

Catalytic activity in methane oxidation of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ ($x = 0-1$) perovskites prepared by mechanochemical route

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Abstract

A number of perovskite-like oxides $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ ($x = 0-1$) prepared by the mechanochemical method were studied in respect of their catalytic activities to methane oxidation. Mechanochemical route as compared with ceramic route results in increase a substitution degree in $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ oxides from $x=0.3$ up to $x=0.5$ even at lower temperature and duration of calcination. The introduction of calcium resulted in a non-monotonic decrease in the catalytic activity upon an increase in x with the intermediate maximum at $x=0.3-0.5$. The catalytic activities decreased in the series: $\text{LaCoO}_3 > \text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3 > \text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3 > \text{Ca}_2\text{Co}_2\text{O}_5$. The observed changes in the catalytic activity of the calcium-containing samples correlate with variations in the proportion of weakly bonded oxygen species (or Co^{4+} cations) only in the composition range $x=0.1-0.4$. The higher activity of lanthanum cobaltite may be accounted for by the presence of cobalt oxide particles on the perovskite surface, while the decrease in the activity at $x>0.4$ by the emergence of calcium oxide on the perovskite surface and by the appearance of the less active brownmillerite phase.

Introduction

The high thermal and chemical stability of transition and rare earth metal oxides with the perovskite structure $\text{La}_{1-x}\text{Me}_x\text{Me}^2\text{O}_{3-\delta}$ ($\text{Me}^1=\text{Ca}, \text{Sr}, \text{Ba}; \text{Me}^2=\text{Fe}, \text{Co}, \text{Mn}, \text{Ni}$) make them widely applicable for high temperature processes such as catalytic combustion of hydrocarbons, steam reforming of methane, ammonia oxidation, reduction of sulfur dioxide and a number of the other processes [1-3]. Properties of the oxides depend on the nature of the transition (Me^2) and substituting (Me^1) cations, as well as on the preparation conditions.

Substituted perovskites $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ are highly active to propane oxidation [4,5], attract interest as bifunctional oxygen electrodes [6], and demonstrate exiting magnetic and electric behavior [7]. Literature data in the field give evidence of the substantial dependence of the phase composition and catalytic properties of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ on the preparation conditions. It was shown that the homogeneity range in substituted lanthanum cobaltites $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ is expanded upon temperature elevation during the ceramic synthesis. For example, calcinations of the initial reactants at 885°C allowed the one-phase samples to be produced at $x=0-0.25$ [8], while calcinations at 1100°C resulted in an increase in the solubility up to $x=0.3$ [9,10] that agrees with the statement [11] on the impossibility of the preparation of solid solutions with $x>0.3$ by the ceramic method (calcination temperature 1100°C). The temperature elevation up to 1200°C led to the expansion of the solubility range to $x=0.5$ [12]. Synthesis from solutions allows perovskites with a higher substitution degree to be prepared at lower calcinations temperatures [4,11,13-17]. For example, the solid solutions with x up to 0.8 can be prepared at $700-900^\circ\text{C}$ of the calcinations temperature according [16,17].

The differences in the phase composition of perovskites $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ prepared by different methods are reported in literature; these differences can be the result of the different degrees of homogeneity of initial components at their mixing, calcinations duration and atmosphere. Again, by analogy with the studied earlier $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ system [18,19], the reason may be a change in the

calcium solubility due to ordering of the oxygen vacancies upon temperature elevation.

The observed diversity of catalytic properties of the oxides under consideration prepared using different methods may be accounted for by their different phase compositions, microstructures, textures, and surface composition. The non-linear changes in the catalytic activity to propane oxidation depending on x were shown [4,5] abandon for the one-phase perovskites prepared by the citrate method, the least active being the sample with $x = 0.2$ ($0.5 > 0.4 > 0 > 0.2$). Generally, the activity increased with an increase in the proportion of weakly bonded oxygen (detected using TPR and XPS techniques) whiles the sample with $x=0.2$ fell out of the dependence. Enrichment of the surface of all the prepared samples with lanthanum compounds and a high stability of the oxides in the reaction medium was reported. Another series of the activity to methane oxidation was observed with the samples prepared by the Pechini method: $0.3 > 0.2 = 0.6 > 0.4 > 0 > 1$ [20,21]. The surface enrichment with calcium compounds due to the destruction of perovskite surface layers during the reaction to release calcium oxide was established. The authors reported correlation between the initial catalytic activity (at $x=0-0.3$) and the amount of the weakly bonded oxygen that indicated the stepwise (suprafacial) mechanism of the reaction, the sample with $x=0.2$ being most stable.

The mechanochemical method implies calcination of a mechanically pre-activated mixture of initial reactants; the better disintegration, homogenization and formation of defects to accelerate sintering

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makes it possible to synthesize complex oxides at low temperature and shorter treatment times against those of the ceramic method [22,23]. The energy effective and environmentally friendly mechanochemical method is expected to provide the preparation of wide latitude of homogeneous solid solutions in the $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ system. The present work was aimed at mechanochemical preparation of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ ($x=0-1$) samples and at characterization of their physicochemical and catalytic properties.

Experimental

Initial compounds for synthesis were La_2O_3 , CaO , Co_3O_4 of the chemical purity grade.

The mechanochemical (MC) method for synthesis of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ ($x=0; 0.1, 0.2; 0.3, 0.4; 0.5, 0.6; 0.7, 0.8; 0.9, 1$) included the stage of mechanical treatment of initial oxides in the necessary proportion followed by the stage of thermal treatment. The mechanical treatment was carried out in air using a centrifugal planetary ball mill APF-5; the weight ratio of the loaded powder and 5 mm steel balls was 5:10. The mill drums provided the acceleration equal to ~ 40 g. The mechanical treatment (MT) took 3 min. The mechanically activated mixture underwent thermal treatment at 1100°C in air for 5 hours.

The phase composition was studied using a X'TRA (Thermo ARL, Switzerland) instrument. The spectra were acquired at the 2θ range of $10^\circ-80^\circ$ at 0.05 step and 43 s accumulation time. BET surface area, S_{sp} , was determined using argon desorption at 300°C .

Thermoprogrammed reduction with hydrogen (H_2 -TPR) was carried out using a flow setup equipped with a thermal conductivity detector for the 0.25-0.5 mm fraction. The samples were pretreated in oxygen at 500°C for 0.5 h and cooled in oxygen to room temperature. The sample weight was 50 mg; flow rate of the reducing mixture (10% H_2 in Ar) was $40\text{ cm}^3\text{min}^{-1}$. The samples were heated to 900°C at the rate of 10°min^{-1} . The Origin 6.0 program package was used for calculation of the peak areas underneath the TPR curves. H_2 consumption of MC prepared $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ was calculated for peaks in the temperature fields: 40-150 $^\circ\text{C}$, 40- 500 $^\circ\text{C}$, 500-900 $^\circ\text{C}$ and 40-900 $^\circ\text{C}$.

The catalytic activity to methane oxidation was studied at 350-600 $^\circ\text{C}$ in a flow reactor using 1 g (0.6 cm^3) 0.25-0.5 mm fraction of the catalyst. The reaction mixture (0.5 CH_4 + 9 % O_2 in He) was fed at the rate of 2.4 l/h. The reaction rate for the initial methane concentration $C_0=0.5$ was calculated by formula (1):

$$W, [\text{molecules of } \text{CH}_4 \text{ m}^{-2}\text{s}^{-1}] = k \cdot C_0 \cdot 2.69 \cdot 10^{19}, \quad (1)$$

Where k is effective rate constant of the first order reaction calculated for a plug-flow reactor using equation $k = -2.3 \cdot \lg(1-x) / (\tau \cdot S_{\text{sp}} \cdot q)$ (x is the conversion of CH_4 , q is weighed sample, τ is contact time). The chromatographic error of measuring concentrations of the gas mixture components was no more than 20%.

Results and Discussion

Phase composition and specific surface area of MC prepared $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ ($0 \leq x \leq 1$)

From XRD data (Figure 1), the prepared samples with $x \leq 0.5$ are practically one-phase perovskites with a small admixture of cobalt oxides. The lattice parameter and unit cell volume decreased with increasing the x value to 0.4, which indicated the intercalation of Ca cations into lanthanum sublattice (Table 1). In the samples with $x \geq 0.6$, the phase of calcium cobaltite with the brownmillerite structure

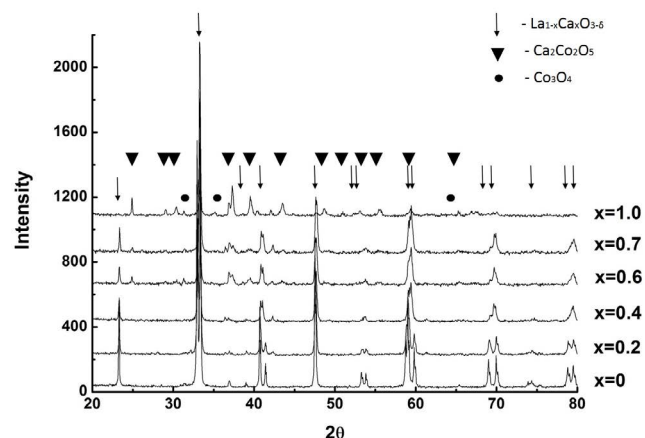


Figure 1. X-ray data for MC prepared $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$

Table 1. Specific surface area (S_{sp} , m^2g^{-1}) of MC prepared $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ samples and unit cell parameters for the perovskite phases

Sample	aÅ	cÅ	$V\text{\AA}^3$	S_{sp} , m^2g^{-1}
LaCoO_3	5.444	13.097	56.027	0.24
$\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$	5.443	13.104	56.018	0.16
$\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$	5.437	13.109	55.938	0.14
$\text{La}_{0.7}\text{Ca}_{0.3}\text{CoO}_3$	5.429	13.120	55.825	0.26
$\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$	3.818		55.652	0.2
$\text{La}_{0.5}\text{Ca}_{0.5}\text{CoO}_3$	3.816		55.564	0.4
$\text{La}_{0.4}\text{Ca}_{0.6}\text{CoO}_3$	3.818		55.669	0.34
$\text{La}_{0.3}\text{Ca}_{0.7}\text{CoO}_3$	3.819		55.702	1.0
$\text{La}_{0.1}\text{Ca}_{0.9}\text{CoO}_3$	3.819		55.700	0.36
CaCoO_3				0.35

is detected along with the perovskite phase, the former phase being increased in proportion with increasing x to become the main phase with cobalt and calcium oxides as impurities at $x=1$. The XRD data indicate the morphotropic phase transition from hexagonal ($x < 0.4$) to cubic ($x > 0.4$) modification of the perovskite structure. Thus, the mechanochemical method, against the ceramic method, allows really the substituted solutions with larger x to be prepared during shorter time of the calcination at 1100°C . The data on the specific surface area of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ samples (no more than $1\text{ m}^2/\text{g}$) show their good sintering (Table 1).

Microstructure of MC prepared $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$

From HRTEM data, samples of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ at $x = 0-0.3$ are mainly built up by particles of rhombohedral perovskite phase of 100 nm to micron in size (Figure 2). There are ensembles (10–50 nm in size) of fine cobalt oxide particles ($x=0$), as well as lanthanum and calcium oxides ($x=0.2-0.4$ and $x>0.5$, respectively) on the perovskite surface. With an increase in the amount of calcium, the amount of admixtures in the samples (Figure 2) increases. The size of such particles is ca. 10 nm (Figure 2). Sample with $x=0.4$ is cubic perovskite. The cubic phase is $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-\delta}$ with some deviations (5-7 at %). In the samples with $x \geq 0.5$ an additional brownmillerite phase (figure 3b) along with the cubic perovskite modification (figures 2 and 3a) occurs. From HRTEM and EDX data, the composition of the rhombohedral phase is changes according to the Vegard rule up to $x < 0.4$. The HRTEM data allow the compositions at $x=0.3-0.4$ to be assigned to the region of morphotropic phase transition.

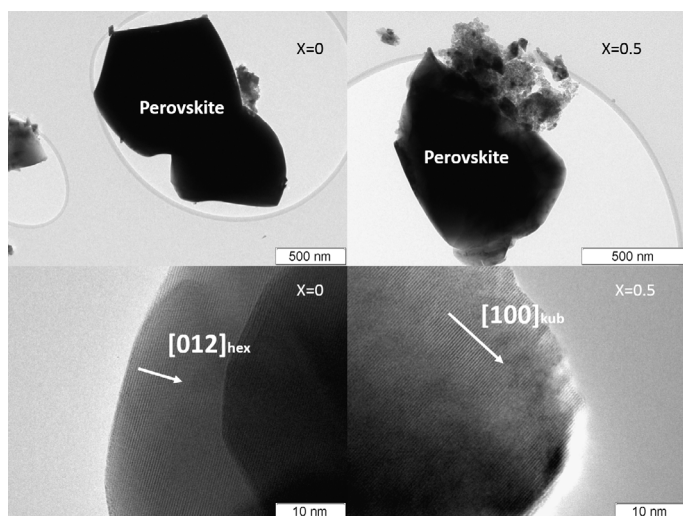


Figure 2. Microstructure of two kinds of particles of MC prepared: $\text{LaCoO}_{3-\delta}$ particle with R3m perovskite structural modification (a); particle $\text{La}_{0.5}\text{Ca}_{0.5}\text{CoO}_{3-\delta}$ with Pm3m perovskite structural modification (b)

H_2 -TPR of MC prepared $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$

TPR curves (dependencies of hydrogen absorption on the temperature of sample reduction) are shown in Fig. 4. The complex shapes of the TPR curves indicate the stepwise process of the sample reduction with hydrogen with the temperature rise; the first low-temperature peak is observed at ca. 400°C, and the second high-temperature peak at 600°C. The substitution leads to splitting and increasing in intensity of the first peak, to lowering of the reduction onset temperature at increasing x , while the high-temperature peak is shifted towards low temperature region. The reduction of cations $\text{Co}^{3+} \rightarrow \text{Co}^2$ and $\text{Co}^{4+} \rightarrow \text{Co}^0$ at below 500°C, and $\text{Co}^{2+} \rightarrow \text{Co}^0$ at above 500°C is reported elsewhere [24]. By analogy with literature data [25], we calculated quantities of hydrogen absorption at the ranges assigned, formally, to different steps of the sample reduction:

- The lowest-temperature hydrogen absorption corresponds to removal of no more than one surface oxygen monolayer (40-150°C)
- The low-temperature absorption with maxima at the range no more than 500 °C corresponds quantitatively to the reduction of cations $\text{Co}^{4+} \rightarrow \text{Co}^0$ and $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ (40-500°C)
- The high-temperature absorption with maxima at above 500°C corresponds quantitatively to the reduction $\text{Co}^{2+} \rightarrow \text{Co}^0$ in the sample bulk and is accompanied by the perovskite destruction (500-900°C).

Figure 5 illustrates hydrogen absorption as dependent on the catalyst compositions calculated for the identified TPR ranges. The data argue for an increase in the total hydrogen absorption and, correspondingly, for an increase in the oxygen contents; in accordance with the rule of preserving electroneutrality, this must result in an increase in the charge of a part of cobalt cations, i.e. in an increase in the number of Co^{4+} cations at increasing the calcium content (x). Similar changes were observed before in the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ system [25]. However, the absorption in the low-temperature range related to the reduction $\text{Co}^{4+} \rightarrow \text{Co}^0$ and $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ goes through a maximum to indicate the corresponding change in the quantity of Co^{4+} cations. The discrepancy in the Co^{4+} contents calculated from the total or low-temperature absorption may result from incorrect calculation of the absorption at low temperature because of overlapping of the low- and high-temperature peaks.

Notice that the lowest-temperature hydrogen absorption, which is assigned to variations in the most weakly bonded oxygen upon calcium introduction, also changes in non-monotone manner but, in general, increases with increasing x in the calcium-containing samples after its initial decrease at $x=0.1$.

Catalytic activity of MC prepared $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ in methane oxidation

Figures 6 and 7 show dependencies of the methane conversion and catalytic activity (CA) on the composition (x) of samples $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ at $T=350-600^\circ\text{C}$. The substitution of calcium for lanthanum results in a non-monotone (with an intermediate maximum at $x=0.2-0.5$) decrease both in the methane conversion (Figure 6) and in CA (Figure 7). The maximal conversion at 600°C ($x=0$) is ca. 60% but no more than 40% over the calcium-substituted perovskites ($x>0$). The temperature elevation leads to an increase in the conversion to reach 100% at 750°C even over the least active sample ($x=0.9$).

The observed variations in the catalyst activity to methane oxidation do not correlate with variations in the quantity of the most weakly bonded surface oxygen species, probably, due to the absence (desorption) of these species under conditions of the catalytic studies. Again, in general, the catalyst activity correlates neither with calcium content nor with an increase in the proportions of weakly bonded oxygen and Co^{4+} cations (determined from the total absorption and from the first peak). Hence, not only quantity of weakly bonded oxygen determined the catalyst activity. For example, some researchers [4,5] reported the correlation between the catalytic activity to propane oxidation and the quantity of oxygen removed during TPR but

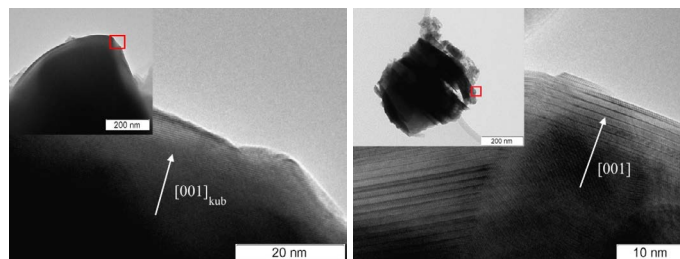


Figure 3. Microstructure of two kinds of particles of MC prepared $\text{La}_{0.4}\text{Ca}_{0.6}\text{CoO}_{3-\delta}$: particle with Pm3m perovskite structural modification (a); particle with bawnmillerite structural modification (b)

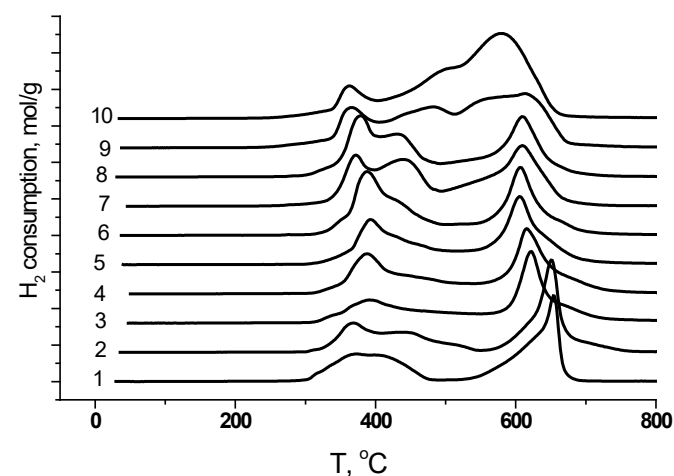


Figure 4. H_2 -TPR curves of MC prepared $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$: 1- $x=0$; 2- $x=0.1$; 3- $x=0.2$; 4- $x=0.3$; 5- $x=0.4$; 6- $x=0.5$; 7- $x=0.6$; 8- $x=0.7$; 9- $x=0.9$; 10- $x=1$

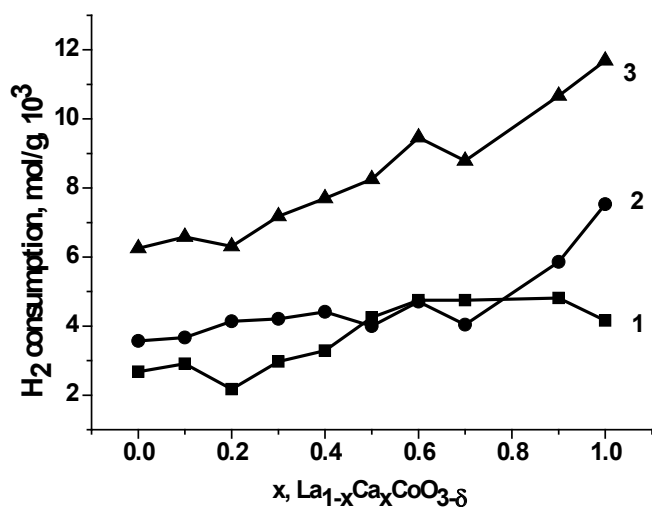


Figure 5. H₂ consumption of MC prepared $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ versus x in the temperature fields: 40-500°C (1), 500-900°C (2) and 40-900°C (3)

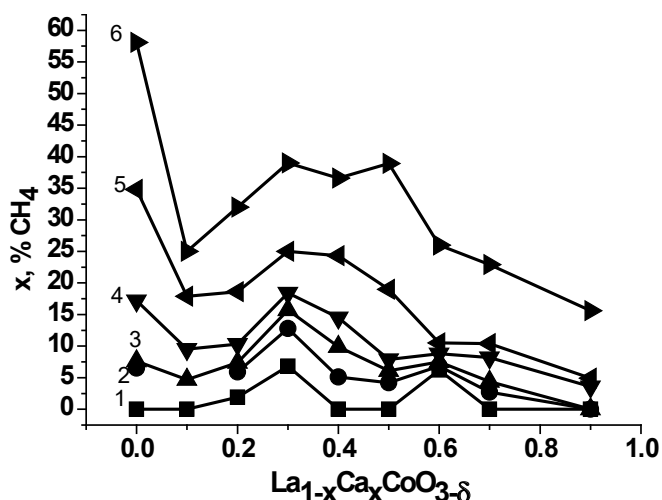


Figure 6. Conversion of methane of MC prepared $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ versus x at: 350°C (1), 400°C (2), 450°C (3), 500°C (4), 550°C (5), 600°C (6)

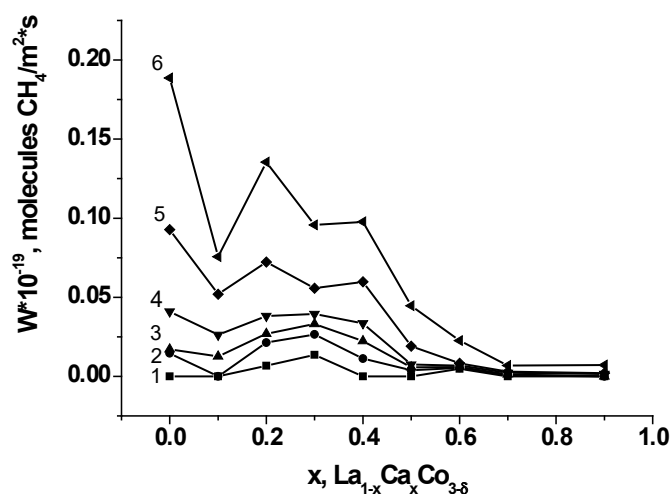


Figure 7. Catalytic activity (reaction rate) in methane oxidation of MC prepared $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ versus x at: 350°C (1), 400°C (2), 450°C (3), 500°C (4), 550°C (5), 600°C (6)

mentioned also that this is not the case of the sample at $x=0.2$, probably, for some additional reasons.

Apart from the sample with $x=0$, there is observed the correlation between the activity of calcium-containing catalysts and the content of Co^{4+} in the range of compositions $x=0.1-0.4$. At the same time, the correlation was observed with the catalysts prepared by the Pechini method at all $x=0-0.3$ range including the sample with $x=0$ free of surface cobalt [20]. The further decrease in the activity at an increase in the Co^{4+} content may be accounted for by the appearance of calcium oxide on the particle surface [20]. The activity of the prepared by us sample of lanthanum cobaltite is $20 \cdot 10^{16}$ CH₄ molecules/m²*s against $7 \cdot 10^{16}$ CH₄ molecules/m²*s showed by the Pechini sample [20]; this is almost 3 times difference. The catalytic activity of the other samples is only a little higher than that of the Pechini samples.

It is not impossible that the higher catalytic activity of lanthanum cobaltite prepared by the mechanochemical method is the result of presence of dispersed cobalt oxide on the surface while the other samples of the series are free of this oxide. Enrichment of the surface with cobalt oxide also was observed before upon mechanochemical treatment of lanthanum cobaltite [26]. It seems like this is the specific feature of the mechanochemical method since the other methods, e.g. the Pechini method, produce lanthanum cobaltite enriched with surface lanthanum compounds. It is reasonable to suppose that the initial decrease in the activity observed upon calcium introduction results from the decrease (absence) in the content of cobalt oxide on the surface of calcium-containing samples. The further increasing activity up to the intermediate maximum at $x=0.3-0.5$ may be accounted for by an increase in the content of Co^{4+} cations, while the activity lowering at $x>0.5$ by the emergence of the less active brownmillerite phase in the samples and calcium oxide on the surface. Hence it was shown that catalytic activity in oxidative process depends not only content of low bounded oxygen form but on surface enrichment with different oxides that may increase (LaCoO_3) or decrease ($\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ $x>0.4$) activity.

Conclusion

The mechanochemical method followed by thermal treatment at 1100°C was demonstrated to allow preparation of homogeneous solid solutions in the $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ system at $x \leq 0.5$. Among the prepared samples, non-substituted lanthanum cobaltite is the most active to methane oxidation due to, probably, the presence of disperse cobalt oxide on the sample surface. This phenomenon is the specific feature of the mechanochemical method. With substituted perovskites, introduction of calcium results in lower activity probably due to absent of cobalt oxide on the sample surface and appearance of calcium oxide impurity. An increase in the catalytic activity at the composition range of $x=0.1-0.3$ up to the intermediate maximum at $x=0.3-0.5$ correlates with increase of low bounded oxygen form in perovskites or Co^{4+} content. The further decrease in the activity may be accounted for by the formation of the vacancy-ordered less active brownmillerite phase. The following series of the catalyst activity is discovered: $\text{LaCoO}_3 > \text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3 > \text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3 > \text{Ca}_2\text{Co}_2\text{O}_5$

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References

- Tejuga LG, Fierro JLG, Tascon JMD (1989) Structure and Reactivity of Perovskite-Type Oxides. *Adv Catal* 36: 237.

2. Baran EJ (1990) Structural Chemistry and Physicochemical Properties of Perovskite-like Materials. *Catal Today* 8: 133.
3. Yamazoe N, Teraoka Y (1990) Oxidation Catalysis of Perovskites – Relationships to bulk structure and Composition (Valence, Defects, etc.). *Catal Today* 8: 175.
4. Merino N, Barbero BP, Grande P, Cadus LE (2005) $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ Perovskite-Type Oxides: Preparation, Characterization, Stability, and Catalytic Potentiality for the Total Oxidation of Propane. *J Catal* 231: 232.
5. Merino N, Barbero BP, Eloy P, Cadus LE (2006) $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ perovskite-type oxides: Identification of the surface oxygen species by XPS. *Appl Surf Sci* 253: 1489.
6. Haas O, Holzer F, Muller S, McBreen JM, Yang XQ, et al. (2002) X-Ray Absorption and Diffraction Studies of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ Perovskite, a Catalyst for Bifunctional Oxygen Electrodes. *Electrochimica Acta* 47: 3211.
7. Yazdanbakhsh M, Tavakkoli H, Hosseini SM (2011) Electrical and Optical Properties of Nanosized Perovskite-type $\text{La}_{0.5}\text{Ca}_{0.5}\text{MO}_3$ ($\text{M}=\text{Co}, \text{Ni}$) prepared using Sol-Gel Method. *Afr J Chem* 64: 71.
8. Wong NW, Lawz WJ, Yan YG (2013) Phase diagram and crystal chemistry of the $\text{La}-\text{Ca}-\text{Co}-\text{O}$ system. *Solid State Sci* 17: 107.
9. Cherepanov VA, Gavrilova LY, Barkhatova LY, Voronin VI, Trifonova MV, et al. (1998) Phase Equilibria in the $\text{La}-\text{Me}-\text{Co}-\text{O}$ ($\text{Me}=\text{Ca}, \text{Sr}, \text{Ba}$) Systems. *Ionics* 4: 309.
10. Gavrilova LY, Cherepanov VA, Surova TV, Baimistruk VA, Voronin VI (2002) Phase equilibria and oxygen nonstoichiometry in complex oxide phases of the $\text{La}-\text{Ca}-\text{Co}-\text{O}$ system. *Russian J Phys Chem* 76: 150.
11. Mastin J, Einarsrud MA, Grande T (2006) Crystal Structure and Thermal Properties of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ ($0 \leq x \leq 0.4$). *Chem Mater* 18: 1680.
12. Kononyuk IF, Tolochko ASP, Lutsko VA, Anishchik VM (1983) Preparation and properties of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($0.2 \leq x \leq 0.6$). *J Solid State Chem* 48: 209.
13. Melo DS, Marinho EP, Soledade LEB, Melo DMA, Lima SJG, et al. (2008) Lanthanum-based perovskites obtained by the polymeric precursor method. *J Mater Sci* 43: 551.
14. Pathak S, Kuebler J, Payzant A, Orlovskaya N (2010) Mechanical behavior and electrical conductivity of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ($x = 0, 0.2, 0.4, 0.55$) perovskites. *J Power Sources* 195: 3612.
15. Merino NA, Barbero B, Eloy P, Cadus LE (2006) $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ perovskite-type oxides: Identification of the surface oxygen species by XPS. *J Appl Surf Science* 253: 1489.
16. Kumar DA, Selvasekarapandian S, Nithya H, Leiro J, Masuda Y (2013) Effect of calcium doping on LaCoO_3 prepared by Pechini method. *Power Technology* 235: 140.
17. Haas O, Ludwig C, Bergmann U, Singh RN, Braun A, Graule T (2011) X-ray absorption investigation of the valence state and electronic structure of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ in comparison with $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ and $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$. *J Solid State Chem* 184: 3163.
18. Nadeev AN, Tsybulya SV, Belyaev VD, Yakovleva IS, Isupova LA (2008) Weakly bound oxygen and its role in stability of solid solutions $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$. *Russ J Structural Chem* 49: 1077.
19. Gerasimov EY, Isupova LA, Tsybulya SV (2015) Microstructural features of the $\text{La}_{1-x}\text{Ca}_x\text{FeO}_{3-\delta}$ solid solutions prepared via Pechini route. *Mater Res Bull* 70: 291.
20. Isupova LA, Kulikovskaya NA, Saputina NF, Gerasimov EY (2018) Catalytic activity of $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ ($x = 0-1$) perovskites prepared by Pechini route in deep oxidation of methane. *Kinetics Catalysis* 59: 407.
21. Gerasimov E, Kulikovskaya N, Chuvilin A, Isupova L, Tsybulya S (2016) Microstructural Changes in $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ Solid Solutions Under the Influence of Catalytic Reaction of Methane Combustion. *Top Catal* 59: 1354.
22. Boldyrev VV (1988) Mechanical activation and its application to technology. *J Chem Phys* 11: 821.
23. Avvakumov EG, Senna M, Kosova NV (2001) Soft Mechanochemical Synthesis: A Basis for new Chemical Technologies; Kluwer Acad. Publ: Boston-Dordrecht-London.
24. Futai M, Yonghua C (1986) Characterization of perovskite-type oxide catalysts RECoO_3 by TPR. *React Kinet Catal Lett* 31: 47.
25. Yakovleva IS, Isupova LA, Rogov VA (2009) Oxygen species and their reactivity in the mechanochemically prepared substituted perovskites $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$ ($x = 0-1$). *Kinetics Catalysis* 50: 275.
26. Pauli IA, Avvakumov EG, Isupova LA, Sadykov VA, Poluboyarov VA (1993) Effect of mechanical activation on synthesis and catalytic properties of lanthanum cobaltite. Conference on Mechanochem. (InCoMe -93 Kosice); Cambridge Intersci. Publ.