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

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Abstract
A number of perovskite-like oxides La\(_{1-x}\)Ca\(_x\)CoO\(_{3-\delta}\) (\(x = 0\text{--}1\)) 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 La\(_{1-x}\)Ca\(_x\)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 \(x=0.3\text{--}0.5\). The catalytic activities decreased in the series: LaCoO\(_3\) \(>\) La\(_{0.8}\)Ca\(_{0.2}\)CoO\(_3\) \(>\) La\(_{0.6}\)Ca\(_{0.4}\)CoO\(_3\) \(>\) Ca\(_2\)Co\(_2\)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\(_{\beta}\) cations) only in the composition range \(x=0.1\text{--}0.4\). 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 La\(_{1-x}\)Me\(_{x}\)\((\text{Me}1)\)CO\(_3\) (Me\(_1\)=Ca, Sr, Ba; Me\(_2\)=Fe, Co, Mn, 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\(_1\)) and substituting (Me\(_2\)) cations, as well as on the preparation conditions. Substituted perovskites La\(_{1-x}\)Ca\(_x\)CoO\(_3\) 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 La\(_{1-x}\)Ca\(_x\)CoO\(_3\) on the preparation conditions. It was shown that the homogeneity range in substituted lanthanum cobalites La\(_{1-x}\)Ca\(_x\)CoO\(_3\) 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 \(x=0\text{--}0.25\) [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°C of the calcinations temperature according [16,17].

The differences in the phase composition of perovskites La\(_{1-x}\)Ca\(_x\)CoO\(_3\) 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 La\(_{1-x}\)Ca\(_x\)FeO\(_3\) 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] for the one-phase perovskites prepared by the citrate method, the least active being the sample with \(x=0.2\) (0.5>0.4>0.2). 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 \(x=0.3\)) 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 La$_{1-x}$Ca$_x$CoO$_{3-δ}$ system. The present work was aimed at mechanochemical preparation of La$_{1-x}$Ca$_x$CoO$_{3-δ}$ ($x=0-1$) samples and at characterizing their physicochemical and catalytic properties.

**Experimental**

Initial compounds for synthesis were La$_2$O$_3$, CaO, Co$_3$O$_4$ of the chemical purity grade.

The mechanochemical (MC) method for synthesis of La$_{1-x}$Ca$_x$CoO$_{3-δ}$ ($x=0; 0.1, 0.2; 0.3, 0.4; 0.5, 0.6; 0.7, 0.8; 0.9, 1$) 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 20 range of 10°-80° 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% oxygen at 500°C for 0.5 h and cooled in oxygen to room temperature). The Origin 6.0 program package was used for calculation of the peak areas underneath the TPR curves. H$_2$ consumption of MC prepared La$_{1-x}$Ca$_x$CoO$_{3-δ}$ was calculated for peaks in the temperature fields: 40-150°C, 40-500°C, 500-900°C and 40-900°C.

The catalytic activity to methane oxidation was studied at 350-600°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 rate of 2.4 l/h. The reaction rate for the initial methane concentration was determined using argon desorption at 300°C.

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$$ W_r [\text{molecules of CH}_4 \cdot \text{m}^2 \cdot \text{s}^{-1}] = k \cdot C_0 \cdot \frac{2.69 \cdot 10^{-11}}{\tau S_{sp} q} \cdot (x) $$

Where $k$ is effective rate constant of the first order reaction calculated for a plug-flow reactor using equation $k = \frac{-2.3 \cdot \lg (1-x)}{(\tau S_{sp} q)}$ ($x$ is the conversion of CH$_4$, q is weighed sample, $\tau$ 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 La$_{1-x}$Ca$_x$CoO$_{3-δ}$ ($0 \leq x \leq 1$)**

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 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 La$_{1-x}$Ca$_x$CoO$_{3-δ}$ samples (no more than 1 m$^2$/g) show their good sintering (Table 1).

**Microstructure of MC prepared La$_{1-x}$Ca$_x$CoO$_{3-δ}$**

From HRTEM data, samples of La$_{1-x}$Ca$_x$CoO$_{3-δ}$ 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 $x>5$, 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 La$_{1-x}$Ca$_x$CoO$_{3-δ}$ 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.
Formally, to different steps of the sample reduction: is reported elsewhere [24]. By analogy with literature data [25], we indicate the corresponding change in the quantity of Co\(^{4+}\) cations. Co\(^{3+}\) → Co\(^{2+}\) and Co\(^{4+}\) → Co\(^{0}\) at below 500°C, and Co\(^{2+}\) → Co\(^{0}\) at above 500°C is shifted towards low temperature region. The reduction of cations onset temperature at increasing \(x\), while the high-temperature peak increasing in intensity of the first peak, to lowering of the reduction temperature peak at 600°C. The substitution leads to splitting and temperature peak is observed at ca. 400°C, and the second high-reduction with hydrogen with the temperature rise; the first low-temperature peak is shifted towards low temperature because of overlapping of the low- and high-temperature absorption may result from incorrect calculation of the 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 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 weakly bonded surface oxygen species, probably, due to the absence (desorption) of these species under conditions of the catalytic studies.

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...
Catalytic activity (reaction rate) in methane oxidation of La$_{1-x}$Ca$_x$CoO$_3$$_\delta$ versus x at: 350°C (1), 400°C (2), 450°C (3), 500°C (4), 550°C (5), 600°C (6)

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 20·10$^{16}$ CH$_4$ molecules/m$^2$·s against 7·10$^{16}$ CH$_4$ molecules/m$^2$·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 mechanochanical 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 up to the intermediate maximum at x=0.3-0.5 correlates 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].

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Conclusion
The mechanochemical method followed by thermal treatment at 1100°C was demonstrated to allow preparation of homogeneous solid solutions in the La$_{1-x}$Ca$_x$CoO$_3$$_\delta$ system at x ≤ 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 absence 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: LaCoO$_3$ > La$_{0.6}$Ca$_{0.4}$CoO$_3$ $>$ La$_{0.8}$Ca$_{0.2}$CoO$_3$ > Ca$_2$Co$_2$O$_5$

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