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Synthesis and microstructure of $La_{1-x}Ca_xCoO_3$ nanoparticles and their catalytic activity for CO oxidation

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Abstract

Perovskite nanoparticles of $La_{1-x}Ca_xCoO_3$ ($x = 0$, 0.2, 0.3, 0.5) were synthesized by the combustion method using polyvinyl alcohol (PVA) and corresponding metal nitrates. Microstructure of samples was characterized by high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) combined with x-ray diffraction (XRD). The nanoparticles were characterized by thermogravimetric and differential thermal analysis (TG-DTA) and BET (Brunauer–Emmet–Teller). A high surface area (15–21 $m^2\,g^{-1}$) at low temperature (600 °C) of samples was obtained. The optimal preparative conditions were PVA/metals 2:1 by mole, pH = 3 and 80 °C for gel formation. Perovskites exhibit a good catalytic activity in total oxidation of CO at the low temperature (<250 °C) of reaction.

Keywords: nanoparticles, catalytic properties, microstructure, TEM, SAED
Classification numbers: 4.02, 5.06, 5.07

1. Introduction

The use of automobiles has increased exponentially day by day, and hence also the tremendous increase in emissions of CO, HC, NO_x particulate matters etc. These pollutants have negative impact on air quality, environment and human health leading to stringent norms of pollutant emission. Perovskite type oxides of general formula ABO_3 (A is lanthanide and/or alkaline earth metal ion and B is transition metal ion) promising alternatives to support noble metals have attracted much attention for exhaust gas depollution because of their low cost, thermal stability at rather high temperatures, great versatility and excellent redox properties [1]. The quality such as the crystalline structure, grain size and morphology of a material depends on the synthetic approach and doping metal ion. Of perovskites, $LaCoO_3$ as well as compounds with an alkali-earth element partly substituted for La was found to be one of the most active catalysts in conversion of pollutant [2, 3].

For the synthesis of perovskite at low temperature with small particle size and large specific square area, heterogeneous catalysis is very interesting. Conventionally, perovskites were synthesized via solid state reaction by heating constituent metal carbonates, or sometime precipitates (co precipitation method). The method required heating of the solid reactants at high temperature, usually higher than 1000 °C, so the specific surface area is low (<5 $m^2\,g^{-1}$) [4–6].

In recent years, combustion synthesis (CS) has become an effective, low cost method for production of various industrially useful materials. Today, CS has become a very popular approach for preparation of nanomaterials. The extensive research carried out in the last five years emphasized the CS capabilities for materials improvement, energy saving and environmental protection [5, 7, 8].

In this paper we present the results of a study on microstructure and their catalytic activity for CO oxidation of $La_{1-x}Ca_xCoO_3$ ($x = 0$, 0.2, 0.3 and 0.5) perovskites which

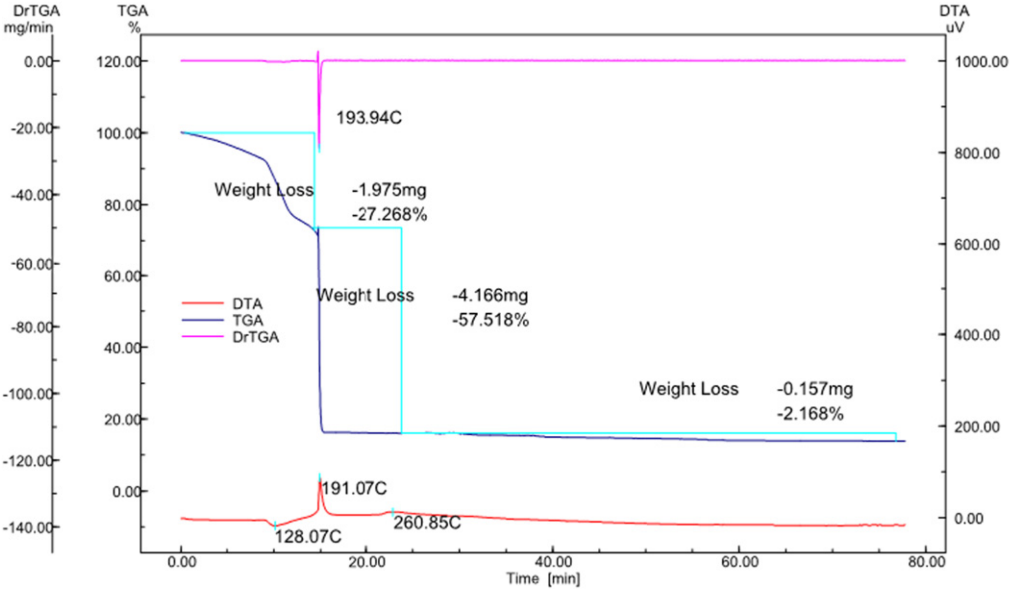

Figure 1. TGA-DTA curves of gel sample prepared under the conditions: temperature 80 °C, pH = 3 and PVA/metal mole ratio of 3:1.

were synthesized by combustion method using polyvinyl alcohol (PVA) and metal nitrates.

2. Experimental

The metal nitrate solutions in the predetermined molar ratio La:Ca:Co were mixed with the PVA solution (PVA/metal mole ratio of 3:1). The solution pH is adjusted to about 3 with NH_3 and HNO_3 solutions. The mixture was magnetically stirred at 80 °C. As water was evaporated, the solution turned into a very viscous gel. After drying, gel was further heated to form crystal phase.

The structures of nanocrystallites were characterized on an x-ray diffractometer (XRD) Bragg-Brentano with Cu-Kα in the range $2\theta = 20$–$80°$ with a step size = 0.02. The grain size, grain distribution and morphology of all the samples were analyzed and estimated by means of a high resolution transmission electron microscope (HRTEM) Philip CM20-FEG operated at 200 kV and a Hitachi H-8100 operated at 200 kV by using the bright field transmission electron microscopy (BF-TEM), dark field transmission electron microscopy (DF-TEM) and HRTEM images. The structure of nanocrystallites was also characterized by selected area electron diffraction (SAED) technique. The energy dispersive x-ray (EDX) spectrum of the oxides was obtained by EDAX equipment attached to the Hitachi H-8100 TEM. The sample preparation for TEM and SAED investigations was done by using an amount of about 5 mg of the powder dissolved in the solvent ethanol (99%). This solution was continuously stirred by using the ultrasonic machine for 30 min. After that a drop of solution was dropped on a Cu grid, which was covered by a carbon film of about 5 nm. Finally, the sample was dried in a clean box at 60–70 °C.

The thermal analysis was performed on a TGA/DTA Analyzer DTG 60 H (Shimadzu, Japan) in air with the heating rate of 10 °C $\min^{-1}$. The BET specific surface areas were determined by nitrogen adsorption at 77 using Autosorb iQ Station 1 instrument (Quantachrome Instruments, USA), operating in a multi-point mode.

Activity tests for catalytic oxidation of CO over $La_{1-x}Ca_xCoO_3$ nanomaterials were performed in a continuous-flow fixed-bed reactor containing 100 mg of catalyst samples. A standard reaction gas containing 396 ppm CO and 20% (V/V) O_2 in N_2 was fed with a total flow rate of 3 l h^{-1}. The concentration of CO in the reaction gas was controlled by the flow rate of nitrogen and were analyzed online using Lancom II. The conversion of CO was calculated as follows

$$X\,(\%) = \frac{C_{\mathrm{CO(in)}} - C_{\mathrm{CO(out)}}}{C_{\mathrm{CO(in)}}} \times 100\%,$$

where $C_{\mathrm{CO(in)}}$, $C_{\mathrm{CO\ (out)}}$ are the concentrations of CO in the inlet and outlet, respectively.

The effect of temperature on CO conversion was studied by increasing the reactor temperature from 100 °C to 300 °C.

3. Results and discussion

The pyrolysis of the gel-precursor was monitored by thermal analyses, as in figure 1. According to the TGA curve, the weight loss terminated around 400 °C. Before 150 °C, the weight loss of about 27.3% was associated with the removal of residual water. In the range of temperature 150–200 °C, the weight loss (accompanying exotherms in the DTA thermogram) showed the ashes of PVA being left in the gel with nitrates acting as an oxidizer. During the combustion, large amounts of gases such as H_2O, CO, CO_2 and NO were released. For temperatures higher than 200 °C, the weight remains nearly constant and the sample can be considered to consist completely of crystalline phase.

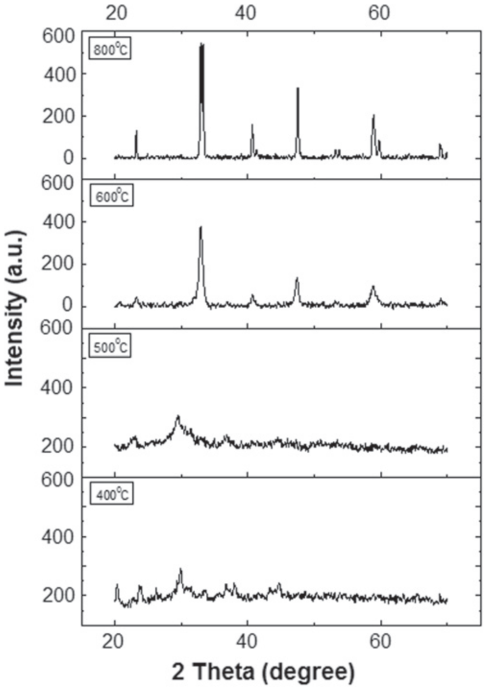

Figure 2. XRD patterns of, $La_{1-x}Ca_xCoO_3$ with $x = 0$ samples prepared by heating the precursor at designated temperature for 60 min.

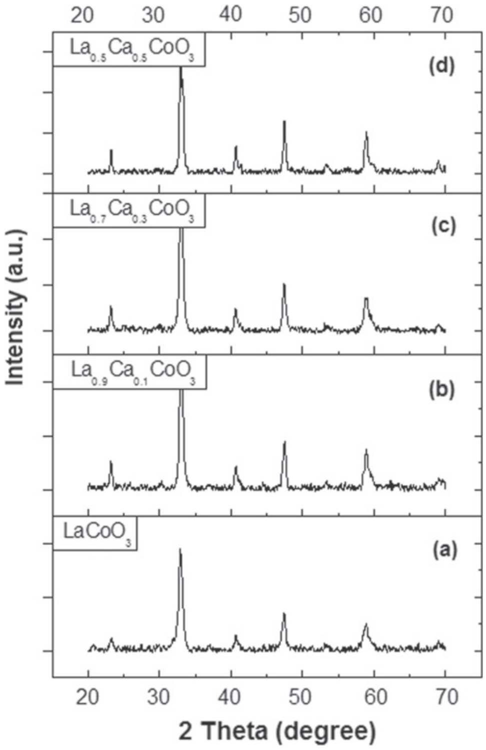

Figure 3. XRD patterns of the $La_{1-x}Ca_xCoO_3$ samples prepared with different Ca contents: (a) $x = 0.00$, (b) $x = 0.1$, (c) $x = 0.3$ and (d) $x = 0.5$.

To find the heating temperature for formation of perovskite phase, gels with PVA/metal mole ratio of 3:1 were prepared at 80 °C, pH = 3, gel formation temperature 80 °C, followed by annealing at 300, 400, 600 and 800 °C, respectively. Figure 2 presents XRD patterns of the obtained powders. Heating in the temperature range from 400–500 °C results in an amorphous pattern. The samples above 500 °C gave the characteristic XRD pattern of perovskite phase (PDF card 01-075-0279).

From the results above, $La_{1-x}Ca_xCoO_3$ with $x = 0$, 0.1, 0.3, 0.5 was synthesized under gel formation temperature of 80 °C, PVA/metal mole ratio of 3:1, annealing temperature of 600 °C for 60 min and pH = 3. The XRD patterns of $La_{1-x}Ca_xCoO_3$ are shown in figure 3. All the samples have the cubic system structure of $LaCoO_3$ from PDF card 01-075-0279. No traces of impurity peaks other than $LaCoO_3$ were observed. These confirmed the formation of single phase of hexagonal $LaCoO_3$ in all the samples.

The particle sizes and morphologies of $La_{1-x}Ca_xCoO_3$ nanoparticles prepared at different conditions have been determined by means of bright field transmission electron microscopy (BF-TEM), dark field transmission electron microscopy (DF-TEM) and HRTEM imaging. Morphology and particle size of nanoparticles of $La_{1-x}Ca_xCoO_3$ were found to be greatly affected by calcination and also Ca concentration. Figure 4 shows BF-TEM images of of $La_{1-x}Ca_xCoO_3$ samples with $x = 0$, $x = 0.3$ and $x = 0.5$ (figures 4(a)–(c), respectively) synthesized under conditions at: pH = 3, PVA/metal mole ratio = 3:1 and annealing at 600 °C for 60 min, respectively. The inset figures in the BF-TEM images are corresponding SAED patterns. Average particle sizes of $La_{1-x}Ca_xCoO_3$ samples annealed at 600 °C for 60 min, as estimated from the BF-TEM and DF-TEM images, are 27, 25, 20 and 23 nm for $x = 0$, 0.2, 0.3 and 0.5, respectively. The morphology of crystalline particles appeared in two types: sphere and peanut-bulb. The sphere-shaped particles were mainly found in the samples with $x = 0.2$ and $x = 0.3$ (figure 4(b)). The other shape was found in the samples with $x = 0$ and $x = 0.4$ (figures 4(a) and (c)). Figure 4(d) is the radial distribution of the diffracted intensity (analyzing from SAED pattern by Beugung software) for the sample with $x = 0.3$. The diffracted peaks in this distribution are corresponding to (012), (110), (104), (202), (024), (122), (214) and (208) lattice planes of perovskite crystalline phase ($a = 0.407$ nm). The diffracted rings of SAED patterns shown in the inset figures of figures 4(a)–(c) are similar, which means the crystalline phase in the samples is the perovskite phase.

EDX analysis was used to determine the composition of the samples. Energy dispersive x-ray spectra (EDXS) of some grains taken from both undoped (sample with $x = 0$) and Ca-doped (sample with $x = 0.3$) samples annealed at 600 °C are shown in figure 5. It shows peaks corresponding to Co, La and O in the spectrum of the undoped sample (figure 5(a)) and peaks corresponding to Co, La, O and Ca in the spectrum of the sample with $x = 0.3$ (figure 5(b)); no trace amount of other impurities could be seen within the detection limit of the EDXS. The result of quantitative analysis from the spectra is presented in the table 1. These results correspond to the $LaCoO_3$ (figure 5(a)) and $La_{0.7}Ca_{0.3}CoO_3$ (figure 5(b)) composition, respectively. The quantitative analysis is consistent with the synthesis conditions. The specific surface areas

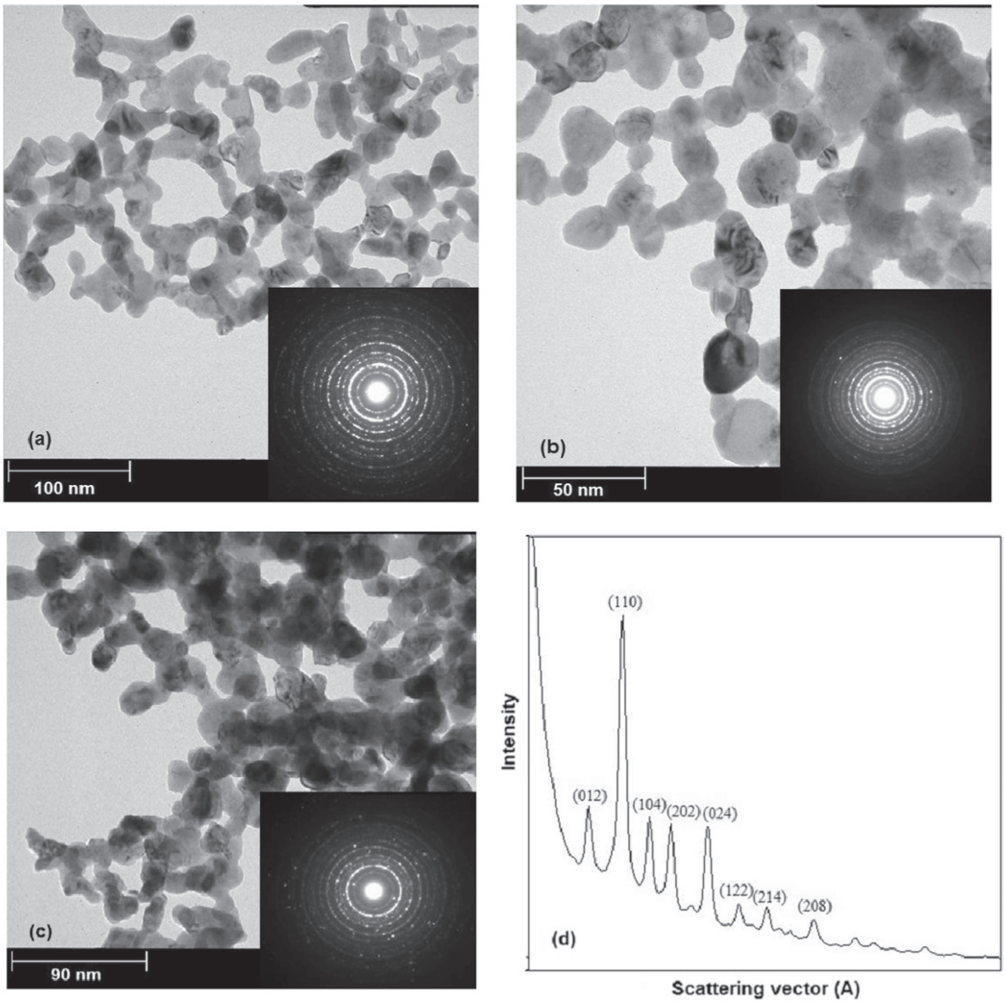

Figure 4. BF-TEM micrographs of $La_{1-x}Ca_xCoO_3$ nanoparticles with (a) $x = 0$, (b) $x = 0.3$ and (c) $x = 0.5$ synthesized under conditions at: pH = 3, PVA/metal mole ratio = 3:1 and annealing at 600 °C for 60 min, respectively, and corresponding SAED patterns (inset figures) and radial intensity distribution of SAED for sample with $x = 0.3$ (d).

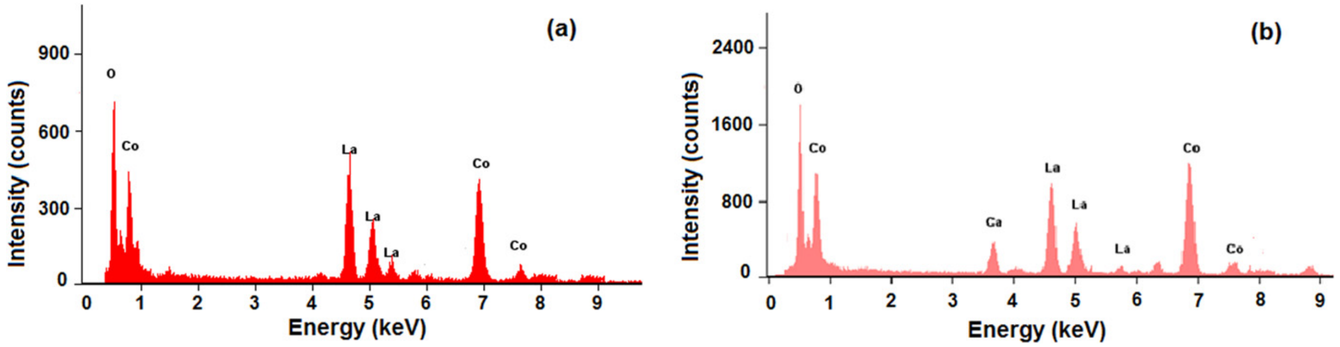

Figure 5. Energy dispersive x-ray (EDX) spectra of $La_{1-x}Ca_xCoO_3$ samples with $x = 0$ (a) and $x = 0.3$ (b).

(BET) of the $La_{1-x}Ca_xCoO_3$ ($x = 0$, 0.2, 0.3 and 0.5) samples are listed in table 2.

The CO oxidation over catalysts was investigated in the temperature range of 100–300 °C (figure 6). The results show that the catalytic activity of perovskites was performed as a function of temperature. The catalytic activity of Ca doped $LaCoO_3$ (for samples with $x = 0.2$, 0.3 and 0.5) catalyst for the oxidation of CO is higher than that of pure $LaCoO_3$. Among all studied catalysts for CO conversion of $La_{0.7}Ca_{0.3}CoO_3$ sample is the most active one.

4. Conclusion

The combustion method was successfully applied to synthesize Ca-doped $LaCoO_3$ nanoparticles with different sizes from

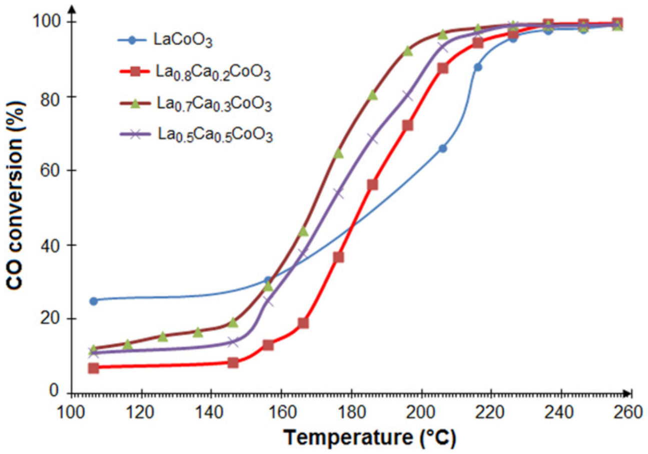

Figure 6. CO conversion as function of temperature for $La_{1-x}Ca_xCoO_3$ nano perovskites synthesized under conditions at: pH = 3, PVA/metal mole ratio = 3:1 and annealing at 600 °C for 60 min.

Table 1. Composition of $La_{1-x}Ca_xCoO_3$ samples with $x = 0$ and $x = 0.3$.

	Weight %		Atomic %	
Element	$x = 0$	$x = 0.3$	$x = 0$	$x = 0.3$
La	56.2	46.5	19.9	15.1
Ca	0	5.2	0	5.8
Co	24.7	27.3	20.6	20.1
O	19.4	21.2	59.5	59.0

Table 2. Measured BET surface areas of $La_{1-x}Ca_xCoO_3$ samples.

Samples	BET ($m^2\ g^{-1}$)	Average grain size (nm)	Annealing temperature (°C)
$LaCoO_3$	15.5	27	600
$La_{0.8}Ca_{0.2}CoO_3$	19.6	25	600
$La_{0.7}Ca_{0.3}CoO_3$	20.5	20	600
$La_{0.5}Ca_{0.5}CoO_3$	17.0	23	600

polyvinyl alcohol and metal nitrate by varying the calcination temperature and Ca concentration. Under synthetic conditions of gel formation at 80 °C, pH = 3, PVA/metal mole ratio of 3:1 and heating temperature 600 °C, an average particle size of 20–27 nm was obtained. Combining XRD, SAED patterns, bright-field, dark-field and HRTEM micrographs, the grain size, crystalline phase and morphology of the nanoparticles have been investigated. Good catalytic activity in total oxidation of CO at a low temperature of reaction below 250 °C of all the nanoparticles of perovskite samples was obtained.

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