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

Qiang Wu^{a,*}, Li Zhao^a, Meixia Wu^b, Weifeng Yao^a, Meixue Qi^a, Xiaoyan Shi^{c,d}

^a College of Environmental and Chemical Engineering, Shanghai University of Electric Power, Shanghai 200090, China

^b Department of Chemistry, Shanxi Datong University, Datong 037009, China

^c State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, China

^d Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

ARTICLE INFO

Article history:

Received 2 July 2013

Received in revised form 2 December 2013

Accepted 16 December 2013

Available online 25 December 2013

Keywords:

- A. Oxides
- B. Vapor deposition
- C. X-ray diffraction
- D. Catalytic properties

ABSTRACT

Fabrication of nanofibrous $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05, 0.1, 0.2$) and $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.2, 0.5, 0.8$) 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 $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05$) and $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.5$) 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.

© 2013 Elsevier Ltd. All rights reserved.

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 [10,11] (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

* Corresponding author. Tel.: +86 21 35303902; fax: +86 21 35303902.

E-mail addresses: qiangwu@shiep.edu.cn, imqiangwu@gmail.com (Q. Wu).

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 $\text{Ni}(\text{NO}_3)_2$ 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 $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ 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, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}:\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}:\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} = (1-x):x:1$, 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 $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ on silica fiber. For comparison, the immobilization of LaCoO_3 on silica fiber from CNfS templates was also prepared. The yield of the resulting $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ was calculated by the following equation: yield (%) = 100 × weight of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ /weight of silica fiber. In addition, the specific surface areas of the resulting $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ were calculated by subtracting the surface areas of pure silica fiber (~1 m² g⁻¹) from the total surface areas of the silica fiber immobilized- $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$.

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

The procedure for the immobilization of $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ on silica fiber is similar to that of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$. While the precursor

solution consisted of the desired amount of mixed metal nitrate (0.3 M as total metals, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}:\text{Mn}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}:\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} = 1:x:(1-x)$, 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 $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ on silica fiber. In addition, the yields and specific surface areas of $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ were calculated by using the similar method as $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$.

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-K α 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, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}:\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O} = 1:1$) 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

Fig. 1. (a) FE-SEM image of pure silica fiber, (b and c) FE-SEM images of CNFs immobilized on silica fiber, (d) cross-sectional TEM image of CNFs immobilized on silica fiber, and (e) TEM image of CNFs.

fiber was observed at $2\theta = 22.3^\circ$. In contrast, XRD measurements reveal that the predominant peak responsible for the diffraction of the graphite (0 0 2) plane was pretty clear for the obtained CNFs (Fig. 2b), indicating that CNFs were highly graphitized. It was found that the interplanar distance $d(002)$ values of CNFs were 0.337 nm, which is slightly higher than that of the ideal graphite (0.335 nm).

3.2. Characterization of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05, 0.1, 0.2$) perovskite-type oxides immobilized on silica fiber

As revealed by our previous studies [16,18], surface functionalization of silica fiber is a necessary prerequisite to getting mass

and uniform target materials immobilization on its surface, due to its very low surface area (ca. $1 \text{ m}^2 \text{ g}^{-1}$) and chemical inertness. Once silica fiber was functionalized with CNFs on its surface via CVD process, the surface area of the obtained composites material can be achieved at ca. $80 \text{ m}^2 \text{ g}^{-1}$, which can act as “sponge” and supply much more “reservation” room for the precursor solution than pure silica fiber does. Thus, CNFs immobilization on silica fiber can be adopted as the promising and effective templates for novel material coatings.

Immobilization of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05, 0.1, 0.2$) perovskite-type oxides on silica fiber was firstly characterized by FE-SEM measurements and the representative images are indicated in Fig. 3. The corresponding yield of the resulting A-sites substitution of LaCoO_3 perovskite-type oxides was calculated to be 146% for $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05$), 150% for $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.1$), and 148% for $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.2$), respectively (Table 1). As can be seen from Fig. 3, applying CNFs as templates, thick and uniform immobilization of the desired samples on silica fiber were demonstrated for each case, and there was no obvious difference in the morphologies among the as-prepared three samples. In addition, in the corresponding high magnification FE-SEM images (Fig. 3b, d and f), the typical nanofibrous structures of the immobilized samples with uniform morphology are clearly evident, and this unique nanofibrous structure material is well depicted with FE-SEM and TEM measurements in our previous papers [16,18]. Furthermore, the BET surface areas were calculated to be $15.6 \text{ m}^2 \text{ g}^{-1}$ for $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05$), $17.5 \text{ m}^2 \text{ g}^{-1}$ for $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.1$), and $20.8 \text{ m}^2 \text{ g}^{-1}$ for $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.2$), respectively (Table 1). It was worth noting that CNFs template method is a facile and economy fabrication technique for novel material formation on the substrate surface, and the resulting as-prepared materials basically duplicate the shapes of CNFs templates. Thus, it is reliable to control the properties of the resulting as-prepared material by tuning the formation of CNFs.

The phase purity and crystallinity of the as-prepared samples were further examined by XRD patterns and the results are shown in Fig. 4. As a reference, the XRD pattern of LaCoO_3 immobilized on

Fig. 2. XRD patterns of (a) pure silica fiber, and (b) CNFs immobilized on silica fiber.

Fig. 3. FE-SEM images of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ immobilized on silica fiber (a and b) $x = 0.05$, (c and d) $x = 0.1$, (e and f) $x = 0.2$.

silica fiber from CNFs templates was also indicated in Fig. 4a, whose diffraction peaks can be assigned to a perovskite-structured phase and no other feature were observed. Fig. 4b shows the XRD pattern of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05$) obtained from CNFs templates,

and all the diffraction peaks can be well indexed to the perovskite-structured phase. However, in cases of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.1, 0.2$) derived from CNFs templates (Fig. 4b and c), we can see that the main perovskite-structured phase coexisted with small minor impurity phase of CeO_2 (JCPDS 34-0394). That means the solubility of cerium metal in LaCoO_3 perovskite structure is relatively low, and it is possible to obtain single phase of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ perovskite oxides if x content was controlled below 0.05. In addition, two intense and well-resolved peaks were observed at around $2\theta = 33^\circ$ for LaCoO_3 sample (Fig. 5), and the separation of the two peaks became smaller with the increasing cerium content and eventually merged and shifted to higher angle, indicating that cerium metal was incorporated into the perovskite structure under the applied conditions.

3.3. Characterization of $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.2, 0.5, 0.8$) perovskite-type oxides immobilized on silica fiber

FE-SEM images in Fig. 6 exhibit $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.2, 0.5, 0.8$) perovskite-type oxides immobilized on silica fiber resulted from CNFs templates. Similarly, thick and uniform nanofibrous $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.2, 0.5, 0.8$) perovskite-type oxides was formed on

Table 1
Physicochemical properties of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ and $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$.

Sample	Yield ^a (%)	Phase identification ^b	BET surface areas ^c (m^2g^{-1})
$\text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3$	146	Single P	15.6
$\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$	150	P + CeO_2	17.5
$\text{La}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$	148	P + CeO_2	20.8
$\text{LaMn}_{0.2}\text{Co}_{0.8}\text{O}_3$	148	Single P	16.2
$\text{LaMn}_{0.5}\text{Co}_{0.5}\text{O}_3$	151	Single P	23.6
$\text{LaMn}_{0.8}\text{Co}_{0.2}\text{O}_3$	147	Single P	28.2

^a Yield (%) = $100 \times \text{weight of } \text{La}_{1-x}\text{Ce}_x\text{CoO}_3 \text{ (or } \text{LaMn}_x\text{Co}_{1-x}\text{O}_3) / \text{weight of silica fiber}$.

^b P, perovskite.

^c BET surface areas calculated by subtracting the surface areas of pure silica fiber ($\sim 1\text{ m}^2\text{g}^{-1}$) from the total surface areas of the silica fiber immobilized $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ (or $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$).

Fig. 4. XRD patterns of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ immobilized on silica fiber (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, (d) $x = 0.2$.

silica fiber, and there was no too much difference in the morphologies among the as-prepared three samples. Note that the corresponding yield of the resulting B-sites substitution of LaCoO_3 perovskite-type was 148% for $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.2$), 151% for $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.5$), and 147% for $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.8$), respectively (Table 1). Moreover, XRD patterns (Fig. 7) indicate that the as-prepared three samples show diffraction peaks in good agreement with perovskite-structured phase, without other detectable secondary phase. This is a confirmation of single phase $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.2, 0.5, 0.8$) perovskite-type oxides immobilized on silica fiber by using CNFs as templates. On the other hand, this result also exhibits that the solubility of manganese metal in LaCoO_3 perovskite structure is high, and it is easy to control the single phase formation of $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ perovskite oxides through the above mentioned method. In addition, as shown in Fig. 8, the separation of the two typical peaks (around $2\theta = 33^\circ$) became smaller with increasing manganese content and they were eventually merged above the manganese content of 0.5. Another observable phenomenon is that the peaks shifted to lower angle by increasing manganese content. These results demonstrate that the added manganese metal was incorporated into perovskite structure under the applied conditions [23]. In addition, the BET surface areas were calculated to be $16.2 \text{ m}^2 \text{ g}^{-1}$ for $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.2$), $23.6 \text{ m}^2 \text{ g}^{-1}$ for $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.5$), and $28.2 \text{ m}^2 \text{ g}^{-1}$ for $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.8$), respectively (Table 1).

3.4. Plausible immobilization mechanism

Plausible immobilization mechanism of uniform nanofibrous A- or B-sites substituted LaCoO_3 perovskite-type oxides on silica fiber is as follows: during the impregnation stage, the mixed metal precursor can rapidly diffuse into the whole layer of CNFs by capillary force. In this process, CNFs act as a “sponge”, it can supply enough “reservation” room for the precursor solution to fill the pores of its fibrous structure. By heating process, the precursor can undergo some chemical reactions: hydrolysis, and condensation or polymerization to form small perovskite-type mixed oxides particles, meanwhile, functional groups (such as $-\text{COOH}$, and $-\text{C}=\text{O}$) can be generated by nitrates oxidation on the surface of CNFs. Note that such functional group can serve as the anchor sites for the small metal oxide solid particles, thus would play an important

Fig. 5. XRD patterns of ($2\theta = 30\text{--}35^\circ$ extended) of $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ immobilized on silica fiber (a) $x = 0$, (b) $x = 0.05$, (c) $x = 0.1$, (d) $x = 0.2$.

role for coatings for the first cycle, but after the second coating cycle, the hydroxyl groups reproduced on the metal oxide surface can further act as the anchor sites for the metal precursors [24], just as effected in a typical sol-gel process. Over time, the small metal oxide solid particles can link together and three-dimensional networks can be formed. Finally, further calcination in air contributes to the removal of CNFs templates and the formation of the desired nanofibrous samples immobilized on silica fiber.

3.5. Catalytic activity

Catalytic activity of the immobilized nanofibrous $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05$) and nanofibrous $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.5$) perovskite-type oxides for carbon particle combustion was tested using the TG-DTA apparatus. Fig. 9 shows the TG-DTA curves of carbon black particles in the presence of the immobilized nanofibrous $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05$), nanofibrous $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.5$), as well as the reference samples of α -alumina and powder LaCoO_3 , under air flow (30 mL min^{-1}) and at a heating rate of 10 K min^{-1} . As for α -alumina (Fig. 9a), it was shown that the weight-loss of carbon black particles started at ca. 770 K, and T_{50} (temperature where half of the carbon black particles were burned) with α -alumina was 820 K. When using powder LaCoO_3 as a catalyst (Fig. 9b), it was found that the weight loss of carbon black particles started ca. 640 K, and T_{50} shifted to 750 K. In the case where the immobilized nanofibrous $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05$) was present as catalyst (Fig. 9c), the weight loss of carbon black particles was found to be decrease to ca. 600 K, and T_{50} shifted to 720 K. In term of the immobilized nanofibrous $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.5$) perovskite-type oxides acting as catalyst (Fig. 9d), it was shown that the weight loss of carbon black particles decreased to ca. 620 K, and T_{50} shifted to 730 K. From Fig. 9, we can infer that the catalytic performance of the immobilized nanofibrous $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05$) and nanofibrous $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.5$) was slightly higher than powder LaCoO_3 sample, and follows the order of immobilized nanofibrous $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05$) > immobilized nanofibrous $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.5$) > powder LaCoO_3 . The above results well demonstrated an advantage of nanofibrous $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05$) and $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.5$) perovskite-type oxides immobilization on silica fiber for the combustion of carbon black particles. This was in good

Fig. 6. FE-SEM images of $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ immobilized on silica fiber (a and b) $x = 0.2$, (c and d) $x = 0.5$, (e and f) $x = 0.8$.

agreement with the result in literature [25], where the immobilized nanofibrous LaMnO_3 catalyst was proved to take an advantage over the corresponding powder sample in soot combustion. In that literature, the author assumed that the immobilized nanofibrous LaMnO_3 catalyst has both function of trapping soot and combustion of soot, which is responsible for the high catalytic performance. In our case, we also think the unique nanofibrous morphology of samples plays a very important role in their high catalytic performance. Two reasons will be considered for its high catalytic activity in soot combustion, as for the obtained immobilized nanofibrous catalyst. One is that the pore is big enough to permit soot to enter their pores, and the other is that the macroporous network of the immobilized materials allows easy mass transfer and less diffusion resistance during catalytic reaction. And the detailed catalytic reaction mechanism requires further investigation. Thus it is rationally concluded that such

materials with direct macroscopic shapes would hold promise as highly functionalized materials for its practical applications in diesel exhaust treatment.

4. Conclusions

In summary, nanofibrous $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05, 0.1, 0.2$) and $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.2, 0.5, 0.8$) perovskite-type oxides with macroscopic shapes can be successfully prepared by using CNFs as sacrificial template. It is worthwhile to emphasize that the above strategy could be applicable to a large number of materials that possess direct macroscopic shapes. By tuning the formation of CNFs, it is possible to control the properties of the resulting novel materials. Furthermore, we have demonstrated that the immobilized nanofibrous $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05$) and $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.5$) perovskite-type oxides possess higher catalytic

Fig. 7. XRD patterns of $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ immobilized on silica fiber (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 0.8$.

Fig. 8. XRD patterns of ($2\theta = 30\text{--}35^\circ$ extended) of $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ immobilized on silica fiber (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 0.8$.

performance for the combustion of carbon black particles, which is a model of PM exhaust from diesel engines. Further attempts to fabricate a better PM combustion system are also under way.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21107069 and 21103106), the Shanghai Pujiang Program (12PJ1403800), the Innovation Program of Shanghai Municipal Education Commission (14ZZ153), the Open Project of Shanghai Key Laboratory of Rare Earth Functional

Fig. 9. TG-DTA curves of (a) α -alumina mixed carbon black, (b) powder LaCoO_3 mixed with carbon, (c) immobilized nanofibrous $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$ ($x = 0.05$) mixed with carbon black, and (d) immobilized nanofibrous $\text{LaMn}_x\text{Co}_{1-x}\text{O}_3$ ($x = 0.5$) mixed with carbon black.

Materials (Z-2011-050), and State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex (SCAPC201302).

References

- [1] N. Russo, D. Fino, G. Saracco, V. Specchia, *J. Catal.* 229 (2005) 459–469.
- [2] N. Guilhaume, B. Bassou, G. Bergeret, *Appl. Catal. B* 119 (2012) 287–296.
- [3] B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, *Catal. Rev.* 43 (2001) 489–564.
- [4] D. Fino, V. Specchia, *Powder Technol.* 180 (2008) 64–73.
- [5] Y.X. Wen, C.B. Zhang, H. He, Y.B. Yu, Y. Teraoka, *Catal. Today* 126 (2007) 400–405.
- [6] M. Oishi, K. Yashiro, K. Sato, J. Mizusaki, T. Kawada, *J. Solid State* 181 (2008) 3177–3184.
- [7] Y. Teraoka, K. Kanada, S. Kagawa, *Appl. Catal. B* 34 (2001) 73–78.
- [8] J.F. Xu, J. Liu, Z. Zhao, J.X. Zheng, G.Z. Zhang, A.J. Duan, G.Y. Jiang, *Catal. Today* 153 (2010) 136–142.
- [9] K. Taniguchi, N. Okinaka, T. Akiyama, *J. Alloys Compd.* 509 (2010) 4084–4088.
- [10] S. Cimino, R. Pirone, L. Lisi, *Appl. Catal. B* 35 (2002) 243–254.
- [11] J.F. Xu, J. Liu, Z. Zhao, C.M. Xu, J.X. Zheng, A.J. Duan, G.Y. Jiang, *J. Catal.* 282 (2011) 1–12.
- [12] N.M. Rodriguez, *J. Mater. Res.* 8 (1993) 3233–3250.
- [13] H. Cui, S.V. Kalinin, X. Yang, D.H. Lowndes, *Nano Lett.* 4 (2004) 2157–2161.
- [14] H.S. Qian, M. Antonietti, S.H. Yu, *Adv. Funct. Mater.* 17 (2007) 637–643.
- [15] H. Ogihara, M. Sadakane, Y. Nodasaka, W. Ueda, *Chem. Mater.* 18 (2006) 4981–4983.
- [16] H. Ogihara, M. Sadakane, Q. Wu, Y. Nodasaka, W. Ueda, *Chem. Commun.* 39 (2007) 4047–4049.
- [17] Q. Wu, H. Ogihara, M. Sadakane, Y. Nodasaka, W. Ueda, *Bull. Chem. Soc. Jpn.* 81 (2008) 380–386.
- [18] Q. Wu, H. Ogihara, M. Sadakane, Y. Nodasaka, W. Ueda, *Mater. Res. Bull.* 45 (2010) 1330–1333.
- [19] Q. Wu, H. Ogihara, M. Sadakane, Y. Nodasaka, W. Ueda, *J. Nanosci. Nanotechnol.* 10 (2010) 5431–5436.
- [20] K.K. Zhu, J.M. Sun, H. Zhang, J. Liu, Y. Wang, *J. Nat. Gas Chem.* 21 (2012) 215–232.
- [21] S. Takenaka, T. Kato, Y. Tomikubo, K. Otsuka, D.H. Lowndes, *J. Catal.* 219 (2003) 176–185.
- [22] K. Otsuka, S. Takenaka, H. Ohtsuki, K. Otsuka, *Appl. Catal. A* 273 (2004) 113–124.
- [23] J. Wang, Y.G. Su, X.Q. Wang, J.H. Chen, Z. Zhao, M.Q. Shen, *Catal. Commun.* (2012) 106–109.
- [24] H. Ogihara, M. Sadakane, W. Ueda, *Top. Appl. Phys.* 117 (2010) 147–158.
- [25] S.X. Li, R. Kato, Q. Wang, T. Yamanaka, T. Takeguchi, W. Ueda, *Appl. Catal. B* 93 (2010) 383–386.