

Combustion synthesis and characterization of porous perovskite catalysts

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Abstract. Porous perovskite-type complex oxides LaCoO_3 and $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$ were produced by combustion method. The properties of these porous materials such as crystal structures, particle sizes, surface patterns, pore size, surface area and pore volume were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and BET measurements. The results indicated that all porous materials are of the perovskite-type complex oxides. Doping Sr^{2+} ions on site A and doping Ni^{2+} ions on site B entered the crystal lattices of LaCoO_3 in the place of La^{3+} and Co^{3+} , respectively, and the maximum peak of XRD patterns of doping sample was weakened and broadened. Morphological microscopy demonstrated agglomerates involved mostly thin smooth flakes and layers perforated by a large number of pores and its lamella decreased with the introduction of Sr^{2+} and Ni^{2+} . Hysteresis loop in the N_2 adsorption-desorption isotherm of samples indicated its porous structures and the doping effect on its pore size, surface area and pore volume were improved. The porous catalysts have been tested for methane catalytic combustion and the results showed that these catalysts possessed high catalytic activity.

Keywords. Combustion method; porous perovskite catalysts; methane; catalytic combustion.

1. Introduction

Most of catalysts used in the modern chemical industry are the catalyst of complex oxides. Among many available complex oxides materials, perovskite-type complex oxides which have the same structure as natural CaTiO_3 (generally in its orthorhombic form) are particularly noticeable.^{1–4} Perovskite-type complex oxides materials are more and more favoured in many fields due to its design flexibility.^{4–7} But those perovskite-structural complex oxides produced via conventional synthesis methods are found to be with relatively low specific surface areas and low catalytic activity in the reactions, thus its commercialised applications are limited. So it is very important for us to develop a new method to prepare the kind of catalytic materials with large specific surface area values. Porous perovskite-type complex oxides have been recently studied as new catalytic materials for their large specific surface area values, low cost, high catalytic activity and high stability^{8,9}. To our knowl-

edge, here we report for the first time the obtaining of the porous perovskite-structural complex oxides materials by sol-gel combustion method, which were characterized by some measurements.

2. Experimental

2.1 Catalyst preparation

The catalysts, LaCoO_3 and $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$, were prepared by citric acid sol-gel combustion synthesis method. Briefly, lanthanum, strontium, nickel and cobalt nitrates in a desired molar ratio were dissolved in a citric solution at room temperature with constant stirring. At pH 6–7 (ammonia adjuster), acrylamide and other organic crosslinking agent were added in the solution, then the mixer was heated to 90–95°. The stirring was continued until a gel was formed. Then the prepared gel were transferred into a ceramic dish and placed into an oven preheated at 350°C, and then the combustion reactions could be carried out. With the temperature-increasing rate of $2^\circ\text{C}\cdot\text{min}^{-1}$, the obtained precursor was calcined at 700 or 750°C for 2 h.

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2.2 Characterization

Powder X-ray diffractometer (type D-Max-3B made in Japan) over the range $20^\circ \leq 2\theta \leq 80^\circ$, at room temperature, operated at 40 kV and 100 mA, using $\text{CuK}\alpha$ radiation combined with the nickel filter, scanning rate of 0.5°min^{-1} . Scanning electron micrographs of the powders were obtained using a JEOL JSM-5800, scanning electron microscope. BET specific surface areas were measured by nitrogen adsorption-desorption at 78 K using a Micromeritics ASAP 2020 instrument.

2.3 Measurement of catalytic activities

The $\text{CH}_4 + \text{O}_2$ reactions were carried out in a flow microreactor by feeding a gas mixture of CH_4 (1.0 vol.%), O_2 (10.0 vol.%) and N_2 (balanced) over 100 mg catalyst with $20,000 \text{ h}^{-1}$ GHSV and $300\text{--}700^\circ$ reaction temperature. The gas composition was analysed before and after the reaction by an online gas chromatography with thermal conductor detector (TCD), which was connected with a computer integrator system and Porapak Q columns was used. The activity of the catalysts was assigned as conversion.

3. Results and discussion

3.1 XRD measurement

LaCoO_3 (sintered at 700° for 2 h) and $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$ (sintered at 750° for 2 h) mixed oxides was prepared by sol-gel combustion synthesis

method and its XRD patterns are presented in figure 1. The results of phase analysis in figure 1 clearly show that the XRD patterns of $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$ had the same direction as those of LaCoO_3 , such as (110), (020), (112), (220) and (130) peaks thus it can be concluded that both LaCoO_3 and $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$ are perovskite-structural complex mixed oxides and no uncertain phase could be discovered. Meanwhile, it also is found that the peak locations of samples $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$ remained intact with the introduction of Sr^{2+} ($r_{\text{Sr}^{2+}} = 0.1310 \text{ nm}$) and Ni^{2+} ($r_{\text{Ni}^{2+}} = 0.124 \text{ nm}$; $r_{\text{Ni}^{3+}} = 0.074 \text{ nm}$), this implies the completion of crystallization and doping Sr^{2+} ions on site A and doping Ni^{2+} ions on site B entered the crystal lattices of LaCoO_3 , which replace La^{3+} ($r_{\text{La}^{3+}} = 0.1216 \text{ nm}$) and Co^{3+} ($r_{\text{Co}^{2+}} = 0.125 \text{ nm}$; $r_{\text{Co}^{3+}} = 0.075 \text{ nm}$). But the maximum peak of XRD patterns of doping sample is weakened and broadened, and indicates that samples $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$ are single phase with more rhombohedral distorted perovskite structure than undoped samples LaCoO_3 .

3.2 Surface area and porous structure

The results for the nitrogen isothermal sorption at 78 K of LaCoO_3 and $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$ perovskite-type mixed oxides are presented in figure 2, respectively. All the isothermal results show hysteresis loops, whose characteristics exhibit dependence on the structure of the samples, which are confirmed to be with a porous morphology. Such isothermal curves exhibit a intermediate profile between type B and

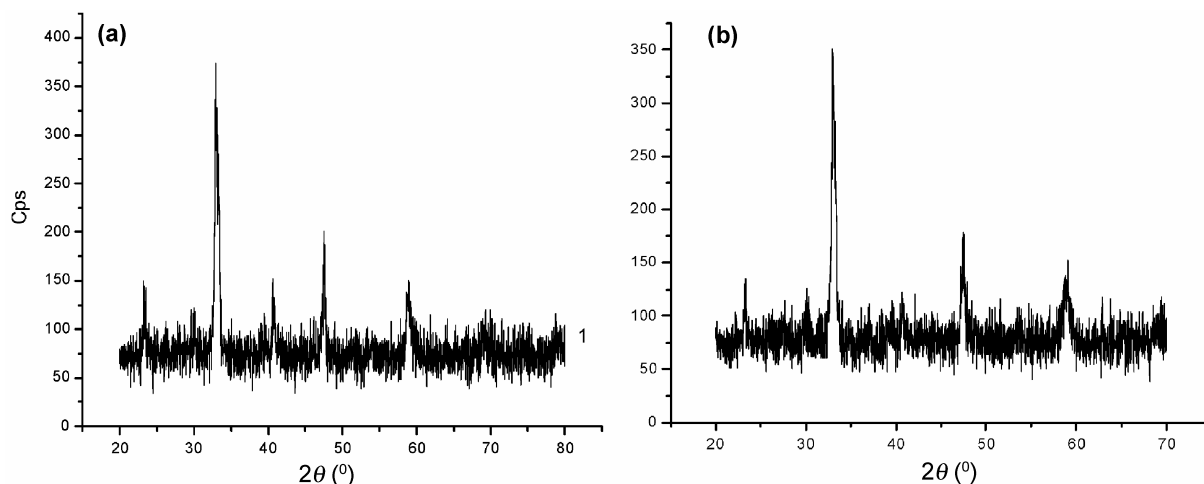


Figure 1. XRD patterns of LaCoO_3 and $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$. **a.** LaCoO_3 . **b.** $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$.

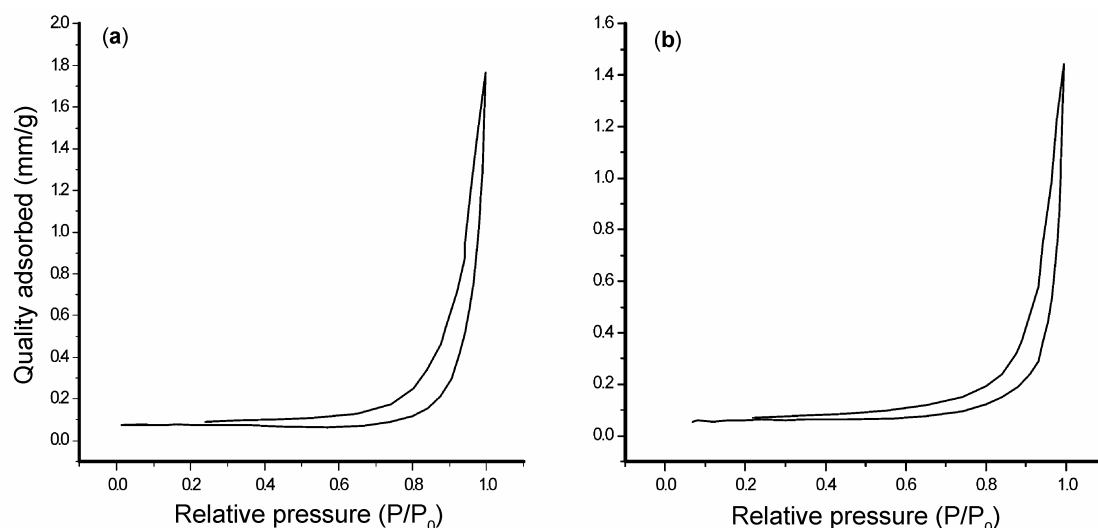


Figure 2. N_2 adsorption-desorption isotherm of $LaCoO_3$ and $La_{0.95}Sr_{0.05}Ni_{0.05}Co_{0.95}O_3$. a. $LaCoO_3$ b. $La_{0.95}Sr_{0.05}Ni_{0.05}Co_{0.95}O_3$.

Table 1. Characteristics of different catalysts samples

Samples	Average pore size (nm)	BET surface area (m^2/g)	BET surface area (cm^3/g)	Pore volume $T_{10}(\square)$	CH_4 oxidation $T_{90}(\square)$
Porous $La_{0.95}Sr_{0.05}Ni_{0.05}Co_{0.95}O_3$	43–65	33.6	0.16	399	628
Porous $LaCoO_3$	45–39	25.4	0.15	418	643
Ordinary $LaCoO_3^{10}$	–	5.6	–	560	750

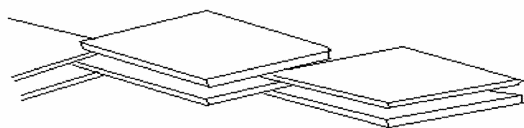


Figure 3. Lamella-structural model of the porous materials.

type D, main typical of lamella structure perforated by a large number of pores. In the other hand, the isothermal curves of samples $LaCoO_3$ and $La_{0.95}Sr_{0.05}Ni_{0.05}Co_{0.95}O_3$ show a slow increase at the relative pressure $P/P_0 = 0.25-0.9$, this indicates that the samples has a broader pore-size distribution. Lamella-structural model of the porous materials is presented in figure 3.

In table 1 some BET data of the samples are presented. The BET results show the surface area of the porous samples, which are prepared by citric acid sol-gel combustion synthesis method, are much larger than that of the samples prepared via conventional synthesis routes. The results also show that the surface area and the pore volume of the porous samples

increase with the introduction of Sr^{2+} and Ni^{2+} , But the average pore size decrease slightly. These results indicate that the introduction of Sr^{2+} and Ni^{2+} in the system can increase the surface area of the catalysts with high porosity and inhibit the congregating process.

3.3 SEM micrographs

Selected microstructures of samples $LaCoO_3$ and $La_{0.95}Sr_{0.05}Ni_{0.05}Co_{0.95}O_3$ are presented in figure 4 and 5, respectively. As shown in figure 4, undoped $LaCoO_3$ perovskite-type mixed oxides is porous and plate-shaped, and the grain size is $\sim 3.0 \mu m$. However, As shown in figure 5, the samples $La_{0.95}Sr_{0.05}Ni_{0.05}Co_{0.95}O_3$ mixed oxides with 0.05% Sr and 0.05% Ni doping has a slightly bigger crystallite size ($\sim 6.0 \mu m$). Meanwhile, morphological microscopy of the explored samples also demonstrated agglomerates involved mostly thin smooth flakes and layers perforated by a large number of pores. The crystallite size has increased from $\square 3.0 \mu m$ to $\square 6.0 \mu m$ whereas the surface area has enhanced from $25.4 m^2/g$ to $33.6 m^2/g$

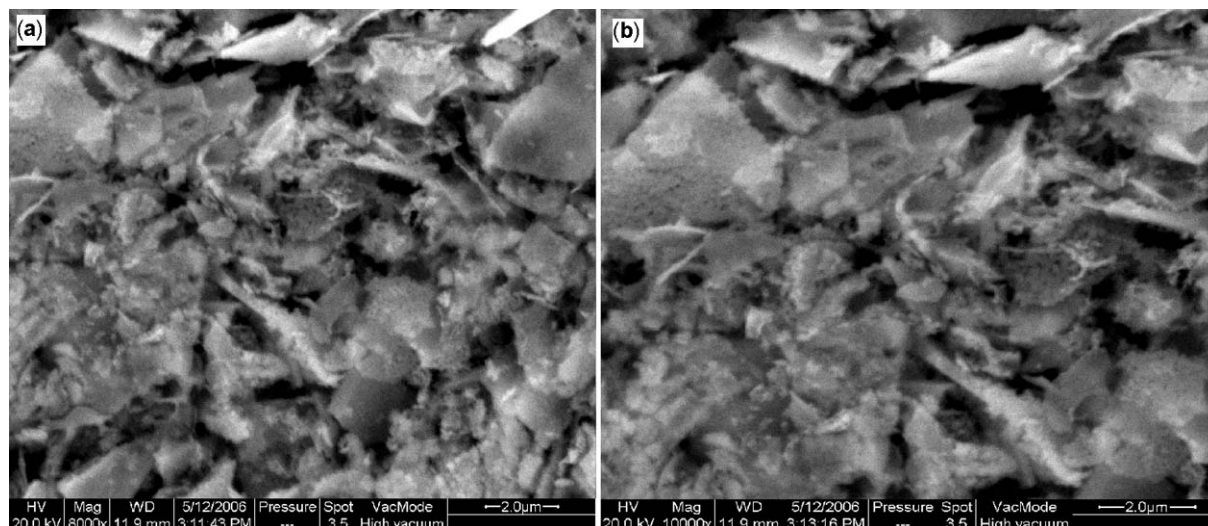


Figure 4. SEM patterns of samples LaCoO_3 . **a.** 8000 times; **b.** 10000 times.

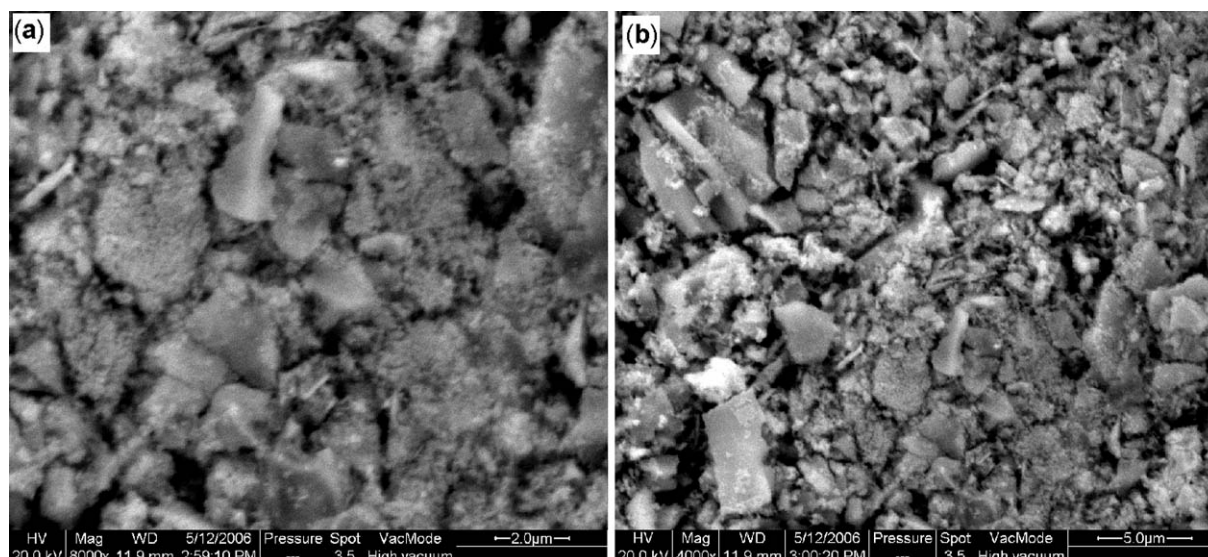


Figure 5. SEM patterns of samples $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$. **a.** 8000 times; **b.** 4000 times.

on substitute which implies the surface area of the catalysts is also related to its high porosity.

The principles of the formation of porous and lamella-structural perovskite-type mixed oxides can be explained as follow,¹¹ all the organic molecules play a double role: they react with the precursors (metal nitrates), to form complexes with metal cations in aqueous solution, they guarantee a good sol-gel homogeneity, probably avoid the preferential precipitation of ionic species. The porous sponge structure is formed by the combustion of the resulting gel and then porous and lamella structural samples was obtained by the following calcinations at high temperature for several hours.

3.4 Activity in methane combustion

The catalytic results of porous LaCoO_3 , $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$ and ordinary LaCoO_3 ¹⁰ for oxidation of CH_4 are summarized in table 1 with 10 and 90% conversion temperatures (T_{10} and T_{90}). The conversion curves of oxidation of CH_4 over these samples are presented in figure 6. By comparing T_{10} , T_{90} and conversion curves of oxidation of CH_4 , we find that the catalytic activities of porous LaCoO_3 and $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$ for CH_4 oxidation are much greater than that of ordinary LaCoO_3 . The T_{10} and T_{90} for porous $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ni}_{0.05}\text{Co}_{0.95}\text{O}_3$ was decreased by 161 and 122°C, respectively, as compared

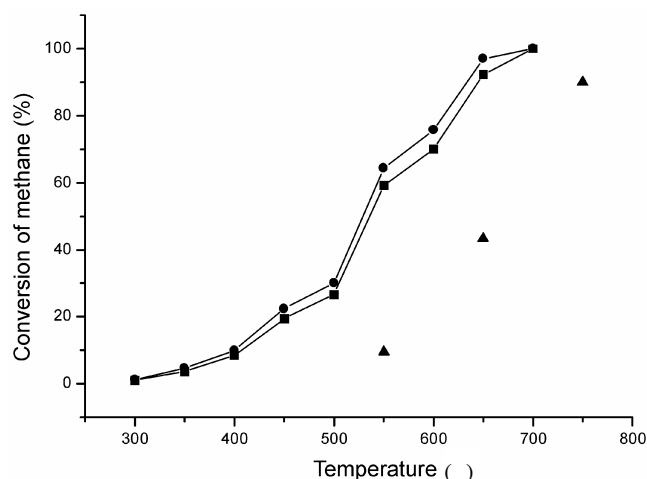


Figure 6. CH₄ conversion as a function of temperature over different catalysts. ● porous La_{0.95}Sr_{0.05}Ni_{0.05}Co_{0.95}O₃ ■ porous LaCoO₃ ▲ Ordinary LaCoO₃.

to the ordinary LaCoO₃ and, again, partial substitution of lanthanum and cobalt in the porous perovskite with strontium and nickel, respectively, resulted in decreasing T₁₀ and T₉₀ values by about 19% as compared to the porous LaCoO₃. The enhancement of catalytic activity may attribute to both the higher BET surface of the perovskite used and to the presence of strontium and nickel.

4. Conclusion

New catalytic materials based on LaCoO₃ and La_{0.95}Sr_{0.05}Ni_{0.05}Co_{0.95}O₃ were developed through a fast and relatively cheap technique. In the technique, the sol-gel combustion synthesis with citric and organical crosslinking agent is used, to synthesize a catalyst with high specific surface area. The obtained oxide powders were investigated by XRD, SEM and BET measurements. The XRD data for the explored sam-

ples showed that all the materials are single phase with more rhombohedral distorted perovskite structure. SEM pictures of LaCoO₃ and La_{0.95}Sr_{0.05}Ni_{0.05}Co_{0.95}O₃ composition showed that all the samples obtained from gel precursors have primary fine particles with tendency of lamella structure and high porosity. The catalytic activities of porous samples for CH₄ oxidation are much greater than that of ordinary LaCoO₃. Therefore, this preparation method is rather simple and the obtained powders are expected for application as catalysts.

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