Influence of Soluble Salt Matrix on Mechanochemical Synthesis of Lanthanum Cobaltate Nanoparticles

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ABSTRACT

Mechanochemical reaction of lanthanum cobaltate ($LaCoO_3$) nanoparticles was performed by milling mixtures of $LaCl_3$, $CoCl_2$ and Na_2CO_3 with no addition and addition of soluble salt matrix (NaCl). The purposes of this work were to synthesize $LaCoO_3$ nanoparticles via mechanochemical process and to study the effect of soluble salt matrix on the average particle size and specific surface area. The three-stage process consisting of mechanical milling, subsequent heating and washing with distilled water was used to synthesize of $LaCoO_3$ nanoparticles. The results indicated that the average particle size (D[4,3]) and the specific surface area are as a function of the soluble salt matrix concentration. Moreover, SEM images revealed that the addition of soluble salt matrix can improve the dispersion of $LaCoO_3$ nanoparticles.

Key words: Mechanochemical; Lanthanum cobaltate; Soluble salt matrix; Nanoparticles.

INTRODUCTION

$LaCoO_3$ has many practical applications owing to its excellent physical and chemical properties. The $LaCoO_3$-based materials have been known to show high catalytic properties for oxidation of carbon monoxide, methane, hexane, and toluene[1-4]. Thus, it can be used as the catalyst for combustion, automobile exhaust and waste gas purification[5-7]. Moreover, it could be used as electrode materials for solid-electrode fuel cells and gas sensors[8,9]. The syntheses of $LaCoO_3$ have been achieved by many methods including conventional ceramic powder technology which leads to low the specific surface area, poorly active materials, requires high temperatures and long calcination periods. To overcome these limitations, several techniques were developed including sol–gel[4,6], amorphous heteronuclear complex decomposition synthesis[10], the polymerizable complex method[11], combustion synthesis[12], the molten chloride flux method[13], the alkaline coprecipitation method[14] and electrochemical oxidation[15]. These methods can provide products of fine and homogeneous particles with high the specific surface area, but the processes are generally complicated and the reagents used are very expensive.

Recently, mechanochemical processing has been used for the synthesis of ultrafine powders. In this process chemical precursors undergo reaction, either during milling or during subsequent

low temperature heat treatment, to form a composite powder consisting of fully dispersed ultrafine particles embedded within a soluble salt by-product. The ultrafine powder is then recovered by removing the salt by-product with a simple washing procedure. This technique has successfully been used to synthesize a wide variety of materials including transition metals[16], magnetic intermetallics[17], sulfide semiconductors[18], and oxide ceramics[19-21]. The mechanochemical processing technique allows significant control to be exercised over the characteristics of the final washed powder. For example, the average particle size can readily be controlled through the use of inert diluents and post-milling heat treatments. Furthermore, the simultaneous formation of ultrafine particles with an intervening salt matrix suggests that agglomerate formation can more readily be avoided than is possible with other synthesis techniques since the salt matrix inherently separates the particles from each other during processing. In addition, Achimovièová *et al.*[22] have been reported that the effect of soluble salt matrix on the nanoparticles of lead sulphide (PbS) prepared by mechanochemical processing. In this study revealed that the addition of soluble salt matrix can be improved the specific surface area, the average particle size and homogeneity of PbS particles were synthesized.

The purpose of this research was to study of the effect of soluble salt matrix addition on the average particle size and the specific surface area

of $LaCoO_3$ nanoparticles which synthesized by mechanochemical method.

EXPERIMENTAL
Materials and synthesis

Starting materials used in the experiment were $LaCl_3$ (Fluka, 99.0%), $CoCl_2$ (Sigma-Aldrich, 97%), Na_2CO_3 (Fluka, 99.0%) and NaCl (Merck, 99.9%). All the starting materials were dried at 80°C for 2 h. The NaCl was used as soluble salt matrix and added to the starting powders at different concentrations. The mixture of starting powders was milled by planetary ball mill (Retsch, PM 100) at speed 300 rpm under atmospheric. The mechanochemical processing was used to synthesis of $LaCoO_3$ nanoparticles under condition with no addition of soluble salt matrix and performed according to the equation (1). On the other hand, the addition of soluble salt matrix was performed according to equations (2) and (3). The weight and the molar ratio between the reactants were selected empirically in the initial powder mixture.

Twenty grams mixture was put in a stainless steel pot of 250 cm^3 inner volume with fourteen stainless steel balls of 20 mm diameter and milled for 2 h. The ground sample was calcined at 600°C with a heating rate of 10°C/min for 90 min, followed by washing with distilled water to remove NaCl phase from by-product. Then, the sample was dried in an oven at 110°C for 2 h.

$$LaCl_3 + CoCl_2 + 2.5Na_2CO_3 + 0.25O_2 \rightarrow LaCoO_3 + 5NaCl + 2.5CO_2 \qquad (1)$$
$$LaCl_3 + CoCl_2 + 2.5Na_2CO_3 + 0.25O_2 + 2NaCl \rightarrow LaCoO_3 + 7NaCl + 2.5CO_2 \qquad (2)$$
$$LaCl_3 + CoCl_2 + 2.5Na_2CO_3 + 0.25O_2 + 4NaCl \rightarrow LaCoO_3 + 9NaCl + 2.5CO_2 \qquad (3)$$

Characterizations

The milled, calcined and washed samples were characterized by X-ray diffraction analysis (Philips X'Pert), using Cu-Kα radiation in an angular range from $2\theta = 5°$ to 80°, to identify the phases existing in the product. The average particle size was determined using a laser diffraction method fitted with a wet sampling system (Mastersizer S, Malvern), this particle diameter reported was calculated using volume distribution ($D^{4,3}$). The specific surface area (SSA) of the sample was measured by a nitrogen gas adsorption instrument

(Quantachrome, Version 1.11) based on the BET method. Morphology and microstructure of the prepared sample was observed by scanning electron microscope (SEM) and analyzed the chemical composition by energy dispersive spectrometer (EDS) technique (JSM-6301F, JEOL).

RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of samples before and after milled at speed 300 rpm for 2 h by grinding mixture of $LaCl_3$, $CoCl_2$ and Na_2CO_3. Fig.
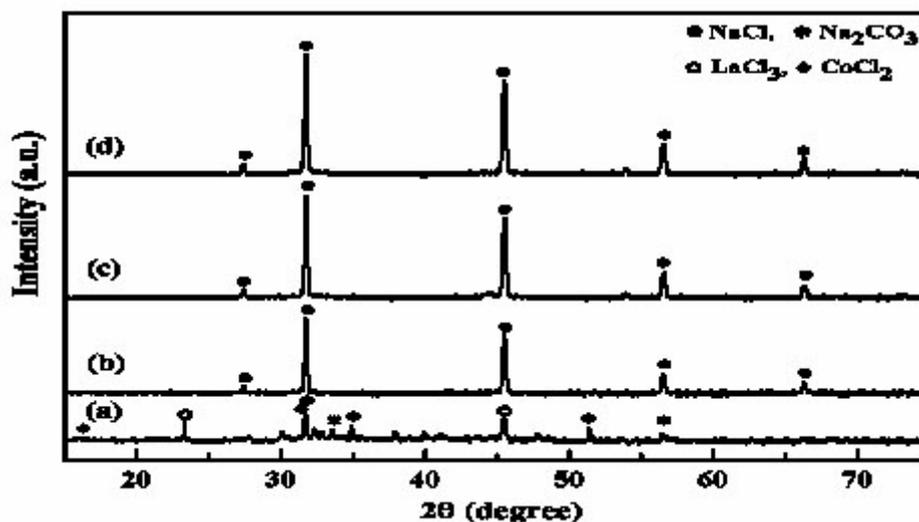
Fig. 1: XRD pattern of reactant mixture and milling samples; (a) starting mixture before milling, (b) no addition of soluble salt and milled for 2 h, (c) addition of 2 mol soluble salt and milled for 2 h and (d) addition of 4 mol soluble salt and milled for 2 h

1(a) shows peaks which associated with $LaCl_3$, $CoCl_2$ and Na_2CO_3 mixture before milling and their peaks intensity decrease gradually and vanished after milled for 2 h. However, Fig. 1(b) shows XRD pattern of sample with no addition of soluble salt matrix accorded to the reaction equation (1). It clearly shows the new peaks of NaCl and these peaks correspond to the standard powder diffraction patterns (JCPDS) of NaCl file No. 05-0628. The appearance of the NaCl phase indicated that displacement reactions between $LaCl_3$, $CoCl_2$ and Na_2CO_3 occurred during milling and 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 product[23]. This reaction occurred indicates that the mechanochemical (MC) solid-state reaction can be proceeded by grinding mixture of starting material powders using a high-energy ball mill at room temperature[19,24-26]. In addition, the NaCl phase was formed in the ground product and it plays a big role to disperse or enable well separate nanoparticles of $LaCoO_3$[27]. Moreover, XRD pattern of sample with addition of soluble salt matrix at the different concentrations which accorded to the reactions equations (2) and (3) also shows high intensity of NaCl diffraction peaks as shown in Figs. 1(c) and 1(d). Increasing of the intensity peaks were

increased the concentration of soluble salt matrix addition, this resulted due to increase in the crystalline volume fraction of NaCl which added into the initial starting mixture during the grinding process[28].

Fig. 2 shows XRD pattern of samples after milled and calcined at 600°C for 90 min. The XRD pattern of all samples clearly revealed the new peaks of $LaCoO_3$ which were observed after heat treatment and associated with the NaCl phase. These results indicate that the reaction between the starting materials occurred during calcinations which can be given by equations (1)-(3). The presence of $LaCoO_3$ phase after heat treatment as shown in Figs. 2(a), 2(b) and 2(c), indicates that the milling of starting powders by mechanochemical processing leads to form of desired phase at low temperature (600°C)[27-30].

Fig. 3 shows XRD pattern of samples after washed with distilled water. It was found that the peaks of $LaCoO_3$ are present in all conditions and do not have any impurities. Therefore, it can be concluded that the NaCl phase in the by-product was removed out by the washing operation[27,28]. Moreover, the intensity of $LaCoO_3$ peaks show slightly broadening peak and decrease gradually
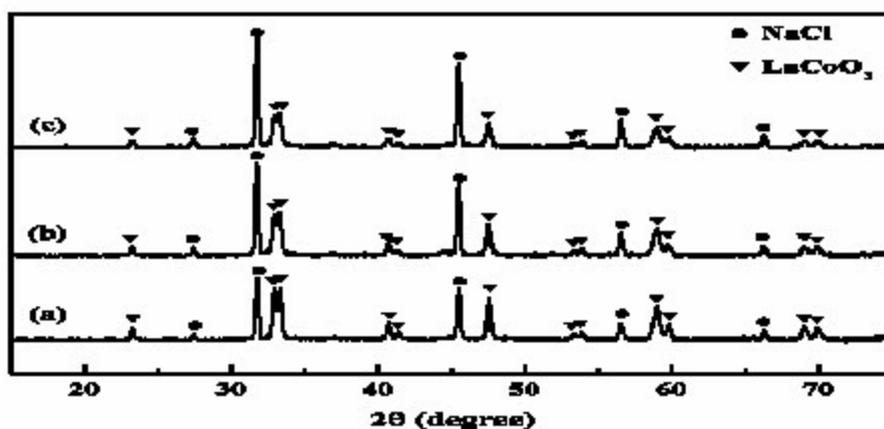
Fig. 2: XRD pattern of samples after milled for 2 h and heated at 600°C; (a) no addition of soluble salt matrix, (b) addition of 2 mol NaCl and (c) addition of 4 mol NaCl
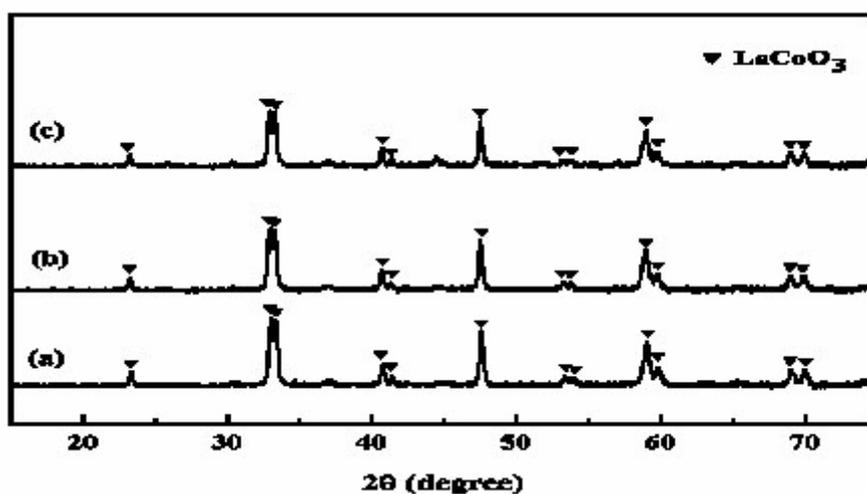
Fig. 3: XRD pattern of samples after washed with distilled water; (a) no addition of soluble salt matrix, (b) addition of 2 mol NaCl and (c) addition of 4 mol NaCl

with an increasing in concentrations of soluble salt matrix addition as shown in Figs. 3(a), 3(b) and 3(c). Decreasing of the intensity attributed that the NaCl phase within the starting powders can be prevent reaction occurring, due to the soluble salt matrix separate the reactants, reducing the reaction volume between the reactant particles, leading to a decrease in reaction rate and the rate of heat generation in the calcination process[25,28]. Furthermore, the XRD patterns of $LaCoO_3$ peaks correspond to the standard powder diffraction patterns (JCPDS) file No. 25-1060 with perovskite-type structure.

Table 1 shows the effect of soluble salt matrix addition on the average particle size ($D^{4,3}$) and the specific surface area of samples. The results show that the average particle size and specific surface area of samples depend on the concentration of soluble salt matrix which added in the initial reactants mixture. The average particle size was decreased with increased in the

Table 1: Average particle size and specific surface area of samples

Samples	Average Particle Size ($D^{4, 3}$) (μm)	Specific Surface Area (m^2/g)
$LaCoO_3$	3.14 ± 0.02	25.67 ± 0.01
$LaCoO_3$ + 2NaCl	2.94 ± 0.02	26.93 ± 0.01
$LaCoO_3$ + 4NaCl	2.63 ± 0.02	27.48 ± 0.01
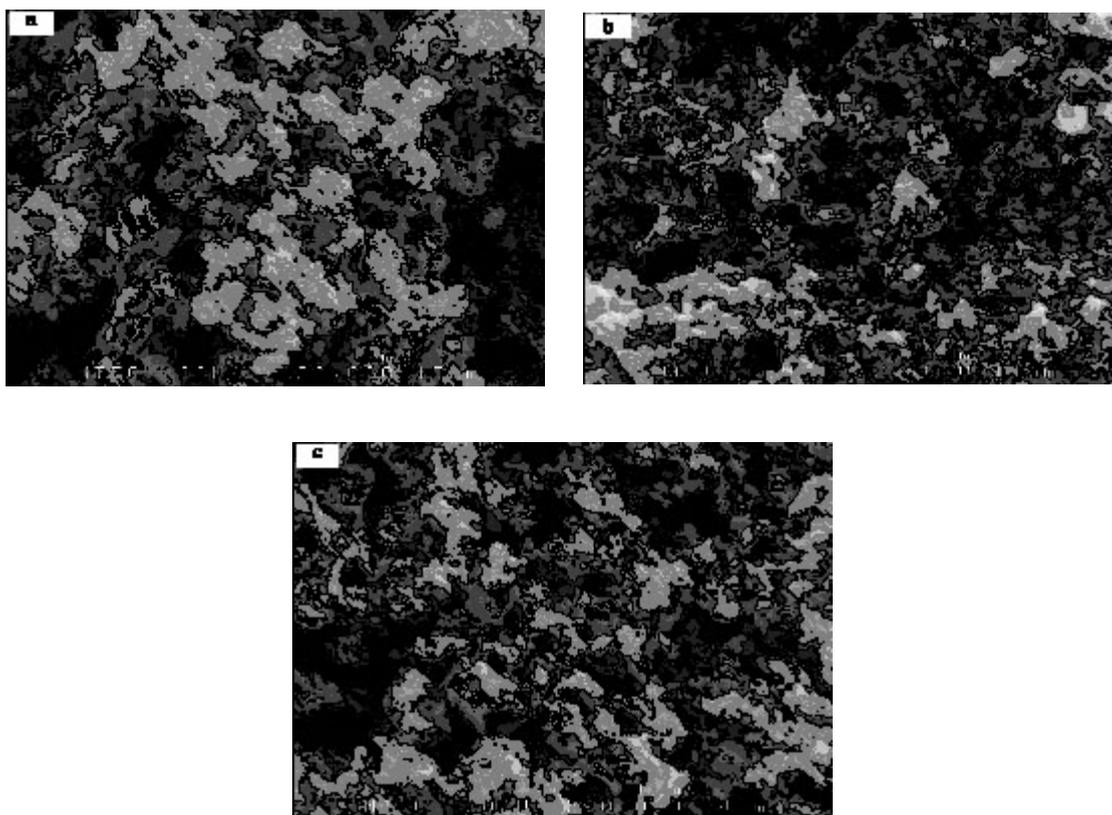
Fig. 4: SEM micrograph of samples after washing; (a) no addition of soluble salt matrix, (b) addition of 2 mol NaCl and (c) addition of 4 mol NaCl

concentration of NaCl, while specific surface area was increased. The results are accordance with previously studies of Dodd and McCormick[28] and Hector *et al.*[31] which found that the addition of soluble salt matrix to the reactant mixtures can be reduced the average particle size and crystallite size. The average particle size of $LaCoO_3$ with no addition of soluble salt matrix is 3.14 mm, while the samples with addition of 2 mol NaCl and 4 mol NaCl decrease down to 2.94 and 2.63 mm,

respectively. On the other hand, the specific surface areas were increased from 25.67 up to 26.93 and 27.48 m^2/g when addition of 2 mol NaCl and 4 mol NaCl, respectively. Decreasing of the average particle size and increasing the specific surface area due to the effect of soluble salt matrix in the initial reactant mixture. The salt matrix is not only separate the $LaCoO_3$ particles to prevent agglomeration, but also enable well dispersed of $LaCoO_3$ particles after calcinations[24,25,28].

The morphology of samples after washing was investigated by scanning electron microscope (SEM). SEM images clearly illustrated that the significant influence of the soluble salt matrix addition can improve the dispersion of $LaCoO_3$ nanoparticles. These results indicated that the existence of soluble salt matrix phase in the initial reactant mixture will prevent the agglomeration of particles or separate the $LaCoO_3$ nanoparticles during calcination. Fig. 4(a) shows SEM micrograph of the $LaCoO_3$ nanoparticles which no addition of soluble salt matrix, is comprised of highly agglomerate particles. In the contrary, Figs. 4(b) and 4(c) show SEM micrographs of $LaCoO_3$ nanoparticles which addition of 2 mol NaCl and 4 mol NaCl show loosely agglomerated of particles and clearly separate of particles. Furthermore, EDS spectrums as shown in Fig. 5 illustrated evident peaks of La, Co and O which accord to chemical elements of $LaCoO_3$ nanoparticles.
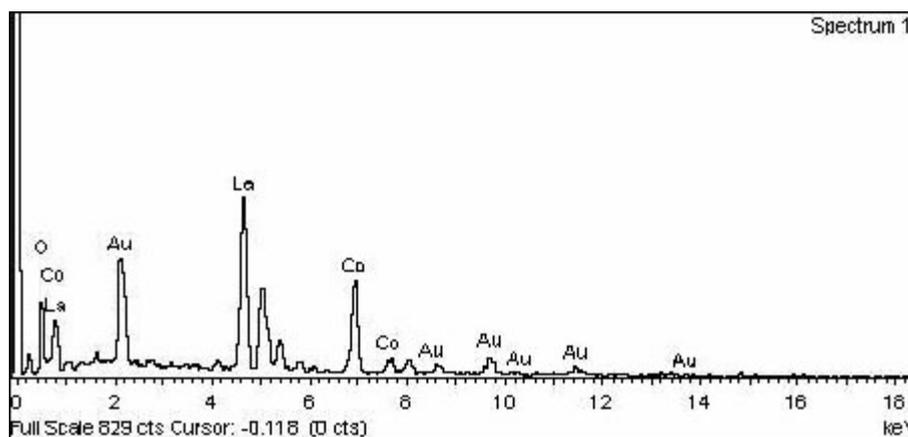
Fig. 5: EDS spectrums of LaCoO$_3$ after washing

CONCLUSIONS

$LaCoO_3$ nanoparticles can be successfully prepared by heat treatment of the milled powder obtained by mechanochemical reaction of $LaCl_3$, $CoCl_2$, and Na_2CO_3 with NaCl as a soluble salt matrix. The soluble salt matrix can separate and prevent the agglomeration of $LaCoO_3$ nanoparticles after calcinations at 600°C. The addition of the soluble salt matrix in the reactant mixture can reduce the average particle size and increase the specific surface area. Moreover, SEM micrographs show loosely agglomerate nanoparticles.

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