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New methods to prepare ultrafine particles of some perovskite-type oxides

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Abstract

This research discusses a technique for the synthesis of ultrafine $LaBO_3$(B: Co, Mn) and $La_{1-x}Sr_xBO_3$ with a perovskite structure, in which a solution of Na_2CO_3-NaOH was adopted as the precipitating agent and the supercritical drying method was applied. By means of this technique, the mean particle size obtained was about 15 nm and its corresponding specific surface area was 30 $m^2\,g^{-1}$. The activity for CO oxidation over $LaBO_3$ increased significantly with a decrease of its particle size. In addition, the substitution of strontium for lanthanum in nanometers $LaBO_3$ increased the activity. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Carbon monoxide; Catalytic oxidation; Ultrafine particles; Perovskite; Supercritical drying; Synthesis

1. Introduction

Perovskite-type oxides (PTOs) have attracted great attention as environment-friendly catalytic materials. They have been used as catalysts mainly in catalytic combustion, automobile exhaust control and SO_2 and NO_x removal. PTOs usually possess much lower specific surface area (SSA), generally $<2\,m^2\,g^{-1}$; consequently, the catalytic activity on specific mass is not sufficiently high, which greatly limits its practical applications [1,2]. Increasing the SSA of PTOs requires a lowering of the calcination temperature of synthesis. In order to lower the calcination temperature of synthesis, the precursor elements should be uniformly dispersed at the molecular level, as this is beneficial for a solid-state reaction. Several kinds of syntheses have been developed on this hypothesis: (1) the spray-freezing/freeze-drying method [3], in which the minimum temperature and time necessary for obtaining a single perovskite phase are 500°C and 15 h, respectively, with the SSA of the product in the range of 8–22 $m^2\,g^{-1}$ and a requirement of a complicated equipment; and (2) the method of complexing with organic agent [4,5]. A typical procedure uses citrate acid as the complexing agent; in synthesizing $LaCoO_3$ and $LaMnO_3$ the minimum calcination temperature and time necessary for obtaining a single perovskite phase are 700°C and 4 h, respectively, and SSA of the product can exceed 10 $m^2\,g^{-1}$; and (3) the cyanides decomposition method [4]. By this method the SSA of the product could exceed 30 $m^2\,g^{-1}$, while noting that cyanides are noxious to human health.

In this research, a technique for the synthesis of $LaBO_3$ (B: Co, Mn) and $La_{1-x}Sr_xBO_3$ was developed, through which ultrafine PTOs with a high surface area could be made.

2. Experimental

The scheme of the synthesis method is presented in Fig. 1. As an example, ultrafine $LaCoO_3$ was made as follows: stoichiometric amounts of lanthanum nitrate and cobalt nitrate [$La(NO_3)_3{\cdot}6H_2O$, 12 g, and $Co(NO_3)_2{\cdot}6H_2O$, 8 g] were dissolved in 400 ml of deionized water, then a precipitating agent, $NaCO_3$–NaOH (in 1:1 molar ratio) was added to give the solution a pH value of 10. The resulting hydrogels were filtered and washed with deionized water to remove Na^+ and $CO_3{}^{2-}$, then the hydrogels were washed four times with ethanol to form alcogels. SCD (SCD stands for supercritical drying [6–9]) was carried out under 80 atm and 523 K with ethanol as an abstracting agent. The ultrafine $LaCoO_3$ was made by calcining the dried product at an appropriate temperature. In the following discussion, this scheme is abbreviated as Na_2CO_3–NaOH–SCD.

X-ray diffraction(XRD) spectra were obtained with a Japanese Rigaku 2038 diffractometer using CuK radiation. Specific surface areas were derived from N_2 adsorption isotherms which were determined with a Chem BET-3000

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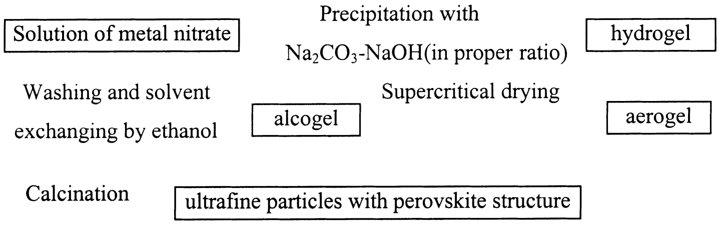

Fig. 1. The scheme of preparation procedure.

sorptiometer. The particle size of the samples were investigated on a JEOL TEM-100XII transmission electron microscope.

The catalytic reaction was carried out in a conventional fixed-bed flow reactor filled with 260 mg catalyst (ultrafine particles with perovskite structure without any further treatment). The feed gas mixtures were composed of 6.0 vol.% CO, 3.0 vol.% O_2 and N_2, and the space velocity was 15 000 ml g^{-1}(catalyst) h^{-1}.

3. Results and discussion

3.1. Synthesis of ultrafine PTOs

The XRD spectra of some samples are shown in Fig. 2. The samples made by the Na_2CO_3–NaOH–SCD method were converted to $LaCoO_3$ with a single perovskite structure after calcination at 700°C for 2 h (Fig. 2, curve 1). When NaOH was used as the substitute for Na_2CO_3–NaOH, the XRD spectra of the resulted samples exhibited not only $LaCoO_3$ diffraction peaks, but also some strong impurity peaks (Fig. 2, curve 3). Fig. 3 indicates that the aerogels (product of SCD) made by Na_2CO_3–NaOH–SCD could be converted to $LaCoO_3$ with a single perovskite structure when calcined at 590°C for 2 h.

These results reveal that the technique of Na_2CO_3–NaOH–SCD can decrease the calcination temperature significantly for synthesizing $LaCoO_3$ perovskite; hence, it could be inferred that the elements La and Co were uniformly dispersed. In synthesizing $LaCoO_3$ using the citrate acid method (components should be dispersed uniformly at the molecular level), the minimum temperature and time necessary for obtaining a single perovskite phase were 650°C (the temperature is >590°C) and 4 h (the calcination time is >2 h), respectively. To synthesize $LaCoO_3$ or $La_{1-x}Sr_xCoO_3$ with a single perovskite phase by the co-precipitation technique, a high-calcination temperature is required [10,11] (usually >1000°C). In this work, $LaCoO_3$ with a single perovskite phase cannot be achieved, when NaOH is used as the precipitating agent and calcined at 700°C. This indicates that some kind of double salt may be formed in the process of precipitating with the Na_2CO_3–NaOH agent, and the double salt allowed the components of metal ions to be uniformly dispersed.

When conventional drying was used as the substitute for SCD, the XRD spectra of the resulting samples (calcined at 700°C) exhibited strong peaks of $LaCoO_3$ perovskite

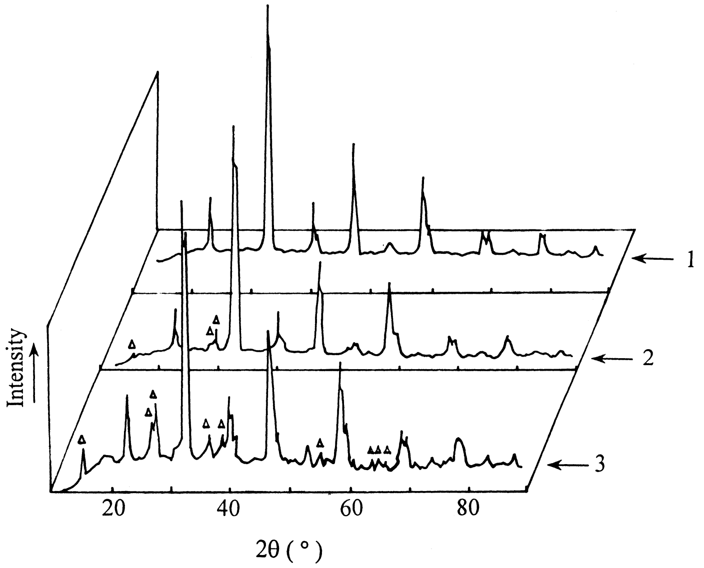

Fig. 2. X-ray diffraction pattern of samples calcined at 700°C. Made by (1) the Na_2CO_3–NaOH–SCD technique; (2) Na_2CO_3–NaOH as co-precipitating agent and conventional drying; and (3) NaOH as co-precipitating agent and supercritical drying. (Δ), Impurity peaks.

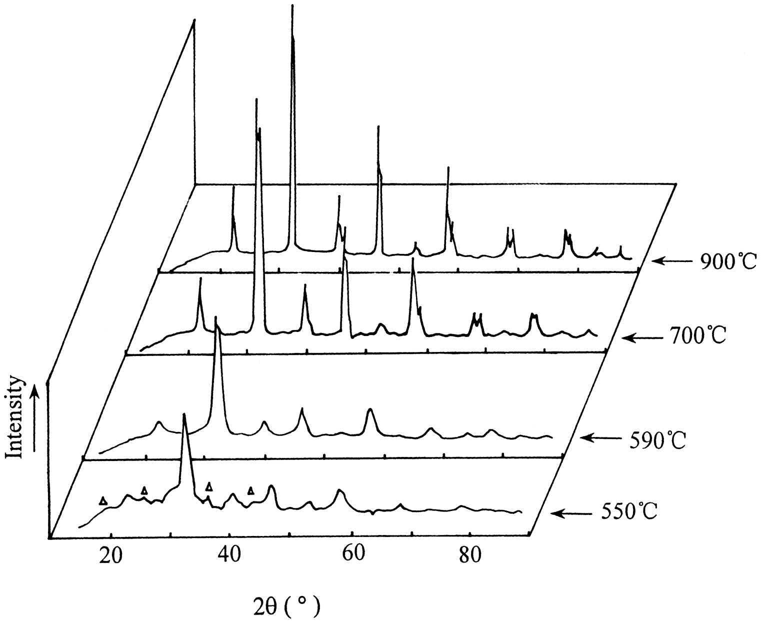

Fig. 3. X-ray diffraction pattern of $LaCoO_3$ calcined at various temperatures. (△), Impurity peaks.

as well as some weak impurity peaks (Fig. 1, curve 2). This indicates that the SCD process facilitates the formation of $LaCoO_3$. This may be due to the special textural structure of aerogel [6]. Firstly, the aggregation of particles in the drying process can be prevented by the SCD method; therefore, the particle size of aerogel is small — several nanometers in most cases — and the nanometer particles possess copious surface defects which are beneficial for the formation of $LaCoO_3$. Secondly, aerogels exhibit a well-developed porous texture and this character facilitates the migration of oxygen during the solid-state reaction process.

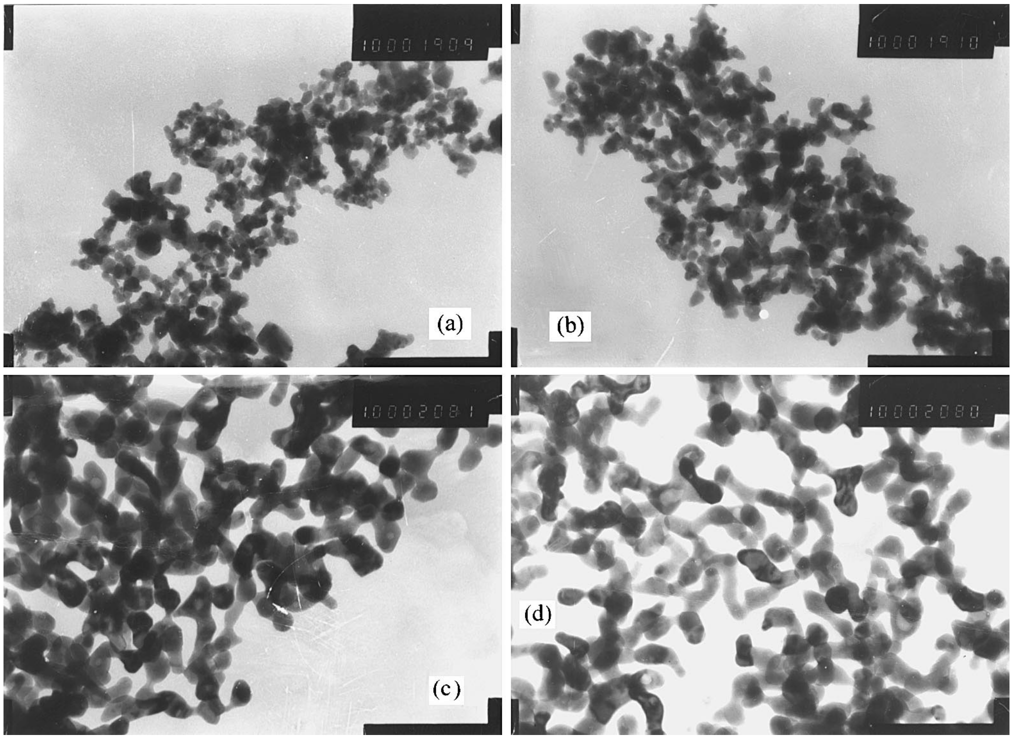

Fig. 4. Transmission electron micrographs (in ratio of 1:100 000). (a) $LaCoO_3$ calcined at 590°C; (b) $LaMnO_3$ calcined at 600°C; (c) $La_{0.8}Sr_{0.2}CoO_3$ calcined at 700°C; and (d) $La_{0.8}Sr_{0.2}MnO_3$ calcined at 700°C.

Table 1
Textural parameters of perovskite $LaCoO_3$ and $La_{1-x}Sr_xCoO_3$ made though Na_2CO_3–NaOH–SCD method

Sample	$LaCoO_3$	$LaCoO_3$	$LaCoO_3$	$LaCoO_3$	$La_{0.9}Sr_{0.1}CoO_3$	$La_{0.8}Sr_{0.2}CoO_3$
Calcination temperature (°C)	590	700	800	900	700	700
D_p[a] (nm)	15	38	75	160		30
S_{BET} ($m^2 g^{-1}$)	29.9	10.5	5.1	3.1	11.9	13.9

[a] Mean particle size derived from TEM diagram.

Table 2
Textural parameters of PTOs made though Na_2CO_3–NaOH–SCD method

Sample	$LaMnO_3$	$LaMnO_3$	$LaMnO_3$	$LaMnO_3$	$La_{0.8}Sr_{0.2}MnO_3$	$La_{0.6}Sr_{0.4}MnO_3$
Calcination temperature (°C)	600	700	800	900	700	700
D_p[a] (nm)	18	30	70	160	25	
S_{BET} ($m^2 g^{-1}$)	27.5	16.2	9.4	3.8	18.9	24.4

[a] Mean particle size derived from TEM diagram.

$La_{1-x}Sr_xCoO_3$ with a perovskite structure was synthesized by the Na_2CO_3–NaOH–SCD technique for $x \leq 0.3$. The minimum temperature and time necessary for obtaining a single perovskite phase are 700°C and 2 h, respectively. When the x reached a value of 0.4, the XRD spectra of the resulting samples exhibited a few weak impurity peaks at the conditions of calcination at 700°C for 2 h.

Using similar procedures, $LaMnO_3$ and $La_{1-x}Sr_xMnO_3$ with perovskite structures were obtained, with the same correlations.

Several transmission electron micrographs of ultrafine perovskite oxides are shown in Fig. 4. The minimum average particle sizes of $LaCoO_3$ and $LaMnO_3$ are about 15 and 18 nm, respectively (>300 particles were measured and the statistical errors were <20%). With an increase in calcination temperature, the particle size increases and the SSA decreases, which indicates that the textural properties are significantly dependent on the calcination temperature. The SSA of $La_{1-x}Sr_xBO_3$ (B: Co or Mn) was larger than that of $LaBO_3$, when they were prepared under equal conditions. This reveals that doping with strontium could prevent the aggregation of ultrafine particles. In the literature [12,13,14], it is stated that zirconia doped with Y_2O_3, La_2O_3 or MgO exhibits much better thermal stability as compared to that of pure zirconia, since the additives dispersed on the surface of zirconia resist surface diffusion and the aggregation of ultrafine particles is brought about mainly by surface diffusion. The X-ray photoelectron spectroscopy results of $La_{1-x}Sr_xCoO_3$ and $La_{1-x}Sr_xMnO_3$ [J. Full Chem. Tech. (China) 1999: 27(3)] showed that the concentration of strontium in surface was much higher than that in the bulk; hence, the aggregation of ultrafine PTOs may be hindered by surface SrO. Textural parameters of perovskite oxides made by Na_2CO_3–NaOH–SCD are listed in Tables 1 and 2. It can be seen that the maximum SSA of $LaCoO_3$ and $LaMnO_3$ with a single perovskite phase are 29.9 and 27.5 $m^2 g^{-1}$, respectively.

3.2. Catalytic performance of ultrafine PTOs

Fig. 5 exhibits the relationship between CO conversion and the reaction temperature on $LaBO_3$ (B: Co or Mn) and $La_{1-x}Sr_xBO_3$. Ultrafine $LaBO_3$ and $La_{1-x}Sr_xBO_3$ exhibit high activity for CO oxidation. On the best catalyst, CO was

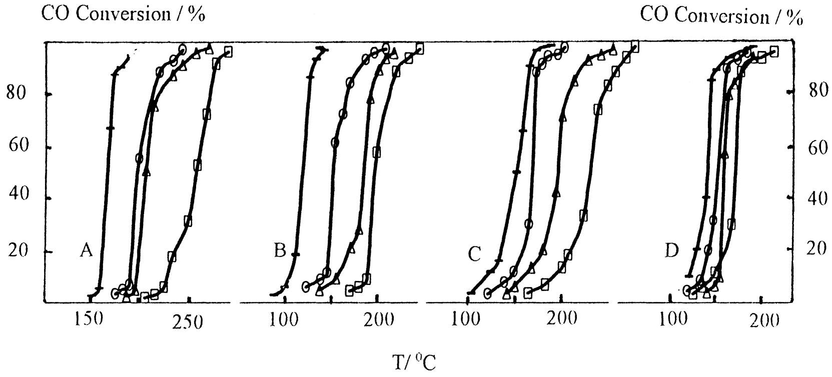

Fig. 5. Conversion vs. temperature. (A) $LaCoO_3$ calcined at (–) 590°C; (○) 700°C, (△) 800°C and (□) 900°C. (B) $La_{1-x}Sr_xCoO_3$ calcined at 700°C, (–) $x=0.1$, (○) $x=0.2$, (△) $x=0.3$, (□) $x=0$. (C) $LaMnO_3$ calcined at (–) 600°C, (○) 700°C, (△) 800°C and (□) 900°C. (D) $La_{1-x}Sr_xMnO_3$ calcined at 700°C, (–) $x=0.4$, (○) $x=0.2$, (△) $x=0.1$, (□) $x=0$.

completely converted to CO_2 before reaction temperature reaches 130°C. With a decrease in particle size, the catalytic activity increases markedly. Partial substitution of Sr for La in $LaBO_3$ could elevate the activity significantly.

PTOs possess certain a crystal structure, consequently, for certain compositions of PTOs, the activity should be directly proportional to SSA. In the literature [14], it is stated that the oxidation activity of PTOs increases linearly with increasing SSA. Our experimental results suggest that the correlation of the activity and SSA is not linear. This might result from the special surface structure of ultrafine TPO. This deserves further investigation.

4. Conclusions

The technique in which Na_2CO_3–NaOH is used as the precipitating agent and the supercritical drying method is adopted can effectively decrease the formation temperature of some PTOs, thus ultrafine $LaBO_3$ (B: Co or Mn) and $La_{1-x}Sr_xBO_3$ with high SSA can be synthesized by this technique.

The oxidation activity of $LaBO_3$ for CO increases with the decrease of particle size. In other words, it increases with increasing SSA (but is not proportional). Partial substitution of Sr for La in $LaBO_3$ increases the activity markedly.

Acknowledgements

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