available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Catalytic oxidation of diesel soot particulates over Ag/LaCoO₃ perovskite oxides in air and NO_x

Qi Fan, Shuai Zhang, Liying Sun, Xue Dong, Lancui Zhang, Wenjuan Shan*, Zaiming Zhu#

Institute of Chemistry for Functionalized Materials, College of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, 116029, Liaoning, China

ARTICLE INFO

Article history:

Received 10 October 2015

Accepted 29 October 2015

Published 5 March 2016

Keywords:

Soot combustion

NO_x

Silver

Perovskite

Thermal stability

ABSTRACT

Ag/LaCoO₃ perovskite catalysts for soot combustion were prepared by the impregnation method. The structure and physicochemical properties of the catalysts were characterized using X-ray diffraction, N₂ adsorption-desorption, H₂ temperature-programmed reduction, soot temperature-programmed reduction, and X-ray photoelectron spectroscopy. The catalytic activity of the catalysts for soot oxidation was tested by temperature-programmed oxidation in air and in a NO_x atmosphere. Metallic Ag particles were the main Ag species. Part of the Ag migrated from the surface to the lattice of the LaCoO₃ perovskite, to form La_{1-x}Ag_xCoO₃. This increased the amount of oxygen vacancies in the perovskite structure during thermal treatment. Compared with unmodified LaCoO₃, the maximum soot oxidation rate temperature (*T*_p) decreased by 50–70 °C in air when LaCoO₃ was partially modified by Ag, depending on the thermal treatment temperature. The *T*_p of the Ag/LaCoO₃ catalyst calcined at 400 °C in a NO_x atmosphere decreased to about 140 °C, compared with that of LaCoO₃. Ag particles and oxygen vacancies in the catalysts contributed to their high catalytic activity for soot oxidation. The stable catalytic activity of the Ag/LaCoO₃ catalyst calcined at 700 °C in a NO_x atmosphere was related to its stable structure.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Soot particles are formed as undesired by-products during combustion, and together with NO_x, CO, and unburned hydrocarbons comprise the main pollutants from diesel engines [1]. Inhaling soot particulates of size less than 2.5 μm can cause pulmonary diseases such as cancer, so soot particulates should be eliminated prior to their release into air. Diesel particulate filters (DPFs) combined with catalytic combustion technology appears to be the most practical method for eliminating soot from diesel exhaust. Soot oxidation catalysts can decrease the temperature required for DPF regeneration. Various catalysts have been used, such as metal oxides, noble metals, spinels, and

perovskite-type oxides [2–15]. Perovskite-type metal oxide catalysts have been extensively investigated and exhibit excellent catalytic performance and chemical, thermal, and structural stability [4,16]. Several studies have reported that perovskite-type oxides are effective for the simultaneous catalytic removal of NO_x and soot [4–6]. La-based perovskites have been the most extensively studied, some of which exhibit excellent performance for soot combustion and NO_x reduction. Their activity follows the trend: LaCoO₃ > LaMnO₃ > LaFeO₃ [17]. Cobalt-based perovskite catalysts doped with metal cations were recently reported for soot oxidation reactions [2–4,16]. Supported metal catalysts employing LaCoO₃ for soot removal have been rarely mentioned.

* Corresponding author. Tel: +86-411-82156852; E-mail: wjshan@dicp.ac.cn

Corresponding author. Tel: +86-411-82156852; E-mail: zhuzaiming@lnnu.edu.cn

DOI: 10.1016/S1872-2067(15)61000-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 3, March 2016

Ag-based catalysts have been used for soot oxidation because of their effective simultaneous removal of carbon particles and NO_x [5,6,16–18]. Yamazaki et al. [5] suggested that Ag is the active species for oxygen activation, even at -70°C . Adsorbed oxygen species on the Ag surface were thought to migrate to the surface of the catalyst support via the Ag/support interface, and then migrate further to the soot particles. Aneggi et al. [19,20] suggested that the catalytic activity of Ag increases when it is supported on CeO_2 and ZrO_2 , and that the active temperature for both supported catalysts was around 300°C . Ag supported on Al_2O_3 exhibits a lower activity than Ag supported on CeO_2 and ZrO_2 , regardless of the presence of Ag nanoparticles. CeO_2 and ZrO_2 are recognized oxygen storage material and oxygen anion conductor, respectively. Lattice oxygen atoms in these materials are thought to contribute to soot oxidation because of the enhanced oxygen exchange between the gas phase and solid. Selecting the appropriate catalyst support can decrease a catalyst's active temperature. Perovskites are thought to be suitable materials for soot oxidation because of their high oxygen storage capability, high lattice oxygen activity, and thermal stability.

In this study, a series of Ag/LaCoO₃ perovskite catalysts were prepared and used to remove soot particles in air and NO_x . The structure of Ag/LaCoO₃ after varying thermal treatments and the role of Ag species in soot oxidation were studied.

2. Experimental

2.1. Catalyst preparation

All chemicals were sourced from Sinopharm Chemical Reagent Co., Ltd., China. LaCoO₃ perovskite was prepared by the citric acid complex combustion method [21]. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99%), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%), and citric acid (99.5%) were dissolved in deionized water. The solution was evaporated, dried, and then calcined at 800°C for 4 h. Co_3O_4 was prepared by the same process and was calcined at 450°C for 3 h in air. LaCoO₃ catalysts containing 4.65 wt% Ag (denoted Ag/LaCoO₃) were prepared by the impregnation method (AgNO_3 , 99.8%), and calcined in air for 3 h. The samples are denoted as Ag/LaCoO₃-400, Ag/LaCoO₃-650, Ag/LaCoO₃-700, Ag/LaCoO₃-750, and Ag/LaCoO₃-800, where the suffix indicates the thermal treatment temperature ($^\circ\text{C}$).

2.2. Catalyst characterization

The catalysts were characterized by powder X-ray powder diffraction (XRD) using a D8 Advance type diffractometer (Bruker AXS LLC, Germany) with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15406\text{ nm}$). The tube pressure was 20–60 kV, tube current was 40 mA, scanning angle was 20° – 60° , and scanning rate was $2^\circ/\text{min}$.

The specific surface areas of the samples were measured by a Sorptometer Coulter SA 3100 apparatus using the Brunauer-Emmett-Teller (BET) method from N_2 adsorption-desorption isotherms at -196°C . Prior to measurement, the samples were degassed at 300°C for 3 h under vacuum.

Transmission electron microscopy (TEM) images were col-

lected using a JEOL JEM-2000EM microscope (Japan) operated at 120 kV. Samples were suspended in ethanol by ultrasonication for 5–10 min, a few droplets of which were then deposited on a microgrid carbon polymer supported on a copper grid, and allowed to dry at room temperature.

Hydrogen temperature-programmed reduction (H_2 -TPR) measurements were performed using a purpose-built apparatus. The sample (25 mg) was heated from room temperature to 910°C at a heating rate of $10^\circ\text{C}/\text{min}$, under a 5% H_2 -95% N_2 (v/v) flow (40 mL/min). H_2O produced from H_2 -TPR was adsorbed by a molecular sieve desiccant and allochroic silica gel, before the outlet reactor gas proceeded through to TCD.

The reactivity of adsorbed O_2 with soot was determined from soot-temperature-programmed reduction (soot-TPR) measurements. In these measurements, catalyst and soot (catalyst:soot mass ratio = 100:1) was placed in a quartz tube and was pretreated by heating at 300°C in He (99.999%) for 1 h to remove adsorbed CO_2 , and then cooled to room temperature. O_2 was then adsorbed by flowing 5% O_2 -95%He over the sample for 1 h, after which the sample was purged with He for 30 min. The temperature was then increased to 850°C at $10^\circ\text{C}/\text{min}$ under a He flow (50 mL/min), and the concentrations of CO_2 ($M_r/z = 44$) and CO ($M_r/z = 28$) in the effluent were continuously monitored by mass spectrometry (MKS CIRRUS 2).

X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 250Xi spectrometer with $\text{Mg } K_\alpha$ radiation ($h\nu = 1253.6\text{ eV}$). Binding energies were referenced to the C 1s peak of adventitious carbon (284.6 eV).

2.3. Catalyst activity test

The catalytic activity of samples was evaluated from temperature-programmed oxidation (TPO) measurements using Printex-U soot (Degussa) as the model reactant. This soot has a specific surface area of $100\text{ m}^2/\text{g}$, average particle size of $25 \pm 3\text{ nm}$, and composition of 92.2 wt% C, 0.6 wt% H, and 6 wt% volatiles. The soot was mixed with the catalyst at a soot:catalyst mass ratio of 20:80. The mixture was heated from 200 to 600°C at a heating rate of $1^\circ\text{C}/\text{min}$ in air or in 0.5% NO -10% O_2 -89.5% N_2 at a flow rate of 50 mL/min. Catalytic performance was indicated by the temperature corresponding to the maximum soot oxidation rate (T_p) derived from the TPO curves, soot ignition temperature (T_{10}), soot complete conversion temperature (T_{90}), and temperature window ΔT ($\Delta T = T_{90} - T_{10}$).

The catalytic stability was evaluated from 200 to 450°C . The used catalyst was mixed with 20 mg of soot again, to investigate the stability of Ag/LaCoO₃-700 in the NO - O_2 - N_2 feed gas at a flow rate of 50 mL/min.

3. Results and discussion

3.1. XRD results

XRD patterns of the Ag/LaCoO₃ perovskite catalysts calcined at different temperatures are shown in Fig. 1. All catalysts exhibit the main diffraction peaks of LaCoO₃ perovskite (JPCDS 75-0279). The diffraction peaks at 36.9° correspond to Co_3O_4

Fig. 1. XRD patterns of the Ag/LaCoO₃ catalysts. (1) Co₃O₄-450; (2) LaCoO₃-400; (3) Ag/LaCoO₃-650; (4) Ag/LaCoO₃-700; (5) Ag/LaCoO₃-750; (6) Ag/LaCoO₃-800; (7) LaCoO₃-800.

(JCPDS 72-2108) and are weaker than the diffractions of LaCoO₃ perovskite. Two weak diffraction peaks at 2θ of 38.2° and 44.4° detected in the XRD patterns of all Ag/LaCoO₃ catalysts are attributed to the (111) and (200) Bragg reflections of face-centered cubic (fcc) Ag [JCPDS 65-2871] [22,23]. The (200) Bragg reflection of body-centered cubic (bcc) Ag₂O [JCPDS 65-6811] exhibits an XRD diffraction peak at 2θ of 38.1°. Thus, it is difficult to exclude the presence of Ag₂O or Ag species within the Ag/LaCoO₃ catalysts from the XRD results, so XPS was used to examine the state of Ag species on the catalyst surface. The intensity of the Ag diffraction peak at 2θ of 38.2° decreases upon calcination at temperatures >700 °C because significant Ag species transfer from the surface to the lattice of the perovskite structure because of the high mobility of Ag at such temperatures [22].

The average crystallite sizes (D_c) and cell parameters of the catalysts were calculated from the XRD patterns using the Scherrer formula and are given in Table 1. Compared with pure LaCoO₃, the cell parameter of Ag/LaCoO₃ increases with increasing thermal treatment temperature until 700 °C. Above this temperature the cell parameter decreases, as Ag⁺ begins to be incorporated into the perovskite lattice because of the high Ag mobility [22,24]. The larger size of Ag⁺ (0.115 nm) com-

Fig. 2. TEM images of Ag/LaCoO₃-400 (a, b) and Ag/LaCoO₃-800 (c, d).

pared with La³⁺ (0.106 nm) and Co³⁺ (0.061 nm) can expand the perovskite lattice. Replacing La³⁺ with Ag⁺ forms oxygen vacancies, so that the electrical neutrality of LaCoO₃ can be maintained. However, more Ag⁺ in the perovskite structure causes structural distortion, which decreases the content of Ag particles on the surface, leads to a separate Co₃O₄ phase, and decreases the lattice parameter at high temperature (>750 °C).

3.2. TEM results

Fig. 2 shows TEM images of the Ag/LaCoO₃ samples. The TEM image of Ag/LaCoO₃-400 indicates a LaCoO₃ particle size of 20–40 nm and an Ag particle size of 5–6 nm. Few Ag particles of 5–6 nm are observed in the TEM image of Ag/LaCoO₃-800, and LaCoO₃ appears highly agglomerated. This is consistent with Ag migrating into the perovskite lattice, rather than sintering on the LaCoO₃ surface.

3.3. H₂-TPR results

Fig. 3 shows H₂-TPR profiles of the Ag/LaCoO₃ catalysts and Co₃O₄. A reduction peak centered at 480 °C with a small shoulder peak at lower temperature is observed in the profile of Co₃O₄. The two reduction peaks of LaCoO₃ indicate that two reduction stages occur, namely the α (350–500 °C) and β (500–700 °C) peaks. The α peak is assigned to the reduction of adsorbed oxygen (O_{ads}) and that of Co³⁺ and Co⁴⁺ to Co²⁺. The β

Table 1

Crystallite sizes, lattice parameters, BET surface areas, and H₂ consumptions for the samples.

Sample	D_c^a (nm)	Lattice parameter ^b (nm)	BET surface area ^c (m ² /g)	H ₂ consumption ^d (μmol/g)		
				Low temperature	High temperature	Total
Co ₃ O ₄ -450	24.1	0.4941	83.2	325.1	—	325.1
LaCoO ₃ -800	31.7	0.3302	32.1	56.4	87.0	143.4
Ag/LaCoO ₃ -400	29.4	0.3303	29.8	54.2	131.6	185.8
Ag/LaCoO ₃ -650	30.0	0.3303	28.7	36.8	97.6	134.4
Ag/LaCoO ₃ -700	26.6	0.3304	27.1	37.3	100.1	137.4
Ag/LaCoO ₃ -750	29.9	0.3299	28.2	36.0	92.9	128.9
Ag/LaCoO ₃ -800	30.1	0.3297	25.3	55.3	89.9	145.2

^a Determined by the Scherrer equation from XRD data.

^b Evaluated in the (200) crystal plane ($2\theta = 47.7^\circ$).

^c Determined by the BET method from N₂ sorption isotherms.

^d Determined from H₂-TPR measurements.

Fig. 3. H₂-TPR profiles of the Ag/LaCoO₃ catalysts. (1) Co₃O₄-450; (2) Ag/LaCoO₃-800; (3) Ag/LaCoO₃-400; (4) Ag/LaCoO₃-650; (5) Ag/LaCoO₃-700; (6) Ag/LaCoO₃-750; (7) Ag/LaCoO₃-800.

peak is assigned to the reduction of lattice oxygen (O_{lat}) and that of Co²⁺ to Co⁰ [2,18].

The α peak at 350–500 °C for Ag/LaCoO₃-400 is weaker and broader than that of LaCoO₃, and the β peak is enhanced greatly. This indicates that Co species exist as Co²⁺, or that more O_{lat} can be reduced because of the presence of Ag species. Increasing calcination temperature reduces the reduction peak intensity of Ag/LaCoO₃ and leads to complexes containing shoulder peaks, compared with the H₂-TPR profile for Ag/LaCoO₃-400. The H₂ consumption of the catalyst calcined at 400 °C is 54.2 μmol/g, which decreases to 36.0–37.3 μmol/g for Ag/LaCoO₃-650, Ag/LaCoO₃-700, and Ag/LaCoO₃-750. This is attributed to the absence of Co₃O₄ on the LaCoO₃ surface, as shown by the XRD patterns in Fig. 1. The H₂ consumption increases to 55.3 μmol/g for Ag/LaCoO₃-800, which is similar to that of 56.4 μmol/g for LaCoO₃, as shown in Table 1. The H₂-TPR results indicate that the reducibility of the catalyst at low temperature is related to the presence of Co₃O₄. They also indicate that the migration of Ag from the LaCoO₃ surface to the lattice during thermal treatment at 400–750 °C restrains the growth of Co₃O₄, which enhances the stability of the perovskite structure.

3.4. XPS results

Fig. 4(a) shows the Ag 3d region of the XPS spectra of Ag/LaCoO₃-400 and Ag/LaCoO₃-800. The two main peaks with binding energy at 368.2 and 374.2 eV correspond to the Ag 3d_{5/2} and Ag 3d_{3/2} states, respectively, with a spin orbital separation of 6.0 eV. The Ag 3d_{5/2} peak appears at 368.2 eV in Ag⁰, 367.8 eV in Ag⁺, and at 367.3–368.6 eV in Ag²⁺ [25]. Therefore, Ag on the Ag/LaCoO₃ surface is likely to be in the metallic state. The high symmetry of the Ag 3d_{5/2} peak suggests a relatively homogeneous environment of Ag⁰. The Ag/La ratios on the surfaces of Ag/LaCoO₃-400 and Ag/LaCoO₃-800 are 0.126 and 0.901, respectively, depending on the XPS analyses. This indicates a surface enrichment in Ag for Ag/LaCoO₃-400, compared with a theoretical atomic ratio of 0.106 for LaCoO₃ containing 4.65 wt% of Ag.

Fig. 4(b) shows the Co 2p region of the XPS spectra of Ag/LaCoO₃-400 and Ag/LaCoO₃-800. The binding energy of the Co 2p_{3/2} state at 780.0 eV is close to those of Co in LaCoO₃ (779.7 eV) and Co³⁺ in Co₂O₃ (779.6 eV) [16]. Negative shifts of Co 2p_{3/2} XPS peaks arise from the presence of Co⁴⁺. A Co 2p_{3/2} state binding energy of 779.3 eV has been attributed to the presence of Co⁴⁺ in La_{1-x}K_xCoO₃ perovskites [18,26]. The positive shifts in the Co 2p_{3/2} peaks in Fig. 3(b) indicate that Co exists as low-valence Co²⁺ and Co³⁺. This is in accordance with the above XRD and H₂-TPR results.

Fig. 4(c) shows the O 1s region of the XPS spectra of Ag/LaCoO₃-400 and Ag/LaCoO₃-800, with each containing two peaks. The peaks at 528.8 and 531.3–531.6 eV are assigned to O_{lat} and O_{ads}, respectively [18,27]. The O_{ads} content on the surface of Ag/LaCoO₃-400 is as high as 67.7%, which is much higher than those of Ag/LaCoO₃-800 (63.1%) and LaCoO₃ (61.1%). This is attributed to more oxygen vacancies and more Ag⁰ on the surface of Ag/LaCoO₃-400 [28].

3.5. Soot-TPR

Understanding the nature of surface oxygen species is important for catalytic oxidation applications. The catalytic activity of Ag/LaCoO₃ for soot oxidation by surface active oxygen was studied by soot-TPR in the presence of high-purity He (99.999%). Under these conditions, soot can only be oxidized

Fig. 4. XPS spectra of the (a) Ag 3d, (b) Co 2p, and (c) O 1s regions for (1) Ag/LaCoO₃-400 and (2) Ag/LaCoO₃-800.

by surface oxygen species of the catalyst, including surface-adsorbed oxygen and surface lattice oxygen. The amount of active oxygen adsorbed on the catalysts was estimated by integrating the peaks associated with CO_2 and CO formation at temperatures below 700°C in Fig. 5. Only a small amount of CO is detected, compared with CO_2 , which indicates a high selectivity for CO_2 . The soot-TPR profiles are divided into three temperature regions, corresponding to the three kinds of oxygen species: O_2^- ($300\text{--}450^\circ\text{C}$), O^- ($450\text{--}650^\circ\text{C}$), and O^{2-} ($>650^\circ\text{C}$) [29,30]. The reduction temperature for lattice oxygen ($>650^\circ\text{C}$) is much higher than that of other oxygen species, indicating its poor reactivity with soot. The low soot ignition temperature ($<400^\circ\text{C}$) observed in this study (Fig. 6, Section 3.6) suggests that surface-chemisorbed oxygen species (O_2^- , O^-) are the main active oxygen species for soot combustion. Adsorbed oxygen species (O_2^- , O^-) are generally produced through the adsorption of gaseous O_2 at oxygen vacancies, and active oxygen species originating from gas phase oxygen over metallic Ag, which are involved in carbon oxidation [31,32]. The Ag loading likely enhances the catalytic activity because of the increased surface oxygen content. The amount of active oxygen increases with increasing Ag nanoparticle content [33,34]. $\text{Ag/LaCoO}_3\text{-400}$ possesses more adsorbed oxygen species than $\text{Ag/LaCoO}_3\text{-800}$. This is because of its greater oxygen vacancy content, which results from the substitution of Ag^+ and its greater surface Ag particle content.

3.6. Soot oxidation in air and NO_x atmospheres

Fig. 6(a) shows the TPO profiles for soot oxidation over Ag/LaCoO_3 catalysts under an air flow. Soot combustion starts at around 350°C , with a T_p as high as 510°C for LaCoO_3 . The T_p decreases by $50\text{--}70^\circ\text{C}$ when LaCoO_3 is partially modified by Ag, depending on the thermal treatment temperature. A low T_p (435°C) is observed over $\text{Ag/LaCoO}_3\text{-400}$ and $\text{Ag/LaCoO}_3\text{-800}$. The conversion of soot in the presence of Co_3O_4 yields a high T_p (495°C). The addition of Ag significantly improves the catalytic performance for soot oxidation in air. The catalytic performance of Ag/LaCoO_3 for soot combustion in a NO_x atmosphere

Fig. 5. Soot-TPR profiles of the $\text{Ag/LaCoO}_3\text{-400}$ and $\text{Ag/LaCoO}_3\text{-800}$ catalysts.

is shown in Fig. 6(b). The T_p of the Ag/LaCoO_3 samples greatly reduces to about 140°C over $\text{Ag/LaCoO}_3\text{-400}$, compared with the catalyst containing no Ag. The T_p increases from 375 to 510°C as the calcination temperature increases from 400 to 800°C .

Soot conversions as a function of temperature in air and NO_x were derived from the TPO profiles in Fig. 6. The derived values of T_{10} , T_{50} , T_{90} , and ΔT ($\Delta T = T_{90} - T_{10}$) are shown in Table 2. Compared with the catalytic oxidation of soot over Co_3O_4 and LaCoO_3 , the soot conversion curves over Ag/LaCoO_3 shift to lower temperature, and the soot conversion rates increase. The ΔT values of Ag/LaCoO_3 fall in a narrow range ($57\text{--}72^\circ\text{C}$), and are $76\text{--}91$ and $43\text{--}58^\circ\text{C}$ lower than those for Co_3O_4 and LaCoO_3 , respectively. The activation energy for soot oxidation was determined for the catalysts by the Redhead method, using peak temperature data from the temperature-programmed experiments [35]. Table 2 shows the ΔE_a (T_p) values of the catalysts. The ΔE_a (T_p) values for LaCoO_3 and Co_3O_4 are 160.0 and 156 kJ/mol , respectively, and are close to that for non-catalytic soot combustion reported previously [27,36]. Loading with Ag reduces the activation energy for soot oxidation. The calcination temperature has a mild influence on the activation energy for soot oxidation in air.

Fig. 6. TPO profiles of soot oxidation over Ag/LaCoO_3 catalysts in (a) air and (b) NO_x . (1) $\text{Co}_3\text{O}_4\text{-450}$; (2) $\text{LaCoO}_3\text{-800}$; (3) $\text{Ag/LaCoO}_3\text{-400}$; (4) $\text{Ag/LaCoO}_3\text{-650}$; (5) $\text{Ag/LaCoO}_3\text{-700}$; (6) $\text{Ag/LaCoO}_3\text{-750}$; (7) $\text{Ag/LaCoO}_3\text{-800}$.

Table 2

Characteristic temperatures and activation energy during soot combustion over catalysts.

Sample	T_{10} (°C)		T_{50} (°C)		T_{90} (°C)		ΔT (°C)		$\Delta E_a(T_p)$ (kJ/mol)	
	O ₂ -TPO	NO _x -TPO	O ₂ -TPO	NO _x -TPO	O ₂ -TPO	NO _x -TPO	O ₂ -TPO	NO _x -TPO	O ₂ -TPO	NO _x -TPO
Co ₃ O ₄ -450	400	325	481	366	548	395	148	—	156.9	—
LaCoO ₃ -800	433	390	500	490	548	545	115	155	160.0	160.0
Ag/LaCoO ₃ -400	392	311	439	363	464	397	72	86	146.7	131.7
Ag/LaCoO ₃ -650	405	325	450	385	476	425	71	100	148.4	135.7
Ag/LaCoO ₃ -700	405	325	445	375	474	410	69	85	147.3	135.1
Ag/LaCoO ₃ -750	405	325	445	380	471	430	66	105	147.3	142.6
Ag/LaCoO ₃ -800	405	395	437	490	462	545	57	150	145.4	160.0

Much better activity with lower T_p values for soot combustion is achieved over Ag/LaCoO₃ in both NO and O₂, compared with LaCoO₃ and Co₃O₄. NO can be oxidized to NO₂ by surface oxygen species (O²⁻, O⁻), and these species have higher activity for soot oxidation than NO and O₂ [37,38]. The activation energy for soot combustion is much lower than that in air atmosphere. Ag/LaCoO₃-400 is the most active catalyst, with an activation energy of 131.7 kJ/mol. A slight increase in activation energy is observed with increasing calcination temperature. The presence of NO lowers the reaction temperature and improves the catalytic activity for soot oxidation. However, the higher ΔT indicates a slower combustion rate, as shown in Table 2. This wider temperature window may indicate a complex and as yet unknown reaction mechanism.

Catalytic soot oxidation requires oxygen transfer from the catalyst to soot to initiate soot combustion at low temperature. Two kinds of adsorbed oxygen species are involved in soot oxidation. Adsorbed oxygen species on the Ag surface migrate to the support surface via the interface to form oxygen species (partly O₂⁻), and further migrate to soot particles [39]. The enhanced activity of Ag/LaCoO₃ can be ascribed to more oxygen vacancies formed by Ag migrating from the LaCoO₃ perovskite surface to the lattice to form La_{1-x}Ag_xCoO₃, and to the additional active sites of Ag itself.

3.7. Stability of Ag/LaCoO₃ for soot oxidation in NO_x

The melting point of Ag is relatively low (961 °C). The stability of supported Ag catalysts during soot oxidation is therefore an important consideration. Repetitive activity tests were

carried out to investigate the stability of Ag/LaCoO₃. Soot conversion profiles as a function of temperature are shown in Fig. 7. The value of T_{50} in NO-O₂-TPO shifts from 355 to 362 °C during the first cycle and then 366 °C in the second and third cycles, respectively. This indicates that there is no obvious deactivation of Ag/LaCoO₃ after three cycles. Towata' group [6] suggested that sintering of Ag nanoparticles and a loss of active Ag species were responsible for the deactivation of Ag catalysts for soot oxidation. No increase in the XRD peak intensity of Ag species is observed (not shown), and there is no shift to higher 2θ for the XRD peaks of LaCoO₃ (not shown). Therefore, the stable activity of Ag/LaCoO₃-700 in soot oxidation after three cycles is related to the high stability of the Ag/LaCoO₃-700 structure.

4. Conclusions

LaCoO₃ catalysts containing 4.65 wt% Ag were synthesized, characterized, and evaluated for the removal of soot in air or NO_x. All catalysts exhibit lower T_p values than LaCoO₃ for soot combustion. The XRD, H₂-TPR, soot-TPR, and XPS characterizations indicate that the high soot combustion over the perovskite-structured Ag/LaCoO₃ results from the following. First, Ag/LaCoO₃ catalysts possess a uniform particle size (24–32 nm), which is similar to that of soot. This allows efficient contact between the soot particles and Ag/LaCoO₃. Second, Ag/LaCoO₃ exhibits a higher reducibility than LaCoO₃. This facilitates redox circulation during soot combustion, which increases the catalytic activity of Ag/LaCoO₃. Third, partial Ag migration from the LaCoO₃ perovskite surface to the lattice allows oxygen vacancies to form in Ag/LaCoO₃. More oxygen vacancies accelerate the transfer of oxygen species during soot combustion. Finally, more metallic Ag leads to higher oxidation ability because more O²⁻ and O⁻ are formed.

References

- [1] J. P. A. Neef, M. Makkee, J. A. Moulijn, *Fuel Sci. Technol.*, **1996**, 47, 1–69.
- [2] S. Q. Fang, L. Wang, Z. C. Sun, N. J. Feng, C. Shen, P. Lin, H. Wan, G. F. Guan, *Catal. Commun.*, **2014**, 49, 15–19.
- [3] P. Doggali, S. Kusaba, Y. Teraoka, P. Chankapure, S. Rayalu, N. Labhsetwar, *Catal. Commun.*, **2010**, 11, 665–669.
- [4] Z. Q. Li, M. Meng, Q. Li, Y. N. Xie, T. D. Hu, J. Zhang, *Chem. Eng. J.*, **2010**, 164, 98–105.
- [5] K. Yamazaki, T. Kayama, F. Dong, H. Shinjoh, *J. Catal.*, **2011**, 282,

Fig. 7. Soot conversion profiles during repetitive soot oxidation over Ag/LaCoO₃ in NO_x.

Graphical Abstract

Chin. J. Catal., 2016, 37: 428–435 doi: 10.1016/S1872-2067(15)61000-2

Catalytic oxidation of diesel soot particulates over Ag/LaCoO₃ perovskite oxides in air and NO_x

Qi Fan, Shuai Zhang, Liying Sun, Xue Dong, Lancui Zhang, Wenjuan Shan*,
Zaiming Zhu*
Liaoning Normal University

Ag migrated into lattice of LaCoO₃ perovskite to increase oxygen vacancy in the thermal treatment process. Ag/LaCoO₃ catalysts showed high catalytic activity for soot combustion in air and in NO_x.

- 289–298.
- [6] M. Haneda, A. Towata, *Catal. Today*, **2015**, 242, 351–356.
 - [7] Y. X. Liu, H. X. Dai, Y. C. Du, J. G. Deng, L. Zhang, Z. X. Zhao, C. T. Au, *J. Catal.*, **2012**, 287, 149–160.
 - [8] C. Lee, J. I. Park, Y. G. Shul, H. Einaga, Y. Teraoka, *Appl. Catal. B*, **2015**, 174–175, 185–192.
 - [9] G. Y. Yang, Y. J. Li, Y. Men, *Catal. Commun.*, **2015**, 69, 202–206.
 - [10] Y. J. Wang, J. H. Wang, H. Chen, M. F. Yao, Y. D. Li, *Chem. Eng. Sci.*, **2015**, 135, 294–300.
 - [11] S. J. Castillo Marcano, S. Bensaid, F. A. Deorsola, N. Russo, D. Fino, *Fuel*, **2015**, 149, 78–84.
 - [12] Q. Q. Yang, F. N. Gu, Y. F. Tang, H. Zhang, Q. Liu, Z. Y. Zhong, F. B. Su, *RSC Adv.*, **2015**, 5, 26815–26822.
 - [13] W. J. Shan, L. H. Yang, N. Ma, J. L. Yang, *Chin. J. Catal.*, **2012**, 33, 970–976.
 - [14] W. J. Shan, J. L. Yang, L. H. Yang, N. Ma, *J. Nat. Gas Chem.*, **2011**, 20, 384–388.
 - [15] H. L. Zhang, J. L. Wang, Y. Cao, Y. J. Wang, M. C. Gong, Y. Q. Chen, *Chin. J. Catal.*, **2015**, 36, 1333–1341.
 - [16] X. Guo, M. Meng, F. F. Dai, Q. Li, Z. L. Zhang, Z. Jiang, S. Zhang, Y. Y. Huang, *Appl. Catal. B*, **2013**, 142–143, 278–289.
 - [17] H. Shimokawa, Y. Kurihara, H. Kusaga, H. Einaga, Y. Teraoka, *Catal. Today*, **2012**, 185, 99–103.
 - [18] K. Wang, L. Qian, L. Zhang, H. R. Liu, Z. F. Yan, *Catal. Today*, **2010**, 158, 423–426.
 - [19] E. Aneggi, J. Llorca, C. de Leitenburg, G. Dolcetti, A. Trovarelli, *Appl. Catal. B*, **2009**, 91, 489–498.
 - [20] E. Aneggi, M. Boaro, C. de Leitenburg, G. Dolcetti, A. Trovarelli, *J. Alloys Compd.*, **2006**, 408–412, 1096–1102.
 - [21] W. J. Shan, N. Ma, J. L. Yang, X. W. Dong, C. Liu, L. L. Wei, *J. Nat. Gas Chem.*, **2010**, 19, 86–90.
 - [22] S. Imamura, H. Yamada, K. Utani, *Appl. Catal. A*, **2000**, 192, 221–226.
 - [23] Y. Kang, M. Sun, A. M. Li, *Catal. Lett.*, **2012**, 142, 1498–1504.
 - [24] L. L. Murrell, R. T. Carlin, *J. Catal.*, **1996**, 159, 479–490.
 - [25] M. Kumar, G. B. Reddy, *Phys. Status Solidi B*, **2009**, 246, 2232–2237.
 - [26] Z. Q. Li, M. Meng, Y. Q. Zha, F. F. Dai, T. D. Hu, Y. N. Xie, J. Zhang, *Appl. Catal. B*, **2012**, 121–122, 65–74.
 - [27] C. Badini, V. Serra, G. Saracco, M. Montorsi, *Catal. Lett.*, **1996**, 37, 247–254.
 - [28] G. C. Zou, M. X. Chen, W. F. Shangguan, *Catal. Commun.*, **2014**, 51, 68–71.
 - [29] J. Liu, Z. Zhao, C. M. Xu, A. J. Duan, *Appl. Catal. B*, **2008**, 78, 61–72.
 - [30] J. Liu, Z. Zhao, C. M. Xu, A. J. Duan, G. Y. Jiang, *J. Phys. Chem. C*, **2008**, 112, 5930–5941.
 - [31] A. Nagy, G. Mestl, *Appl. Catal. A*, **1999**, 188, 337–353.
 - [32] M. Machida, Y. Murata, K. Kishikawa, D. J. Zhang, K. Ikeue, *Chem. Mater.*, **2008**, 20, 4489–4494.
 - [33] K. Shimizu, H. Kawachi, A. Satsuma, *Appl. Catal. B*, **2010**, 96, 169–175.
 - [34] T. Nanba, S. Masukawa, A. Abe, J. Uchisawa, A. Obuchi, *Catal. Sci. Technol.*, **2012**, 2, 1961–1966.
 - [35] B. Dernaika, D. Uner, *Appl. Catal. B*, **2003**, 40, 219–229.
 - [36] N. Russo, D. Fino, G. Saracco, V. Specchia, *J. Catal.*, **2005**, 229, 459–469.
 - [37] J. Oi-Uchisawa, A. Obuchi, R. Enomoto, J. Y. Xu, T. Nanba, S. T. Liu, S. Kushiya, *Appl. Catal. B*, **2001**, 32, 257–268.
 - [38] S. T. Liu, A. Obuchi, J. Uchisawa, T. Nanba, S. Kushiya, *Appl. Catal. B*, **2002**, 37, 309–319.
 - [39] T. Nanba, S. Masukawa, A. Abe, J. Uchisawa, A. Obuchi, *Appl. Catal. B*, **2012**, 123–124, 351–356.

空气或氮氧化物气氛下 Ag/LaCoO₃ 上的碳黑燃烧性能

樊 琪, 张 帅, 孙礼英, 董 雪, 张澜萃, 单文娟*, 朱再明*

辽宁师范大学化学化工学院功能材料化学研究所, 辽宁大连116029

摘要: 碳黑颗粒是柴油机尾气固体污染物的主要成分, 是大气污染中的主要颗粒状污染物。消除碳黑颗粒物的有效方式之一是在尾气排放前安装柴油机颗粒物过滤器。然而, 尾气排放温度远远低于碳黑燃烧温度, 在过滤器上使用碳黑氧化催化剂能够明显降低碳黑的燃烧温度, 防止过滤器堵塞。钙钛矿类催化剂由于具有良好的储氧能力, 高活性的晶相氧有利于碳

黑燃烧过程中气相氧和晶相氧的转换,具有较高的活性和结构稳定性,从而受到广泛关注.

本课题组曾先后对 LaKNiMnO_x 和 LaMO_3 ($M = \text{Fe, Co, Cu}$) 等钙钛矿体系的碳黑燃烧性能进行了系统研究,其中 LaCoO_3 及掺杂的 LaCoO_3 基钙钛矿在碳黑催化燃烧中表现了较高的催化活性.然而担载型钙钛矿催化剂在该领域的应用很少有报道.银基催化剂由于具有较高的低温氧活化能力在碳黑燃烧反应中具有较高的催化活性,Kiyoshi Yamazaki 等发现在银表面吸附的氧物种能够迁移到银与载体的界面,并可以进一步迁移到碳黑表面氧化碳黑,但是载体的选择对催化活性有较大影响,具有较高储氧能力和氧离子传输能力的 CeO_2 和 ZrO_2 载体上负载银催化剂的碳黑燃烧性能明显高于以 Al_2O_3 为载体的催化剂.

为了进一步提高 LaCoO_3 基钙钛矿的碳黑氧化性能,本文结合 LaCoO_3 基钙钛矿和银基催化剂的特点,以 LaCoO_3 为载体制备了负载型银催化剂,考察了 Ag/LaCoO_3 催化剂结构和催化性能随焙烧温度的变化,并对银物种分布及催化作用进行了讨论.采用 X 射线粉末衍射 (XRD)、高分辨透射电镜 (TEM)、X 射线光电子能谱 (XPS)、氢气程序升温还原 (H_2 -TPR) 和碳黑程序升温还原 (soot-TPR) 等表征手段研究了银物种分布及影响催化剂结构和催化活性的原因.

XRD 测试结果表明,经过 800°C 焙烧的 LaCoO_3 催化剂具有钙钛矿结构,并有少量 Co_3O_4 ,银担载在 LaCoO_3 催化剂上,经 400°C 焙烧后 XRD 测试检测到 Ag 的特征峰,说明银物种主要为单质银而不是以氧化物形式存在.随着焙烧温度的升高 ($400\text{--}700^\circ\text{C}$), Ag 的衍射峰减弱,同时 Co_3O_4 的衍射峰消失,说明在热处理过程中银物种发生了迁移,从表面逐渐迁移进入钙钛矿结构,进而影响 Co 物种的分布.继续升高焙烧温度 ($750\text{--}800^\circ\text{C}$),由于高温烧结,部分银物种从钙钛矿结构中析出,钴物种也发生重新分布, Co_3O_4 的衍射峰出现. XPS 结果表明银物种主要为 Ag^0 ,钴物种主要为低价钴离子, Ag/LaCoO_3 催化剂具有较高的吸附氧浓度. Soot-TPR 结果表明,表面单质银的存在有利于活化气相氧, Ag 物种进入钙钛矿的晶胞增加了氧缺陷有助于气相氧和晶相氧的转移, Ag/LaCoO_3 催化剂能够在低温下完全氧化碳黑.低温焙烧的 Ag/LaCoO_3 表面形成的大量吸附氧物种是其高活性的原因.

在空气气氛和 NO_x 气氛下考察了该系列催化剂上碳黑的催化燃烧性能,发现银的担载使 LaCoO_3 钙钛矿催化活性显著提高,在空气气氛下碳黑燃烧最大速率对应温度 (T_p) 降低了 $50\text{--}70^\circ\text{C}$,碳黑燃烧性能与催化剂的低温还原性相关.在 NO_x 气氛下,银在低温下的高活化氧能力使碳黑燃烧温度进一步降低,其中在 $\text{Ag/LaCoO}_3\text{-}400$ 催化剂上碳黑的燃烧温度降低了 140°C .以 $\text{Ag/LaCoO}_3\text{-}700$ 催化剂为例,考察了在 NO_x 气氛下碳黑燃烧性能的稳定性,发现该催化经历 3 次循环实验后没有明显的失活且其结构稳定.

关键词: 碳黑燃烧; 氮氧化物; 银; 钙钛矿; 热稳定性

收稿日期: 2015-10-10. 接受日期: 2015-10-29. 出版日期: 2016-03-05.

*通讯联系人. 电话: (0411)82156852; 电子信箱: wjshan@dicp.ac.cn

#通讯联系人. 电话: (0411)82156852; 电子信箱: zhuzaiming@lnnu.edu.cn

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).