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Fabrication of nanofibrous A- or B-sites substituted $LaCoO_3$ perovskites with macroscopic structures and their catalytic applications

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ABSTRACT

Fabrication of nanofibrous $La_{1-x}Ce_xCoO_3$ ($x = 0.05$, 0.1, 0.2) and $LaMn_xCo_{1-x}O_3$ ($x = 0.2$, 0.5, 0.8) perovskite-type oxides with macroscopic structures can be successfully achieved by using carbon nanofibers (CNFs) as templates. Field emission scanning electron microscopy (FE-SEM), coupled with X-ray diffraction (XRD) analysis confirmed the template effect and formation of the perovskite-type oxides on the macroscopic substrate. It turned out that this facile method can ensure the desired single-phase perovskite-type oxides formation by controlling the corresponding metal ratio during the preparation procedure. In addition, the immobilized nanofibrous $La_{1-x}Ce_xCoO_3$ ($x = 0.05$) and $LaMn_xCo_{1-x}O_3$ ($x = 0.5$) perovskite-type oxides can greatly decrease the combustion temperature of nanosized carbon black particles, which has the high potential application prospects in the treatment of diesel soot particles.

1. Introduction

The emission of soot from diesel engines is a serious environmental problem, due to its harm to human health and environment [1,2]. It has been well proved that soot can be effectively trapped and removed by diesel particulate filters (DPFs), however, the low temperature and regeneration efficiency of DPFs is the main limitation for its practical feasibility [3,4]. A preferred option to overcome the above disadvantages is to develop efficient and thermally stable catalysts, which can reduce soot ignition temperature and enhance soot combustion rate during regeneration process [3]. Perovskite-type oxides (ABO_3) has a typical structure where A and B represent 12-coordinated and 6-coordinated metals, respectively. Its structure and property is strongly influenced by the chemical nature of the cations at A- or B-sites. By partial substitution of cations at A- or B-sites in ABO_3 perovskite-type oxides, it is possible to get some amounts of structure defects and valence distribution inside [5,6]. It is worth noting that the great diversity, high thermal and mechanical stability, and good oxidation ability of ABO_3 perovskite-type oxides make them good candidates for soot catalytic combustion [7–9].

To date, ABO_3 perovskite-type oxides have been adopted as catalysts exclusively in nano-scale powder shape, and there exist some drawbacks during the catalytic reaction, such as pressure drop, mass/heat transfer, contact efficiency and harsh separation process. An alternative way to avoid such kinds of problems is to immobilize nano-scale ABO_3 perovskite-type oxides on macroscopic materials [10,1,11] (such as honey comb, monoliths, foams, filters, fibers, and so on). It is considered that such materials with direct macroscopic shapes would hold promise as highly functionalized materials for practical applications, taking an advantage over the corresponding nano-scale powder sample.

In recent years, carbon nanofibers (CNFs) have triggered great attention due to their wide application potential, such as candidate materials for electronic components, hydrogen storage, polymer additives, functional composites, catalysts and catalytic supports [12–14]. Furthermore, their versatility is further highlighted by potential acting as efficient templates for novel material fabrication [15–20]. Since CNFs can be easily synthesized through the decomposition of hydrocarbons over metal catalysts. Also, the features of CNFs can be easily controlled by changing different operation parameters. The last but the most important point is that CNFs possess high surface area, chemical inertness and can be easily removed by oxidation or hydrogenation [21,22]. The advantages that CNFs offer as templates for novel material fabrication are (a) the relative stability of the templates during the reaction (b) the relative ease in the removal of the templates by

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oxidation in air (c) the capability of controlling the shapes and morphologies of the desired materials by varying different reaction conditions. With this approach, the properties of the resulting materials can be reliably controlled through selecting different CNFs templates.

In our two recent communications [16,18], we have undertaken the studies on the uniform immobilization of nanofibrous $LaMnO_3$ perovskite-type oxides and its relative compounds on the macroscopic substrate by using CNFs as templates. It turned out that this method is simple and effective and can be extended to prepare a lot of novel materials with macroscopic structures which may find many applications. In this paper, we applied and extended the above facile and effective method to the fabrication of A- or B-sites substitution of $LaCoO_3$ perovskite-type oxides on silica fiber, particular attention is given to the substituted cations effect on the structure and morphology of $LaCoO_3$ perovskite-type oxides, as well as its catalytic performance for carbon black particles combustion. The results could provide new insights into the development of new efficient DPFs system for diesel soot particles treatment.

2. Experimental

2.1. Preparation of CNFs templates

Silica fiber immobilized-CNFs were prepared by chemical vapor deposition (CVD) technique, as reported in our previous papers [18,19]. First, silica fiber was impregnated with 0.3 M $Ni(NO_3)_2$ acetone solution at room temperature. Excess solution was removed by vacuum filtration and the resulting sample was further calcined in air at 573 K for 1 h to obtain NiO/silica fiber catalyst (ca. 1 wt% as NiO). Finally, the decomposition of methane (flow rate = 20 mL min^{-1}) was performed over the NiO/silica fiber catalyst at 873 K for 2 h at atmospheric pressure to obtain silica fiber immobilized-CNFs templates. The yield of the resulting CNFs was calculated by the following equation: yield (%) = 100 × weight of CNFs/weight of silica fiber.

2.2. Immobilization of A-sites substitution of $LaCoO_3$ perovskite-type oxides on silica fiber

The typical immobilization of $La_{1-x}Ce_xCoO_3$ perovskite-type oxides on silica fiber was carried out as follows: silica fiber immobilized-CNFs were first placed into a suction filtration unit. Then, the single precursor solution which consists of the desired amount of mixed metal nitrate (0.3 M as total metals, $La(NO_3)_3{\cdot}6H_2O$:$Ce(NO_3)_3{\cdot}6H_2O$:$Co(NO_3)_3{\cdot}6H_2O$ = $(1-x)$:x:1, where x = 0.05, 0.1, 0.2) in ethanol solution was dropped into the CNFs templates. Excess solution was removed by vacuum filtration. Afterwards, the resulting sample was dried in air at 393 K (30 min) and 573 K (30 min), respectively. Finally, CNFs templates were removed by calcination in air at 923 K for 5 h to obtain the desired immobilization of $La_{1-x}Ce_xCoO_3$ on silica fiber. For comparison, the immobilization of $LaCoO_3$ on silica fiber from CNFs templates was also prepared. The yield of the resulting $La_{1-x}Ce_xCoO_3$ was calculated by the following equation: yield (%) = 100 × weight of $La_{1-x}Ce_xCoO_3$/weight of silica fiber. In addition, the specific surface areas of the resulting $La_{1-x}Ce_xCoO_3$ were calculated by subtracting the surface areas of pure silica fiber (~1 $m^2\ g^{-1}$) from the total surface areas of the silica fiber immobilized-$La_{1-x}Ce_xCoO_3$.

2.3. Immobilization of B-sites substitution of $LaCoO_3$ perovskite-type oxides on silica fiber

The procedure for the immobilization of $LaMn_xCo_{1-x}O_3$ on silica fiber is similar to that of $La_{1-x}Ce_xCoO_3$. While the precursor solution consisted of the desired amount of mixed metal nitrate (0.3 M as total metals, $La(NO_3)_3{\cdot}6H_2O$:$Mn(NO_3)_3{\cdot}6H_2O$:$Co(NO_3)_3{\cdot}6H_2O$ = 1:x:$(1-x)$, where x = 0.2, 0.5, 0.8). After finishing the similar impregnation and drying process, the resulting sample was then calcinated at 923 K for 5 h to remove CNFs templates and obtain the desired immobilization of $LaMn_xCo_{1-x}O_3$ on silica fiber. In addition, the yields and specific surface areas of $LaMn_xCo_{1-x}O_3$ were calculated by using the similar method as $La_{1-x}Ce_xCoO_3$.

2.4. Characterizations

Field emission scanning electron microscopy (FE-SEM) measurements were carried out using a JEOL JSM-7400F instrument. X-ray diffraction (XRD) measurements were recorded on a Rigaku RINT Ultima + diffractometer with a Cu-Kα radiation. Transmission electron microscopy (TEM) was conducted on an H-800 (HITACHI) instrument operated at 200 kV. Cross-sectional specimens for TEM measurements were obtained as follows: samples were first embedded in epoxy resin after polymerization of the matrix by heating at 333 K for 48 h, the samples were then cut in ca. 80 nm thick sections on an ultramicrotome. Brunauer–Emmett–Teller (BET) specific surface areas were estimated by using an AUTOSORB-3 (YUASA IONICS) sorption analyzer after degassing at 473 K for 2 h. Catalytic test was performed using a TG-8120 (Rigaku) thermogravimetric analyzer. The sample consisted of the mixture of carbon black particle and the obtained materials (weight ratio of 1:10) was heated in the TG-DTA apparatus under air flow (30 mL min^{-1}) at a heating rate of 10 K min^{-1} and a temperature region from room temperature to 973 K. In addition, α-alumina and powder $LaCoO_3$ were adopted as the reference samples to do the similar combustion experiments, so as to estimate the combustion feature of the carbon black particle and to evaluate the catalytic activity for the obtained materials. Here it should be noted that powder $LaCoO_3$ was prepared using a typical citrate method, under the similar precursor concentration (0.3 M as total metals, $La(NO_3)_3{\cdot}6H_2O$:$Co(NO_3)_3{\cdot}6H_2O$ = 1:1) and calcination conditions (923 K for 5 h).

3. Results and discussion

3.1. Characterization of CNFs templates

Note that the typical morphology of the pure silica fiber is straight with a relatively smooth surface, and its diameter is ca. 5.0 μm (Fig. 1a). Fig. 1b and c shows the FE-SEM images of CNFs formed on silica fiber through CVD technique. It is obvious that large amounts of fibrous CNFs were entangled and uniformly immobilized on silica fiber after CVD process. The yield of CNFs was calculated to be ca. 102%. The average layer thickness of CNFs was calculated to be 5.0 μm, and its diameters ranged from 30.0 to 70.0 nm. A typical cross-sectional TEM image of CNFs (Fig. 1d) confirmed that CNFs were grown on the outer surface of silica fiber, and the CNF layer thickness was in the range of 5.0–6.0 μm, which agrees well with the FE-SEM results. Note that the absence of silica fiber inside CNFs layer (white hole) in the cross-sectional TEM images was due to the breakage of physically hard silica fiber through cutting by an ultramicrotome, while the black rods in the white hole are broken silica fiber pieces. In addition, the TEM image (Fig. 1e) of CNFs illustrates that the diameters of CNFs varied from 30.0 to 80.0 nm, consistent with the FE-SEM result. Evidence shows that a nickel metal particle was present at the tip of CNFs, indicating CNFs growth follows the common tip-growing mode.

The bulk structure of CNFs-immobilized on silica fiber was further identified with XRD patterns and the result is shown in Fig. 2. As a reference, the XRD pattern of pure silica fiber was also indicated in Fig. 2a. It should be noted that the broad peak of silica