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Short Communication

Promotion effects of $LaCoO_3$ formation on the catalytic performance of Co–La oxides for soot combustion in air

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ABSTRACT

$Co_{1-x}La_xO_y$ catalysts were synthesized by citric acid complex method and their catalytic activities for soot combustion in air were investigated in this study. The best performance was observed over $Co_{0.93}La_{0.07}$ oxide catalysts with $T_{50} = 402$ °C. Co^{4+} in the surface of $LaCoO_3$ leads to the formation of more oxygen vacancies, thus contributing to the activities.

1. Introduction

Diesel engines have experienced a rapid growth in market share mainly owing to their stronger power and better fuel economy than gasoline engines. Besides, they also produce less amount of carbon monoxide and unburned hydrocarbon in the exhaust. However, the diffusion combustion mode of diesel vehicle results in serious emission of nanoparticles (<50 nm) [1,2], which is hazardous to the environment and human health [3,4]. Therefore, many countries set strict limits on particulate matter (PM) emission in laws and regulations. Diesel particulate filter (DPF), an efficient way to trap soot, helps to meet the limits, but it needs to be regenerated when backpressure reaches alarm value. The conventional strategy for DPF regeneration is electrical heating, yet it is energy-consuming. A more economic route, continuous regeneration of DPF by means of coating catalysts, was developed to simplify the post-process system. The performance of DPF regeneration largely depends on the catalytic activity of catalysts; hence it is urgent to find a stable and active catalyst compatible with this route.

Catalysts for soot abatement have been explored for decades [5]. As a typical spinel type catalyst, Co_3O_4 showed high activity in soot removal due to its strong redox ability [6,7]. A redox mechanism was proposed to explain the catalytic behavior of Co_3O_4 [8]. The perovskite-type oxides (ABO_3), where site A generally stands for rare earth elements and site B is filled with transition metal elements, are promising catalysts for soot abatement owing to their high catalytic activity and stability. Among all the perovskite-type catalysts, $LaCoO_3$ have been widely applied for their excellent catalytic performance for soot abatement. Two traditional strategies were reported to promote the activity over $LaCoO_3$ catalysts. One is to replace cations at one or both of the A and B sites. This method leads to the generation of oxygen vacancies or the variation of valence state of metal ions at both sites [9], while the other is preparation into macroporous morphology. The structure can significantly improve the contact conditions between diesel soot and catalysts [10,11]. Although Co_3O_4 and $LaCoO_3$ are common catalysts for soot removal, the combined effects of both the catalysts have not been reported yet.

In this paper, $Co_{1-x}La_xO_y$ catalysts were prepared and their catalytic behaviors were investigated. Based on the experimental results, a possible determinant for the reaction was proposed.

2. Experimental

The catalysts were synthesized by citric acid complex method. $Co(Ac)_2$, $La(NO_3)_3$ and citric acid (triple total amount of metal ions) were dissolved in distilled water. The solution was stirred in water bath at 80 °C till dryness. The viscous mixture experienced pre-calcination at 400 °C for 1 h followed by grinding and by final calcination at 700 °C for 4 h to remove the remaining citric acid. The catalysts were denoted as $Co_{1-x}La_x$, where x (x = 0, 0.02, 0.04, 0.07, 0.17, 1) represented the molar proportion of lanthanum to total metal ions. The physical mixture

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Table 1
T_{50} value and BET surface data of $Co_{1-x}La_x$ catalysts (x = 0.02, 0.04, 0.07, 0.17).

Catalysts	T_{50} (°C)	BET (m^2/g)
Co_3O_4	423	2.8
$Co_{0.98}La_{0.02}$	415	3.8
$Co_{0.96}La_{0.04}$	412	6.2
$Co_{0.93}La_{0.07}$	402	12.2
$Co_{0.93}La_{0.07}$-pm	426	3.2
$Co_{0.83}La_{0.17}$	421	6.3
$LaCoO_3$	430	4.5

of $Co_{0.93}La_{0.07}$ was obtained by grinding $LaCoO_3$ and Co_3O_4 prepared above at the same ratio. It was denoted as $Co_{0.93}La_{0.07}$-pm.

The catalytic activities under air atmosphere were carried out on thermo gravimetric (TG) analysis using STA449F3 (NETZSCH, Germany). The tight mixture of typical model soot (Printex U) and catalyst was prepared at a mass ratio of 1:19 by grinding them together for 15 min. The mixture (20 ± 0.2 mg) was purged with air with a flow rate of 50 ml/min from 200 °C to 600 °C. The catalytic activity was evaluated by temperature named as T_{50}, at which 50% of soot was consumed.

The crystal structure of the materials was recorded by X-ray diffraction (Rigaku D/max-2200/PC Japan) with Cu ka (40 kV, 20 mA) at a scan speed of 6°/min. BET surface area measurements were performed on a Micromeritics BET surface area analyzer. X-ray photoelectron spectroscopy (XPS) was acquired with a Kratos Axis UltraDLD spectrometer (Kratos Analytical — a Shimadzu group company) using a monochromatic Al Kα source (1486.6 eV). All the binding energy (BE) values were calibrated by adopting BE value of contaminant carbon (C1s 284.6 eV) as a reference. Soot temperature programmed reduction (soot–TPR) was conducted on TG instrument mentioned above. The tight catalyst/soot mixture was heated under Ar flow at a flow rate of 50 ml/min from 100 °C to 950 °C. H_2-TPR was performed on Micromeritics Chemisorb 2720 device. 0.1 g samples were pretreated under N_2 at 300 °C for 30 min and cooled down to room temperature in the same atmosphere. Then the samples were exposed to 5% H_2/N_2 at a flow rate of 25 ml/min till the TCD signal was flat. Afterwards the tests were carried out under the same condition from room temperature to 600 °C at a heating rate of 10 °C per minute.

3. Results and discussion

3.1. Catalytic activity

The catalytic activities in air are listed in Table 1. It is shown that the T_{50} value of $Co_{1-x}La_x$ catalysts had an inverse relationship with the loading of lanthanum. The minimum value of T_{50} (402 °C) was achieved over $Co_{0.93}La_{0.07}$ catalysts. Further introduction of lanthanum didn't assist soot oxidation due to the formation of La_2O_3 with lower activity. Thus, $Co_{0.93}La_{0.07}$ had the best performance among all the samples, while activities of $Co_{0.93}La_{0.07}$-pm just lay between those of the Co_3O_4 and $LaCoO_3$.

3.2. XRD and BET

XRD patterns of all the catalysts are displayed in Fig. 1. Two separate phases, spinel type Co_3O_4 and perovskite type $LaCoO_3$, were detected in the $Co_{0.93}La_{0.07}$ catalysts. The positive shifts of $LaCoO_3$ peaks indicated a lattice shrink over $Co_{0.93}La_{0.07}$ samples. This phenomenon may result from substitution of La^{3+} for cation with smaller radius such as bivalent cobalt. Accordingly, no shifts were found over $Co_{0.93}La_{0.07}$-pm sample. All the diffraction peaks of $Co_{0.93}La_{0.07}$ were broadened, which revealed that crystal grain size of this sample was smaller than that of other catalysts.

The results of XRD crystal phase and BET surface area are listed in Tables 2 and 1. The BET value of all the catalysts was rather low due to high temperature calcination. There was a negative correlation between the specific surface area and the amount of lanthanum components, with the exception of $Co_{0.83}La_{0.17}$ owing to a new phase (La_2O_3) introduction (Fig. S1). Although the minimum T_{50} value of $Co_{0.93}La_{0.07}$ corresponded to maximum BET value of 12.2 m^2/g, the BET surface area may play a minor role in soot oxidation since the reaction occurred at the three phase boundary of soot, catalysts and reactant gas [12,13].

3.3. Soot–TPR and H_2-TPR

Soot–TPR tests were applied to analyze the activity of surface oxygen and lattice oxygen. DTG curves are shown in Fig. 2. Two major species of

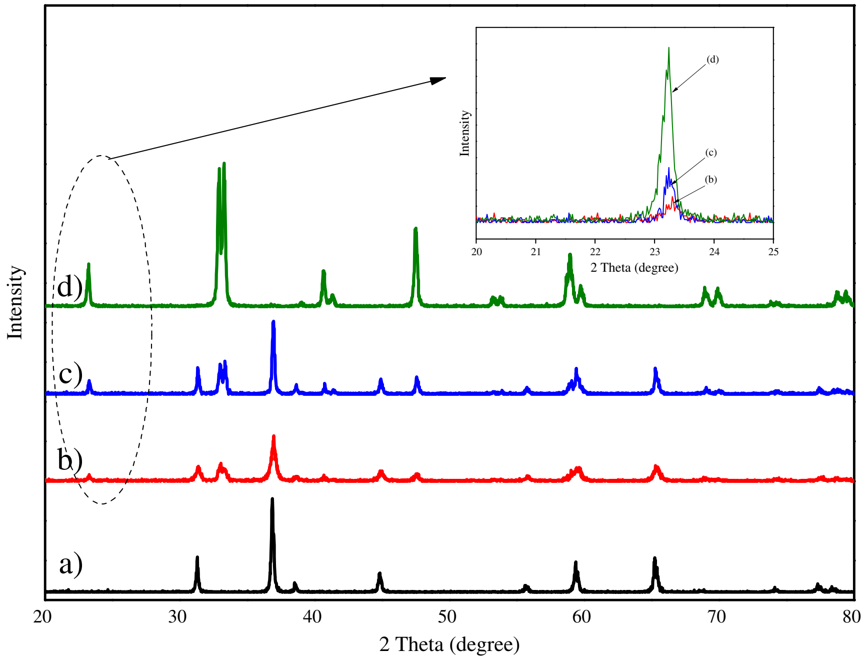

Fig. 1. XRD patterns of (a) Co_3O_4, (b) $Co_{0.93}La_{0.07}$, (c) $Co_{0.93}La_{0.07}$-pm, (d) $LaCoO_3$ and magnified XRD patterns of $LaCoO_3$ (012).