the results are shown in Table 5. The C1s level shows three peaks at 284.6 eV and 285.4 eV (carbon contamination) and 288.6 eV (due to the presence of surface carbonates).¹⁴ The O1s signal was deconvoluted in three peaks: (I) 527.5–529.5 eV, (II) 530–531.5 eV and (III) above 532 eV. Peak (I) corresponds to lattice oxygen (O²⁻), whereas peak (II) is assigned to both hydroxide (OH⁻) and carbonate(CO₃²⁻) species, peak (III) is associated with adsorbed molecular water.^{15–18} The binding energy (BE) value of Ag (3d_{5/2}) before reduction is 367.4 eV,

Table 4. The specific surface area of different catalysts

Catalyst	Specific surface area (m ² g ⁻¹)
La _{0.6} Ce _{0.4} CoO ₃	3.7
La _{0.6} Ce _{0.4} Ni _{0.5} Co _{0.5} O ₃	3.1
La _{0.6} Ce _{0.4} Fe _{0.5} Co _{0.5} O ₃	7.4
La _{0.6} Ce _{0.4} Cu _{0.5} Co _{0.5} O ₃	4.5
5% Ag/La _{0.6} Ce _{0.4} CoO ₃	1.8
5% Ag/La _{0.6} Ce _{0.4} Ni _{0.5} Co _{0.5} O ₃	1.2
5% Ag/La _{0.6} Ce _{0.4} Fe _{0.5} Co _{0.5} O ₃	3.2
5% Ag/La _{0.6} Ce _{0.4} Cu _{0.5} Co _{0.5} O ₃	3.5

Figure 3. XRD patterns of $\text{La}_{0.6}\text{Ce}_{0.4}\text{CoO}_3$ (a) and 5% Ag/ $\text{La}_{0.6}\text{Ce}_{0.4}\text{CoO}_3$ (b) catalysts.

which was consistent with that assigned to Ag^+ ($3d_{5/2}$) in the literature.^{19,20} There is no evidence for the existence of Ag^0 ($\text{BE}=368.2\text{ eV}$). We found that the Ag surface species in CoM ($\text{M}=\text{Fe}, \text{Ni}, \text{Cu}$) supported Ag catalysts was Ag^+ . Perhaps some of the Ag^+ doped on to the surface of CoM partially occupied the sites of La^{3+} due to their similar ionic radii, and thus became stabilized by the perovskite lattice, which would contribute to the prevention of silver aggregation on the surface and enhance the stability of the catalyst. At the same time, Ag^+ also induces some Schottky defects in the form of anionic vacancies, which would be favorable for the adsorption–activation of oxygen on the functioning catalyst and the transport of the lattice and surface oxygen species. All these factors would contribute to the improvement of the activities of these perovskite-type catalysts. Thermodynamically, Ag^+ will be reduced and become metallic Ag in H_2 at 350°C , however, in the case of the 5% Ag/CoNi catalyst, the metallic Ag pattern did not appear, judging from the BE value of Ag ($3d_{5/2}$) (367.6 eV) after reduction.

4 CONCLUSION

The catalytic oxidations of diesel soot over perovskite-

type oxides and derived Ag catalysts were investigated. The activities of the catalysts were decreased with prereduction treatment, while they were pronouncedly improved by adding Ag. The optimal Ag loading is about 5%. Judging from the XRD characterization of Co and 5% Ag/Co catalysts, and also from the XPS result of the 5% Ag/CoNi catalyst, we can conclude that highly dispersed Ag^+ played an important role in improving the catalytic activities of these perovskite-type supported Ag catalysts. Prereduction results in a decrease of the activities of 5% Ag/CoM catalysts.

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Table 5. Binding energy (eV) of surface elements and surface chemical composition of different catalysts

Catalyst	BE (eV)					Content (%)				
	La ($3d_{5/2}$)	Ce ($3d_{5/2}$)	Co ($2p_{3/2}$)	O (1s)	Ag ($3d_{5/2}$)	La	Ce	Co	O	Ag
$\text{La}_{0.6}\text{Ce}_{0.4}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_3$	833.7	881.6	779.7	528.4 530.5 531.8	–	12.7	5.9	4.0	77.4	–
5% Ag/ $\text{La}_{0.6}\text{Ce}_{0.4}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_3$	833.4	881.6	779.3	528.3 530.6 533.3	367.4	10.2	4.6	5.4	76.1	3.7
5% Ag/ $\text{La}_{0.6}\text{Ce}_{0.4}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_3$ (prereduced)	833.8	881.6	779.5	528.2 530.4 532.3	367.6	2.1	1.5	2.6	92.8	1.0

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