

Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 112, No. 5, October 2000, pp. 535–542
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A method for increasing the surface area of perovskite-type oxides

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MS received 13 March 2000; revised 25 April 2000

Abstract. A method based on hydrothermal treatments is described for increasing the surface area of sintered ABO_3 -type perovskite oxides. Influence of hydrothermal treatments, such as water treatment at 125–300°C under autogeneous pressure and steam treatment at 350–800°C, to low surface area (or sintered) $LaCoO_3$ and $LaMnO_3$ perovskite oxides on their surface properties (viz. surface area, crystal size and morphology and surface $La/(Co \text{ or } Mn)$ ratio) and also catalytic activity in complete combustion of methane at different temperatures (450–600°C) has been thoroughly investigated. The hydrothermal treatments result in the activation of the perovskite oxides by increasing their surface area very markedly.

Keywords. ABO_3 -type perovskite oxides; $LaCoO_3$; $LaMnO_3$; hydrothermal treatment; catalytic combustion of methane.

1. Introduction

ABO_3 -type perovskite oxides (A = rare earth element with or without its partial substitution by alkaline earth element, and B = transition element such as Co, Mn, Ni, Fe, etc., with or without its partial substitution by other transition elements) have high potential for their use as catalysts in a number of catalytic reactions^{1–5}. The classical ceramic solid-solid reaction and co-precipitation methods, commonly used for the synthesis of perovskite-type oxide, involve high reaction temperature (> 900°C) and hence yield perovskite-type oxides with a low surface area ($< 2 \text{ m}^2 \text{ g}^{-1}$) due to their sintering¹. The perovskite-type oxides are also deactivated due to sintering or crystal growth during their continuous use in high temperature processes. The catalytic performance of the perovskite-type oxides is well-known to depend on their specific surface area^{1,2,6}, and hence it is of great practical interest to activate low surface area perovskite oxides, which are prepared by the high temperature synthesis methods and/or sintered during their use, by some means. In our very recent communication⁸, we have reported a possibility of activating sintered or low surface area $LaCoO_3$ and $LaMnO_3$ perovskite-type oxides by their hydrothermal treatment with water (under autogeneous pressure) or steam (at atmospheric pressure). The present work was undertaken with the objective of thoroughly investigating the activation of the low surface area perovskite oxides by the hydrothermal treatments for the complete combustion of methane.

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2. Experimental methods

The LaCoO_3 (surface area $\text{SA} = 0.9 \text{ m}^2\text{g}^{-1}$) and LaMnO_3 ($\text{SA} = 1.7 \text{ m}^2\text{g}^{-1}$) perovskite-type oxides were prepared by carbonate coprecipitation method involving calcination at 925°C . The hydrothermal treatment to the perovskite-type oxide with water under autogeneous pressure was carried out in a closed stainless steel bomb, using 1.6 ml water per gram of perovskite-type oxide, at different temperatures for 4 h. The hydrothermal treatment to the LaCoO_3 with steam at atmospheric pressure was carried out in a conventional quartz reactor by passing a mixture of steam and N_2 (60 mole% steam) at a space velocity of $5100 \text{ cm}^3\text{g}^{-1}\text{h}^{-1}$. After the hydrothermal treatment, the perovskite-type oxides were calcined at 600°C for 1 h.

The perovskite-type oxides were characterized by XRD using a $\text{CuK}\alpha$ radiation, by XPS for determining the surface $\text{La}/(\text{Co or Mn})$ atomic ratio, by Scanning Electron Microscope for their crystal size and morphology, and also for their surface area using a Monosorb Surface Area Analyzer (Quantachrome Corp., USA).

The catalytic activity of the perovskite-type oxides in a complete combustion of methane was measured by passing continuously a methane (2.5 mole%)-air mixture at a space velocity of $51,000 \text{ cm}^3\text{g}^{-1}\text{h}^{-1}$ (measured at 0°C and atmospheric pressure) over a 0.1 g catalyst diluted uniformly with 0.4 g inert solid particles in a quartz reactor at different temperatures and analyzing the reaction products by an on-line gas chromatograph as described earlier⁷.

3. Results and discussion

The scanning electron micrographs of LaCoO_3 and LaMnO_3 perovskite oxides with or without hydrothermal treatment are shown in figures 1 and 2. The XRD spectra of LaCoO_3 and LaMnO_3 perovskite-type oxides with or without hydrothermal treatment are shown in figures 3 and 4. Results showing the influence of temperature on the conversion of methane in its complete combustion over hydrothermally treated LaCoO_3 and LaMnO_3 perovskite oxides are presented in figures 5–7. The LaCoO_3 and LaMnO_3 perovskites with or without hydrothermal treatment are compared for their surface area, crystal size and surface $\text{La}/(\text{Co or Mn})$ atomic ratio in tables 1 and 2.

The following observations are made from the results (figures 1–5 and tables 1–2) of the water treatment to LaCoO_3 and LaMnO_3 perovskites and steam treatment to LaCoO_3 perovskite oxide:

- Both the water and steam treatments (at different temperatures) have no significant effect on the structure of perovskite oxides.
- The hydrothermal treatments result in a very significant increase in surface area for LaCoO_3 perovskite oxide, but for LaMnO_3 perovskite, the increase in surface area is relatively less.
- The steam treatment of LaCoO_3 perovskite results in a small increase in its surface area.
- In case of LaCoO_3 , there is a very significant change in the crystal size and morphology due to the hydrothermal treatment (figure 1), depending upon its severity. However, in case of LaMnO_3 , the observed changes in the crystal size and morphology after the hydrothermal treatment are relatively very small (figure 2).

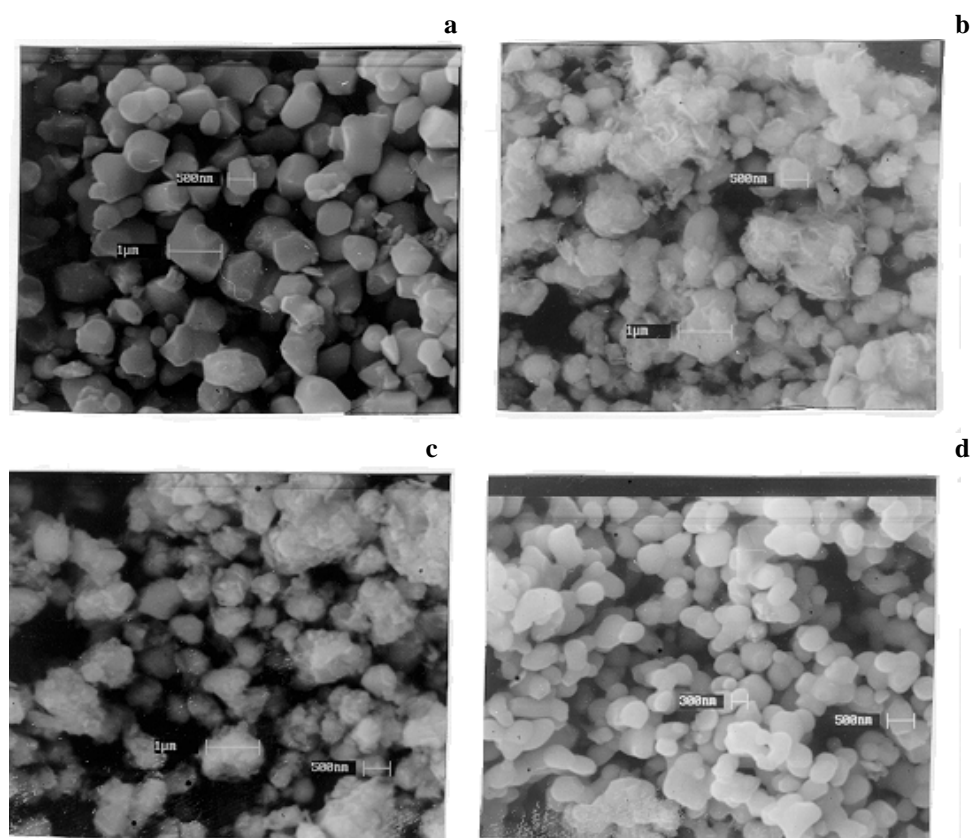


Figure 1. Scanning electron micrograph of $LaCoO_3$ without water treatment (a), treated with water at 175°C (b), at 225°C (c), treated with steam at 800°C (d).

Table 1. Surface area, crystal size and surface La/(Co or Mn) ratio of $LaCoO_3$ and $LaMnO_3$ perovskite oxides treated with water under autogeneous pressure.

Perovskite oxide	Water treatment temperature (°C)	Surface area ($m^2 g^{-1}$)	Crystal size (μm)	Surface La/(Co or Mn) ratio
$LaCoO_3$	Without treatment	0.9	1.1	0.98
	125	7.8	—	—
	175	14.3	0.7	—
	225	16.0	0.6	1.30
$LaMnO_3$	Without treatment	1.7	0.5	1.08
	175	3.0	—	—
	225	3.9	0.45	1.11
	300	4.5	0.4	1.20

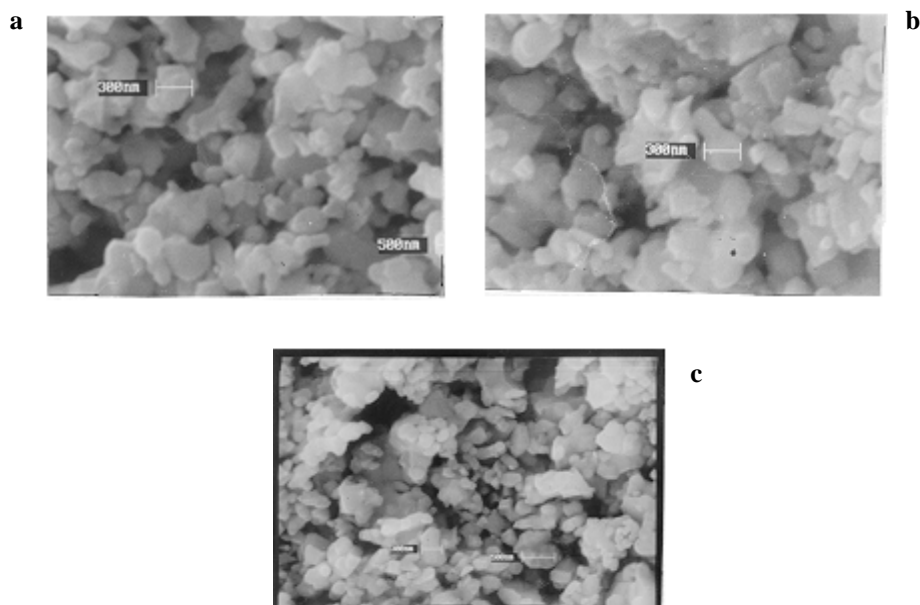


Figure 2. Scanning electron micrograph of LaMnO_3 without water treatment (a), treated with water at 225°C (b) and at 300°C (c).

Table 2. Surface area, crystal size and surface La/(Co or Mn) ratio of LaCoO_3 treated with steam at atmospheric pressure.

Steam treatment temperature ($^\circ\text{C}$)	Surface area (m^2g^{-1})	Crystal size (μm)	Surface La/Co ratio
Without treatment	0.9	1.1	0.98
350	1.4	–	–
500	1.5	–	–
600	1.7	–	–
700	1.9	–	–
800	2.3	0.4	1.08

- The surface La/Co (or Mn) ratio of the perovskite oxides is increased with increasing the severity (i.e. temperature) of the hydrothermal treatment.
- The methane combustion activity of all the water and steam treated catalysts is higher than that of the untreated one. As compared to LaMnO_3 , the increase in the catalytic activity of LaCoO_3 due to the hydrothermal treatments is larger.

These observations clearly indicate a beneficial effect of the hydrothermal treatments and steam treatment to the perovskite-type oxides for their activation or reactivation. This approach may also be employed for activating other low surface area or sintered perovskite-type oxides.

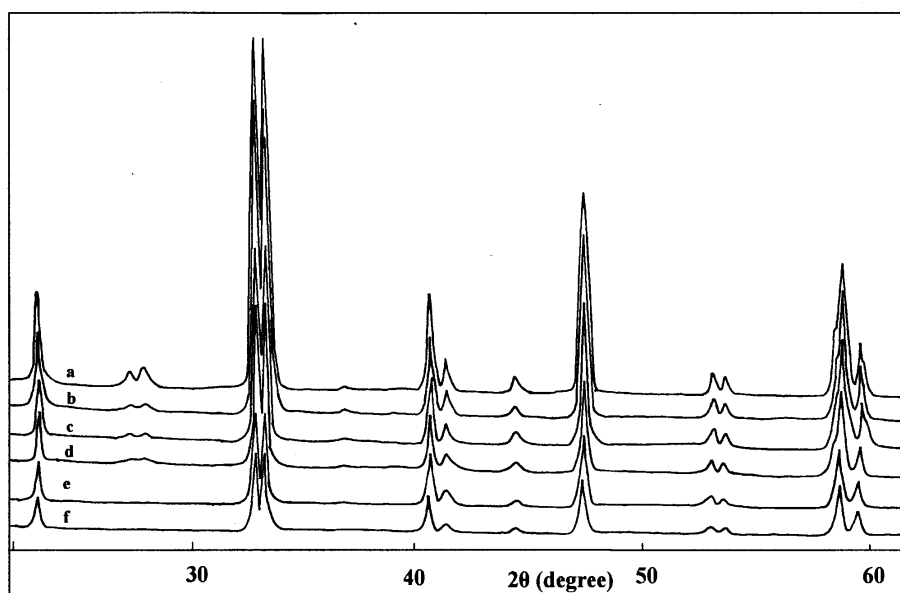


Figure 3. XRD spectra of LaCoO₃ [without treatment (a), treated with water at 125°C (b), 175°C (c), 275°C (d), with steam at 350°C (e) and 800°C (f)].

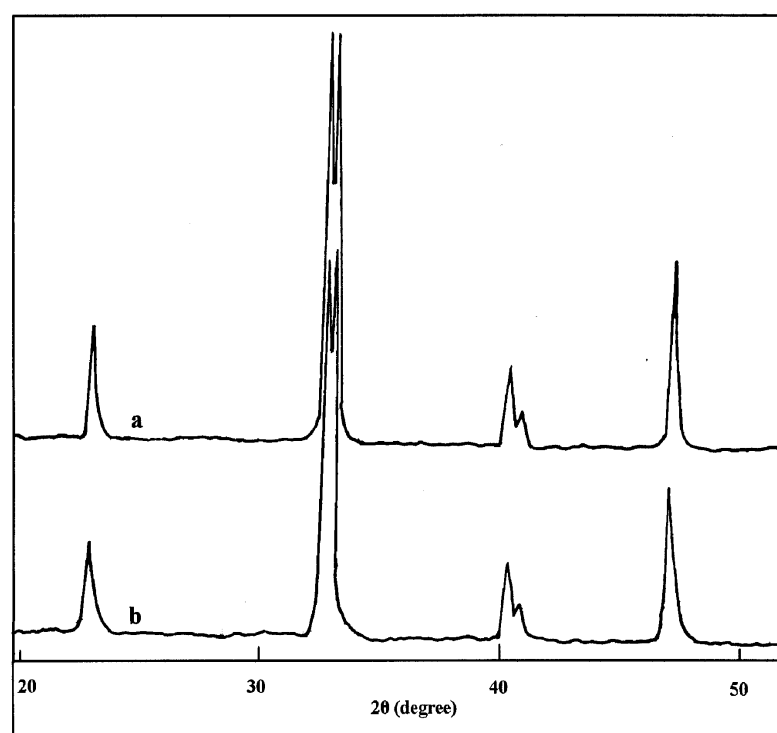


Figure 4. XRD spectra of LaMnO₃ [without treatment (a), treated with water at 225°C (b)].

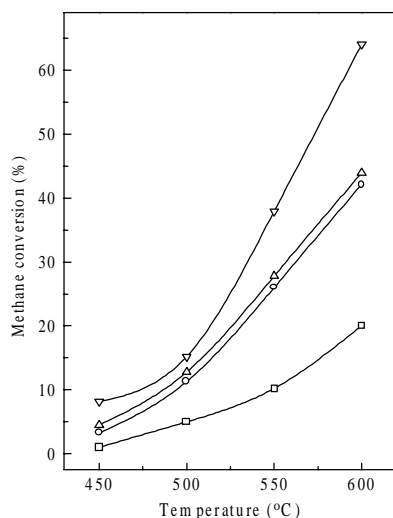


Figure 5. Effect of temperature on the conversion of methane in its complete combustion over LaCoO_3 – treated with water at 125°C (○), 175°C (△), 225°C (▽) and without water treatment (□).

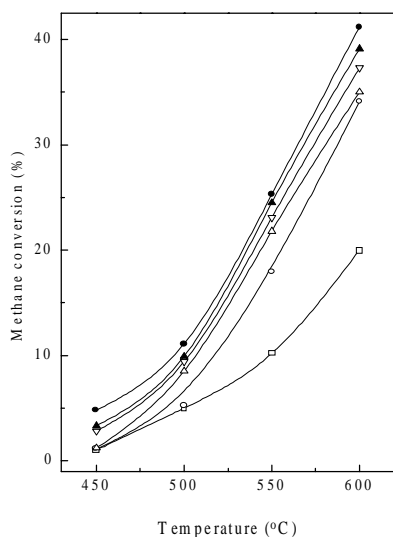


Figure 6. Effect of temperature on the conversion of methane in its complete combustion over LaCoO_3 – treated with steam at 350°C (○), 500°C (△), 600°C (▽), 700°C (▲), 800°C (●) and without water treatment (□).

The increase in the surface area of the perovskite-type oxides and the observed decrease in the crystal size by the steam treatment at 350 – 800°C are expected because of the recrystallization during the high temperature hydrothermal treatment depending upon the steam treatment temperature. Whereas in the water treatment at autogeneous pressure

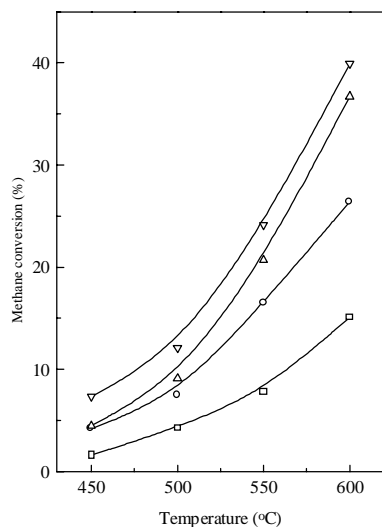


Figure 7. Effect of temperature on the conversion of methane in its complete combustion over LaMnO_3 – treated with water at 175°C (○), 225°C (△), 300°C (▽) and without water treatment (□).

(at 125–300°C), the perovskite-type oxides are expected to be hydrolyzed, at least partially, and recrystallized during the calcination at 600°C, leading to a large increase in their surface area. The hydrolysis followed by the recrystallization may have caused a larger change in the surface area and crystal size in case of the water treatment. The observed increase in the surface La/Co (or Mn) ratio with increasing the severity of the hydrothermal treatment in both the water and steam treatment also indicate the recrystallization of the perovskite-type oxide causing redistribution of La and Co (or Mn).

The methane combustion activity, when expressed per unit mass of the perovskite-type oxide catalyst, is increased due to the hydrothermal pretreatment. However, the catalytic activity, when expressed per unit surface is decreased appreciably, particularly due to water treatment and this is consistent with the increase in the surface La/Co (or Mn) ratio or with the decrease in the surface concentration of Co or Mn (which is responsible for the combustion activity of the catalyst).

4. Conclusions

Surface area and catalytic activity (in the methane combustion for methane emission control) of low surface area (or sintered) LaCoO_3 and LaMnO_3 perovskite type oxides can be increased markedly by hydrothermal treatment of the perovskites with water (under autogeneous pressure) or steam. In the hydrothermal treatments, there is little or no influence on the structure of the perovskite oxide, but its crystal size and surface La/Co (or Mn) ratio are changed significantly; the former is decreased and the later is increased with increasing the severity of hydrothermal treatment.

Acknowledgement

S Banerjee is grateful to the Council of Scientific and Industrial Research, New Delhi, for a fellowship. We are also grateful to Dr Sainkar and Dr Mandale of the Sophisticated Instrumentation Laboratory, for the SEM and XPS of the samples.

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