

Synthesis of perovskite-type lanthanum cobalt oxide powders by mechanochemical activation method

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ABSTRACT: Lanthanum cobalt oxide (LaCoO₃) powders were prepared from mixtures of LaCl₃ · 7H₂O, CoCl₂, and Na₂CO₃ by grinding, heating, and washing operations. The reagents were mixed in a molar ratio of 1:1:2.5 in a planetary ball mill and milled at 300 rpm for 2 h. The milled samples were heated at various calcination temperatures and washed with distilled water. Thermogravimetric and differential thermal analysis were used to evaluate the optimum conditions for calcination. Phase formation was determined by X-ray diffraction (XRD) while specific surface area was measured by the BET method. The average particle size distribution was determined by a particle size analyser and morphology studied by scanning electron microscopy (SEM). The TG and DTA curves of the milled samples indicated that the formation of LaCoO₃ occurred at temperatures in the range of 600 °C to 800 °C. XRD patterns showed clearly the formation of the LaCoO₃ phase with perovskite-type structure at those temperatures. In addition, the results showed that the specific surface areas of the products decreased with increasing calcination temperature, while the average particle size D[4,3] increased. Furthermore, SEM micrographs demonstrated that the particles were in an agglomerated form with mean primary particle sizes in the range of 0.3–0.6 μm.

KEYWORDS: planetary ball mill, specific surface area, particle size, XRD, SEM

INTRODUCTION

The recent enforcement of severe emission controls in auto exhaust and of environmental standards in developing countries have prompted the development of catalytic converters for automobile and industrial emission control during the past decade. However, the most effective catalysts used to date are expensive conventional platinum/rhodium metals. Replacing these costly metal catalysts with cheaper materials has been an interesting and challenging research problem for technologists and material scientists¹. Therefore, many researchers have been searching for alternative materials as the active catalytic phase. One of the most promising active phase for environmental applications is the perovskite group of materials (ABO₃) where A and B are cations of different sizes. The catalytic properties of perovskite-type oxides depend mainly on the nature of the A and B ions and on their valence states². LaCoO₃ has many practical applications owing to its excellent physical and chemical properties and has been shown to have high catalytic activity for the oxidation of carbon monoxide, methane, propane,

hexane, and toluene. Thus, it can be used as a catalyst for combustion, automobile exhaust, and waste gas purification. Besides, it can be used as an electrode material for solid-electrode fuel cells and gas sensors³.

As the properties of the final materials obtained are strongly dependent on the method of preparation, it is essential to control the synthesis of homogeneous, highly pure, and high surface area LaCoO₃ materials. Since the activity of a catalyst strongly depends on its surface area, the development of a convenient method for the synthesis of LaCoO₃ with a sufficiently high specific surface area is also essential. The syntheses of LaCoO₃ powders have been achieved by several methods such as the conventional method based on solid-state reactions at high temperature. The main advantages of this method are its simplicity and the use of inexpensive oxides as starting materials, but it also has some drawbacks such as high reaction temperature, large particle size, and limited degree of chemical homogeneity. Other methods of preparation include the sol-gel process⁴, solid-state thermal decomposition of precipitated precursors⁵, flame hy-

drolysis of an aqueous solution⁶, Pechini and Schiff based methods⁷, amorphous heteronuclear complex decomposition synthesis⁸, the polymerizable complex method⁹, the molten chloride flux method¹⁰, the alkaline co-precipitation method¹¹, and electrochemical oxidation¹². These methods can produce fine and homogeneous particles with a high specific surface area but the processes are generally complicated and the reagents used are very expensive. To overcome these drawbacks, some researchers have developed another route based on mechanochemical activation for the synthesis of LaCoO₃ powders to produce nanoparticles and homogeneous particles. Recently, it has been reported that nanoparticle materials can be synthesized by this mechanochemical activation method^{13–15}. In this method, the chemical precursors undergo reactions, either during milling or during subsequent low temperature heat treatment, to form a composite powder consisting of fully dispersed nanoparticles embedded within a soluble salt by-product. The nanoparticles are then recovered by removing the salt by-product by a simple washing procedure.

Zhang et al^{16–18} have successfully synthesized a single perovskite phase of ABO₃ (A = La, Nd, Pr, Sm; B = Mn, Co, Fe, Ni) by grinding the mixture of constituent oxides using a planetary ball mill at room temperature. In this direct method for the synthesis of nanoparticle materials, it has been found that the reactivities of the starting oxides plays a significant role in the completion of the mechanochemical solid reaction. The reactivities of the starting oxides is found to be dependent on the preparation conditions and the reaction proceeds with the grinding time. The ground samples were formed with a single perovskite phase after a milling time of about 120–180 min but they were agglomerated giving large particles with low specific surface areas. Consequently, attempts have been made to increase the specific surface area of the final product by a combination method¹⁹. This method, which is termed the indirect method for the synthesis of nanoparticle materials, produced powders consisting of weak agglomerates which were well dispersed and which had high specific surface areas. Moreover, this combination method has been recommended as a novel mechanochemical approach for preparing nanoparticle materials.

The purpose of this present study was to synthesize LaCoO₃ powders from mixtures of LaCl₃ · 7 H₂O, CoCl₂, and Na₂CO₃ by the mechanochemical activation method. The microstructure, average particle size distribution, specific surface area, and morphology of the nanoparticles obtained have been investigated.

MATERIALS AND METHODS

Materials and preparation

The starting materials were LaCl₃ · 7 H₂O (Fluka, 99.0%), CoCl₂ (Sigma-Aldrich, 97%), and Na₂CO₃ (Fluka, 99.0%). The powders were dried at 70 °C in air for 2 h prior to use. The starting materials were mixed in a molar ratio of 1:1:2.5 before milling. A planetary ball mill (Retsch, PM 100) was used to mill the starting mixture at 300 rpm under atmospheric conditions. A 20 g portion of the mixture was placed in a stainless steel pot of 250 cm³ inner volume with 14 stainless steel balls of 20 mm diameter and milled for 2 h. The milled sample was calcined at 600, 700, and 800 °C at a heating rate of 10 °C/min for 90 min. After that, the calcined samples were washed with distilled water several times to remove the NaCl phase from the by-product. Then, 15 g of each calcined powder were dispersed in 300 ml of distilled water and stirred continuously with a magnetic stirrer for 1 h at room temperature. Subsequently, the samples were filtered and dried at 110 °C for 3 h and labelled as LaCoO₃_600, LaCoO₃_700 and LaCoO₃_800, respectively.

Characterization

The thermal behaviour of the milled samples was investigated by thermogravimetry from room temperature to 1000 °C in static air with α-Al₂O₃ as a reference. A simultaneous thermogravimetric and differential thermal analysis (TG-DTA) apparatus (Netzsch, STA 409 C/CD) at a heating rate of 10 °C/min was used. The milled, calcined, and washed samples were characterized by X-ray diffraction (XRD) analysis (Philips, X'Pert Pro MPD) using Cu-Kα radiation over the angular range of 2θ = 5° to 80° to identify the various phases present in the product. The average particle size distribution was determined using the laser diffraction method fitted with a wet sampling system (Malvern, Mastersizer S). The particle diameters reported were calculated using volume distribution (D[4,3]). The specific surface areas of the samples were measured by the BET nitrogen adsorption method (Quantachrome, Version 1.11) at the liquid nitrogen temperature using nitrogen gas as an absorbent. The samples were degassed at 120 °C for 4 h before BET analysis. The morphologies of the samples were observed by scanning electron microscopy (Jeol, JSM-6301F).

RESULTS AND DISCUSSION

Examples of the TG and DTA curves of the milled samples are shown in Fig. 1. In the TG curve, the

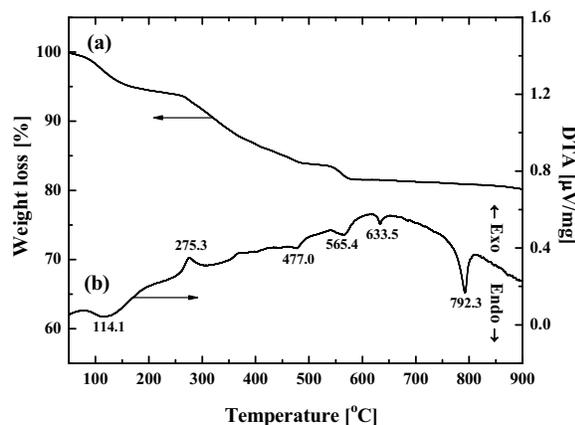


Fig. 1 TG-DTA curves of a sample after milling for 2 h: (a) TG curve and (b) DTA curve.

weight loss step of about 5.98% in the range of 90 °C to 160 °C accompanied by the endothermic peak at 114.1 °C in the DTA curve that can be ascribed to the loss of water (H₂O). In addition, the weight loss step of about 12.54% in the range of 250 °C to 570 °C accompanied by the exothermic peak at 275.3 °C in the DTA curve is due to the decomposition of the carbonates, and the endothermic peaks at 477.0 °C and 565.4 °C are attributed to the release of CO₂. The evaporation of H₂O and CO₂ are consistent with the overall reaction given below. In addition, the DTA curve also shows an endothermic peak at 633.5 °C, without accompanying weight loss, indicating the formation of a perovskite-type LaCoO₃ phase at this temperature¹⁹. The sharp endothermic peak at 792.3 °C corresponds to the melting of NaCl (the reference melting point of NaCl is about 801 °C)²⁰.

The XRD patterns of samples before and after milling for 2 h at a speed of 300 rpm are shown in Fig. 2. The XRD pattern in Fig. 2a shows only the peaks of the three starting materials: LaCl₃ · 7H₂O, CoCl₂, and Na₂CO₃. After milling, the intensities of these peaks decreased gradually until they disappeared completely after a milling time of 2 h. After milling, Fig. 2b clearly shows only the new peaks of NaCl which correspond to the standard powder diffraction pattern of NaCl (JCPDS file No. 05-0628). The appearance of this NaCl phase indicated that displacement reactions between chlorides and Na₂CO₃ occurred during milling and that other phases, such as various types of carbonate and possibly unreacted starting compounds, are present in the form of amorphous or minor phases in the ground product²⁰. The NaCl phase formed in the ground product plays an important role in the dispersion

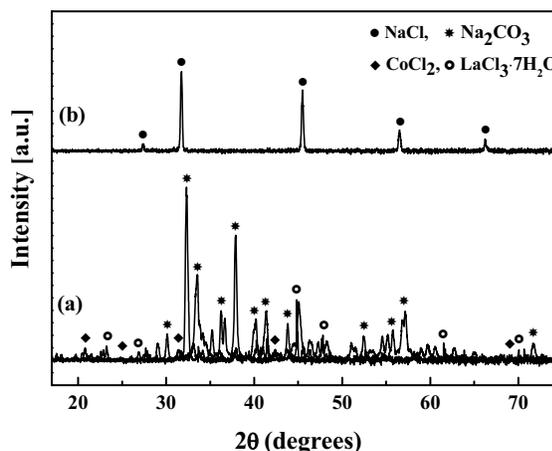
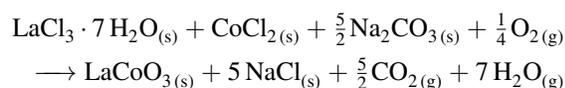


Fig. 2 XRD patterns of samples before and after milling: (a) starting mixture before milling and (b) sample milled for 2 h.

of the fine LaCoO₃ particles after subsequent heat treatment^{13, 14, 21}. This occurrence of this reaction indicated that the mechanochemical solid-state reaction can proceed during milling of the powder mixture of starting materials using a high-energy ball mill at room temperature^{22–24}. Moreover, the XRD patterns in Fig. 3 reveal new peaks of the LaCoO₃ phase after heat treatment at 600, 700, and 800 °C for 90 min which are associated with the NaCl phase. This indicates that a reaction between the starting materials occurred during calcination which can be represented by the following equation:



Normally, the LaCoO₃ phase is synthesized from the constituent oxides as starting materials by heating at around 1000 °C²⁵. In comparison, the temperature of about 600 °C used in this present work is considerably lower, which may be due to the mechanochemical effect induced by the milling. These results have therefore demonstrated that the LaCoO₃ phase can be synthesized successfully through this process.

Fig. 4 shows the XRD patterns of samples after washing with distilled water. It was found that only the main peaks of the LaCoO₃ phase together with minor impurities of Co₃O₄ are present for all conditions, indicating that the NaCl phase in the product was successfully removed by the washing and filtration operations. The XRD patterns also show sharper peaks with increasing calcination temperature,

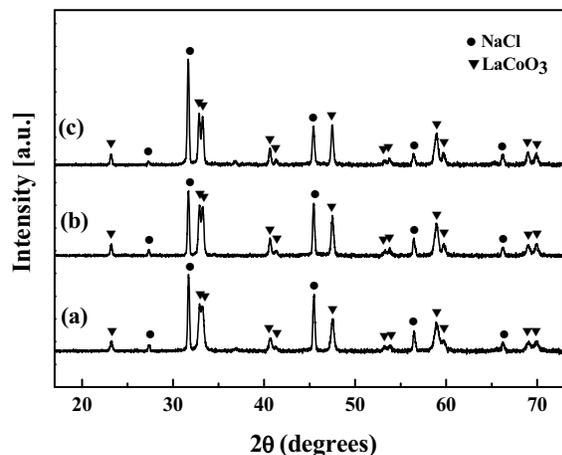


Fig. 3 XRD patterns of a milled sample after heat treatment at different temperatures: (a) at 600 °C, (b) at 700 °C, and (c) at 800 °C.

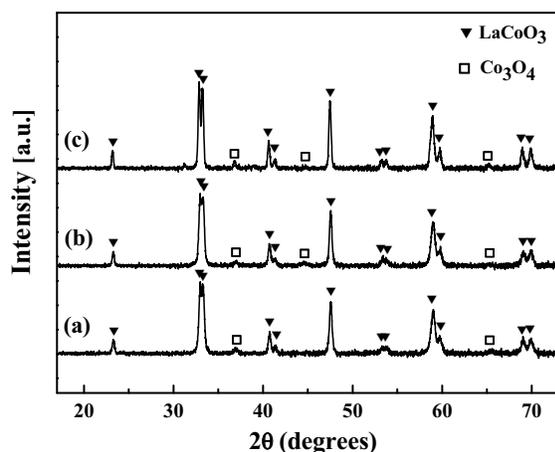


Fig. 4 XRD patterns of samples after heat treatment and washing with distilled water: (a) at 600 °C, (b) at 700 °C, and (c) at 800 °C.

suggesting that the powders were well crystallized after heat treatment. In addition, the peak positions and their relative intensities correspond to the standard powder diffraction pattern of a LaCoO_3 phase (JCPDS file No. 25-1060) with perovskite-type structure³.

The average particle size (D[4,3]) and specific surface area of a LaCoO_3 powder depend on the calcination temperature, (Fig. 5). The results show that the average particle sizes of the LaCoO_3 powders increased rapidly with increasing calcination temperature from 3.14 to 7.96 and 9.87 μm after calcination at 600, 700, and 800 °C, respectively (Fig. 5a). This is in accordance with the XRD patterns which

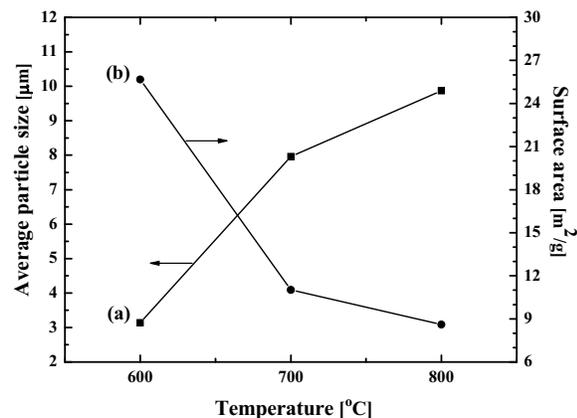


Fig. 5 Average particle size and specific surface area of samples after heat treatment and washing with distilled water: (a) average particle size and (b) specific surface area.

show slightly sharper peaks with increasing calcination temperatures, indicative of larger particles sizes. In contrast, the specific surface area decreased with increasing calcination temperature, decreasing from 25.67 down to 11.02 and 8.61 m^2/g after calcination at 600, 700, and 800 °C, respectively (Fig. 5b). The increasing average particle size and decreasing specific surface area are also confirmed by the SEM micrographs showing grain growth and increasing degree of particle agglomeration at higher temperatures.

The morphology of the samples was investigated by scanning electron microscopy (SEM). Fig. 6 shows the SEM images of the microstructures of the LaCoO_3 powders obtained by calcination at 600, 700, and 800 °C and after washing with distilled water. These SEM micrographs clearly demonstrate that the particles have different shapes from different calcination temperatures but are generally quite spherical and clustered together. The SEM micrographs also demonstrate what are obviously polycrystalline particles composed of many crystallites with a uniform grain size distribution and homogeneous microstructure. In addition, it was found that both the mean primary particle size and degree of agglomeration of the particles tended to increase with the calcination temperature. In Fig. 6a, the SEM micrograph of the LaCoO_3 _600 powder shows a mean primary particle size in the range of 0.3–0.4 μm with a low degree of agglomeration of the particles. However, Fig. 6b and c show the LaCoO_3 _700 and LaCoO_3 _800 powders to have mean primary particle sizes in the ranges of 0.4–0.5 μm and 0.5–0.6 μm , respectively, with higher degrees of agglomeration. The increases in primary particle size and degree of agglomeration were a result

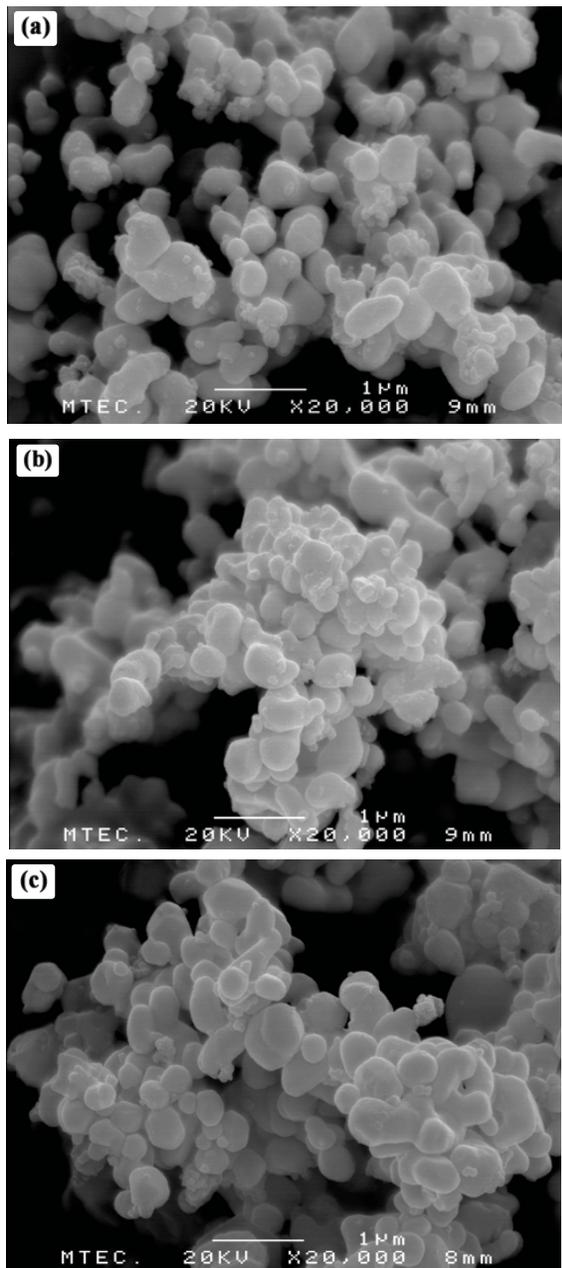


Fig. 6 SEM micrographs of samples after heat treatment at different temperatures and washing with distilled water: (a) at 600 °C, (b) at 700 °C, and (c) at 800 °C.

of the grain growth of the particles after calcination at high temperature.

CONCLUSIONS

LaCoO₃ powders can be synthesized from LaCl₃·7H₂O, CoCl₂, and Na₂CO₃ by milling, heating and washing operations (involving high-

energy ball milling and subsequent heat treatment at low temperatures). The XRD patterns of the samples clearly demonstrated the LaCoO₃ phase formation after heat treatment at 600, 700, and 800 °C, resulting in LaCoO₃ phases with perovskite-type structure. In addition, the LaCoO₃ powders can also be dispersed in a NaCl matrix after heat treatment, while the average particle size and specific surface area of the samples depended on the calcination temperature. Whereas the average particle size increased with increasing calcination temperature, the specific surface area decreased. Furthermore, SEM micrographs revealed spherical particles clustered together with an agglomerate size depending on the calcination temperature.

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