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Sulfur resistance and soot combustion for $La_{0.8}K_{0.2}Co_{1-y}Mn_yO_3$ catalyst

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ABSTRACT

Different Mn-substitution amounts of $La_{0.8}K_{0.2}Co_{1-y}Mn_yO_3$ (y = 0–0.5) catalyst were prepared using the sol-gel method to study the effect of SO_2 on the catalytic combustion of soot. The TPO results show that the $La_{0.8}K_{0.2}Co_{0.7}Mn_{0.3}O_3$ catalyst has the best catalytic performance. After presulfurization (500 ppm SO_2, 3 h, 300 °C), the catalytic performance weakens with higher T_i (310 °C) and T_m (386 °C), increasing by 34 °C and 31 °C. In this paper, the oxygen absorbed from the gas phase and further incorporation of oxygen atoms into a lattice classified as three kinds of oxygen species, O^{2-}, O^- and O_2^-. The results of XPS indicate that there are sulfates on the surface of the catalysts and the catalytic performance of catalysts presulfured weakens mainly due to the decrease of available oxygen source (O_2^- and O^{2-}). However, the oxidation of soot is attributed to the reaction between soot and O_2^- in the surface active site of catalyst. Meanwhile, soot and SO_2 may have a competitive relationship in reacting with O_2^-. These results have significance to research the relation of catalyst poisoning and active oxygen with the aim of improving the stability of perovskite-based catalyst.

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1. Introduction

Nowadays, diesel vehicles have been widely used because of its advantages such as high efficiency, large output, and economical friendly, etc [1]. But, the particulate matters (PM) and nitrogen oxides (NO_x) emitted from diesel engines (70% of the soot particle size is less than 0.3 μm) are detrimental to both environment and human health [2–4]. As described by many studies, activity of catalyst can be inhibited by SO_2 [5–9]. However, SO_2 is inevitable in the combustion products as sulfur is one of the diesel chemical elements [10]. So designing a catalyst that has extraordinary sulfur resistance as well as great performance will be significance for reducing the carbon emissions of diesel exhaust.

$LaCoO_3$ has a unique perovskite structure (ABO_3) and is widely used in soot of diesel vehicle catalytic combustion due to its cost efficiency, strong mechanical stability, thermal stability and amendable redox property [11]. A-ions of $LaCoO_3$, $LaMnO_3$ and $LaFeO_3$ were replaced by K elements in WANG's [12]. They suggest that there was a lot of formative oxygen vacancies in catalyst and the B-ions were promoted to high valence likely after La^{3+} was replaced by low valence K^+. In addition, the variety of Mn ion valence state is capable of balancing charge and multi valence MnO_x has high redox property [13]. Therefore, replacing A-ions and B-ions

of $La_{1-x}K_xCo_{1-y}Mn_yO_3$ greatly reduces the ignition temperature of soot combustion and promotes the catalytic activity. In fact, the soot combustion is mainly based on the spillover mechanism of the surface oxygen. The contact area of catalyst and solid particles is small, so the role of surface oxygen is particularly important. And the oxygen absorbed from the gas phase and further incorporation of oxygen atoms into a lattice lead to three kinds of oxygen species, O^{2-}, O^- and O_2^- [14,15]. Zhu et al. [16] reported the effect of SO_2 on perovskite-type oxides catalyst $LaCoO_3$ and his result shows that perovskite structure of catalyst was destroyed by invading of such sulfur. Moreover, some new phases about La, Co are formed on the surface of catalyst when SO_2 was passed through the soot. That leads to the loss of catalytic activity. However, the report about relationship between the catalyst poisoning and surface oxygen is few. So it is crucial to understand the SO_2 poisoning mechanism with the aim of improving the stability of perovskite-type catalyst.

Previous work suggests that the catalyst has highest activity when x = 0.2. Different Mn-substitution amounts of catalyst $La_{0.8}K_{0.2}Co_{1-y}Mn_yO_3$ was prepared using the sol-gel method [17,18] and best value of Mn-substitution amounts will be determined by TPO activity evaluation. Then, the best catalyst is treated in 500 ppm SO_2 for 3 h at 300 °C. Thus this work investigates the effects of SO_2 on the catalytic activity, structure of catalysts and the surface active oxygen.

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2. Experimental

2.1. Catalyst preparation

A series of perovskite-type $La_{0.8}K_{0.2}Co_{1-y}Mn_yO_3$ (y = 0, 0.1, 0.2, 0.3, 0.4, 0.5) compounds were prepared by sol-gel method. $La(NO_3)_3·6H_2O$, KNO_3, $Co(NO_3)_2·6H_2O$ and $Mn(NO_3)_2$ were used as precursors and citric acid was used as complexing agent. Nitrates and citric acid (mole ratio of nitrates to citric was 1:2) were dissolved in distilled water. The mixed solution was heated and stirred to evaporate water in 80 °C water bath until dried gel was formed. Subsequently, the gel was dried at 120 °C for 2 h and then calcined at 700 °C for 5 h in muffle roaster.

2.2. Catalytic activity measurement and presulfurization

The catalytic activities of the prepared samples were measured with a temperature programmed oxidation (TPO) reaction. Commercially available carbon black Printex-U from Degussa was used as a model of diesel soot. In this paper, loose contact manner is used. We mixed soot particles and catalysts together in a weight ratio of 1:10 and slightly stirred 5 min by used a spatula. And then 555 mg mixture was placed in the quartz tube (Φ = 12 mm, i.d.). Reactant gases containing 10 vol.% O_2 and 500 ppm NO balanced with He were passed through a mixture of the catalyst and Printex-U at a flow rate of 100 mL min^{-1}. O_2, CO and CO_2 of the outlet gas was analyzed via an on-line gas chromatograph (Shanghai Kechuang, GC900A) with columns of TDX-01, equipped with thermal conductivity detector (TCD). The oxidation performance for catalysts was assessed by soot ignition temperature (T_i) and maximum soot oxidation rate temperature (T_m). Presulfurization condition: the feed mixture contain 500 ppm SO_2 balanced with N_2 (Q_{total} = 100 mL min^{-1}) and the treatments were carried out for 3 h at 300 °C.

2.3. Catalyst characterization

XRD patterns were collected by D8 ADVANCE diffractometer (German, Bruker) using the Cu $K\alpha$ radiation at λ = 0.15418 nm. The X-ray tube was operated at 40 kV and 40 mA. The X-ray powder diffractogram was recorded in the 2θ range of 5–90° with a scan step size of 0.02° at the rate of 17.7 s/step.

FT-IR absorbance spectra were obtained in the wave number ranging between 4000 and 400 cm^{-1} via a TENSOR27 spectrophotometer manufactured by Germen Burke Company. The measured wafer was prepared as KBr pellet with the weight ratio of sample to KBr, 1/100. The resolution was set at 4 cm^{-1} during measurements.

BET specific surface areas were determined by N_2 adsorption and desorption using a Micromeritics ASAP 2000 analyzer (America Microsoft) at 196 °C. Prior to analysis, the samples were vacuumed for 2 h at 300 °C.

SEM scanning electron microscopy (Germany ZEISS Merlin) was used to observe the microstructures of catalysts and the distribution of particles.

X-ray photoelectron spectra (XPS) were recorded with a VG Multilab 2000 spectrometer using Mg $K\alpha$ ($h\nu$ = 1253.6 eV) as X-ray source. The binding energies were calibrated internally by the carbon deposit C1s binding energy (BE) at 284.6 eV. Point peak fitting was carried out by XPS Peak 4.1.

3. Results and discussion

3.1. Influence of Mn-substitution amounts on soot combustion

The TPO curves of catalytic activities of samples with different Mn-substitution amounts are shown in Fig. 1. The T_i and T_m of soot
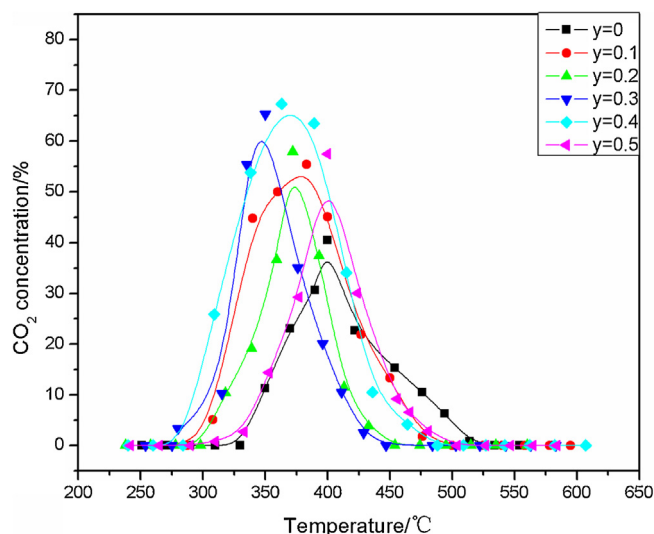

Fig. 1. The catalytic activities of $La_{0.8}K_{0.2}Co_{1-y}Mn_yO_3$ catalysts for soot combustion.

Table 1
TPO results of $La_{0.8}K_{0.2}Co_{1-y}Mn_yO_3$ catalysts.

Catalysts	T_i/°C	T_m/°C
$La_{0.8}K_{0.2}CoO_3$	335	410
$La_{0.8}K_{0.2}Co_{0.9}Mn_{0.1}O_3$	308	383
$La_{0.8}K_{0.2}Co_{0.8}Mn_{0.2}O_3$	300	375
$La_{0.8}K_{0.2}Co_{0.7}Mn_{0.3}O_3$	276	355
$La_{0.8}K_{0.2}Co_{0.6}Mn_{0.4}O_3$	290	365
$La_{0.8}K_{0.2}Co_{0.5}Mn_{0.5}O_3$	310	405
$La_{0.8}K_{0.2}Co_{0.7}Mn_{0.3}O_3$+$SO_2$	310	386

are 335 °C and 410 °C (Table 1) catalyzed by $La_{0.8}K_{0.2}CoO_3$ without Mn-substitution. And the T_i and T_m values of $La_{0.8}K_{0.2}Co_{1-y}Mn_yO_3$ shows a trend of incline and then decline as y (the content of Mn) increases. The catalytic activity of $La_{0.8}K_{0.2}Co_{1-y}Mn_yO_3$ are significantly enhanced with 30–60 °C lower T_i and T_m comparing with $La_{0.8}K_{0.2}CoO_3$.

Mn exists with different higher valance states. The lower state K$^+$ replacing A ion (La) prompt the B ion into higher state($Mn^{2+} \rightarrow Mn^{4+} \rightarrow Mn^{6+}$). Multi valence MnO_X has high redox property. Therefore, both oxidation performance of the catalyst and the performance of soot combustion are improved. Moreover, as shown in Table 1, the best catalytic performance of $La_{0.8}K_{0.2}Co_{0.7}Mn_{0.3}O_3$ comes with the lowest T_i (276 °C) and T_m (355 °C). Thus the $La_{0.8}K_{0.2}Co_{0.7}Mn_{0.3}O_3$ catalyst is selected to perform presulfurization for probing the influence of SO_2 on the catalytic performance.

3.2. The TPO results of $La_{0.8}K_{0.2}Co_{0.7}Mn_{0.3}O_3$ catalyst after presulfurization

The TPO results of presulfided $La_{0.8}K_{0.2}Co_{0.7}Mn_{0.3}O_3$ catalysts are shown in Fig. 2. The catalytic performances of catalysts are slightly lower after presulfurization for 3 h at 300 °C. The T_i and T_m of soot are 310 °C and 386 °C (Table 1) with increase about 34 °C and 31 °C comparing with fresh catalyst. This indicates that the SO_2 affects the catalytic activity of catalysts in some extent. Many studies have found that SO_2 forms sulphite or sulfate with bulk metal of catalyst and occupies the active centers of catalyst causing the decline of the catalytic performances [19,20]. However, the XRD spectra, FT-IR and SEM test results will further reveal the impact of SO_2 on $La_{0.8}K_{0.2}Co_{0.7}Mn_{0.3}O_3$ catalyst.