Mechanochemical Synthesis of Perovskite Deep Oxidation Catalysts $La_{1-x}Ca_xFeO_{3-0.5x}$

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Abstract

XRD, SIMS, BET, MDPD, TPR, and HREM were used to study the effect of time of mechanical treatment (MT) of the mixture of simple La_2O_3, CaO and Fe_2O_3 oxides and the temperature of subsequent calcination on the phase composition, real structure and catalytic properties of substituted $La_{1-x}Ca_xFeO_{3-0.5x}$ ($0 \leq x \leq 1$) perovskites in CO catalytic oxidation. The phase composition and microstructure of MT samples differ significantly from those of ceramic samples: no Grenier phase $La_{0.33}Ca_{0.67}FeO_{2.67}$ were and microheterogeneous solid composite $La_{0.5}Ca_{0.5}FeO_{2.75}$ found in ceramic samples; independently of the time of treatment and Ca content, the MT samples are composed of the perovskite and brownmillerite phases. The microstructure of MT samples ($T_{calc} < 1100$ °C) is distinguished by disordered stacking of microblocks of those phases. An increase in the calcination temperature and MT time does not lead to an increase of the amount of ternary oxides and calcium content in solid solution. The microstructure of samples obtained by ceramic synthesis is suggested to arise due to decomposition of the high-temperature (1100 °C) homogeneous solid solution during its cooling. By contrast, MT does not result in formation of such solution due to short time of thermal annealing. Specific catalytic activity of samples in the reaction of CO catalytic oxidation was found to correlate with the density of extended defects (interphase and intergrain boundaries) and the amount of reactive oxygen easily removed by H_2-TPR at middle (350–400 °C) temperatures.

INTRODUCTION

In a number of catalytic high-temperature processes of deep oxidation (methane combustion, ammonia oxidation to NO_x, toxic wastes incineration) perovskites can be a viable option to the noble metals because they are in expensive and more stable under reaction conditions [1–3]. For the above reactions, perovskite system $La_{1-x}Ca_xFeO_{3-0.5x}$ [4] is one of the most active.

The routine perovskite synthesis as precipitation and ceramic methods suffer from a number of disadvantages: large amounts of waste water in the former case and high process temperature (>1000 °C) and a long period of sintering in the latter case. The method of mechanochemical treatment was shown to be very promising for synthesis of perovskites [5], because it is less power-consuming and wasteless, and high-surface-area samples are obtained. However, this method has not yet been applied for the $La_{1-x}Ca_xFeO_{3-0.5x}$ system.

The data on the structure and phase composition of these perovskites obtained by the ceramic method are contradictory [6–12]. Thus, according to [6, 7], a homogeneous perovskite solid solution forms up to calcium concentration of about 0.5. To the contrary, homologous series of vacancy-ordered phases of $A_nB_nO_{3n-1}$ compositions (A = La, Ca; B = Fe) were suggested to exist between a perovskite phase ($n = \infty$) and a brownmillerite phase ($n = 2$); while for composition with $n = 3$ a new phase $La_{0.33}Ca_{0.67}FeO_{2.67}$ was revealed [8]. According to [8-12], the samples of $La_{1-x}Ca_xFeO_{3-0.5x}$ series have a complex morphological structure, which strongly depends upon conditions of their preparation.

According to our data [13], the ceramic series samples are comprised of three phases: pe-

rovskite $LaFeO_3$, Grenier phase $La_{0.33}Ca_{0.67}FeO_{2.67}$ and brownmillerite $Ca_2Fe_2O_5$. A complex morphological structure of ceramic samples was established: the particles are formed by coherent intergrowth of perovskite and Grenier phases at $0.17 < x < 0.67$ and by Grenier and brownmillerite phases at $0.67 < x < 1.0$. For sample with $x = 0.5$, the thickness of each phase layers is about 40 Å, which permits its assignment to microheterogeneous solid solutions [15]. This sample exhibits the highest catalytic activity in CO oxidation process.

Since the MT permits to prepare perovskites at lower temperatures and shorter calcination times as compared with the ceramic method, it was expected that oxygen vacancy ordering could be hindered under such conditions. Therefore, the region of homogeneous solid solutions formation would probably be extended in comparison with ceramic method and even provide a continuous range of solid solutions in the structure of calcium-substituted lanthanum ferrite.

This work aims at study of the possibility of synthesis of homogeneous solid solutions in the $La_{1-x}Ca_xFeO_{3-0.5x}$ system by using MT method, at analysis of their real structure, and estimation of their catalytic activity in the CO oxidation.

EXPERIMENTAL

Samples of $La_{1-x}Ca_xFeO_{3-0.5x}$ (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) were synthesized by calcinaton at 700, 900 or 1100 °C for 4 h of preliminary activated mixture of reagents taken in required ratios. The mechanical treatment was performed in an APF-5 high-power planetary mill, with acceleration ~40 g. The time of treatment varied from 3 to 10 min, the ratio between masses of the activated powder and milling balls was 1 : 10. As an initial reagent, La_2O_3 (obtained from $La(NO_3)_2$ by calcination at 500 °C for 4–5 h), Fe_2O_3 and CaO ("kh. ch.") were used. The ceramic synthesis method was described elsewhere [13].

An URD-63 diffractometer (Germany) with CuK_a radiation was used to perform XRD. The patterns were recorded at 1 °/min; the angle range was $2\theta = 5–70°$. To refine the phase composition (amounts of admixed phases, weak superstructural reflexes), the patterns were scanned with a scanning step of 0.02° over the scanning range 2θ, the time of accumulation was 30 s in each point.

The phase and stoichiometric compositions of phases were determined by differential phase dissolving (MDPD) which relies on the separation of regions of different phase dissolutions at varying such parameters as temperature (in the range of 20–90 °C) and acidity of the solution (1–10 M HCl) [14]. The solution composition was analyzed by atomic-emission spectroscopy with inductively coupled plasma. The photometry was performed using a BAIRD spectrometer (the Netherlands). The relative experiment error was less than 20 %.

TEM images of samples particles were obtained using a JEM-100X high resolution electron microscope (the resolution 3 Å).

TPR studies were performed in a flow setup equipped with a thermal conductivity detector, the sample fraction varied from 0.25 to 0.5 mm. Before reduction, the samples were pretreated in a flow of oxygen at 500 °C for 0.5 h, then cooled to room temperature in oxygen. The sample mass was 50 mg, the reducing mixture (10 % H_2 in Ar) was fed at 40 cm^3/min. The samples were heated at a rate of 10 °/min to 900 °C. The error of the mixture components determination was below 20 %.

BET surface area was determined by the thermal desorption of argon at 300 °C. The catalytic activity of samples (catalyst fractions 0.5–1 and 1–2 mm) was determined in the reaction of CO oxidation at 400, 450, and 500 °C using a flow reactor with GC analysis of components. The sample mass was 1 g, the rate of circulation was 1200 l/h, the mixture feed rate (1 % CO + 1 % O_2 in He) was 10 l/h. The reaction rate extrapolated to zero conversion was calculated by using the relation (in molecules CO /m^2 s): $w = [x/(1 - x)](7.47\ 10^{17}/S_{BET})$, where x is the degree of CO conversion. The error of chromatographic determination of components concentration in the gas mixture was below 20 %.

RESULTS AND DISCUSSION

Phase composition of $La_{1-x}Ca_xFeO_{3-0.5x}$ samples

The calcination temperature was found to be one of the main factors determining the phase composition and microstructure of samples. Here the effect of calcination temperature will be considered for the samples prepared by mechanical treatment of the initial oxides for 3 min.

X-ray patterns of end samples ($x = 0$ and $x = 1$) calcined at 700 °C exhibit broadened reflexes of perovskite ($x = 0$) and brownmillerite ($x = 1$) phases and a lot of peaks corresponding to initial oxides (Table 1). The intermediate samples contain two complex oxide phases $LaFeO_3$ and $CaFeO_{3-x}$ along with the initial oxide. The shape of MDPD patterns suggests that the product particles are likely to be composed of La–Fe–O and Ca–Fe–O conglomerate particles. Moreover, the surface of particles is enriched by the Ca–Fe–O oxide phase. In this surface layer the concentration of calcium decreases with depth. The formation of only two-component perovskites and the absence of ternary mixed oxides for those samples annealed at 700 °C can be explained by too low temperature of calcination.

According to MDPD and XRD data (including the small angles scanning), the samples of the end compositions ($x = 0$ and $x = 1$) calcined at 900 °C are nearly single-phase systems consisting of perovskite and brownmillerite, respectively, with the amount of product around 93–96 % (Table 2), which is similar to the results of ceramic synthesis [13]. As revealed by XRD, the samples of intermediate compositions are composed of perovskite (samples with $x < 0.5$) and perovskite and brownmillerite (samples with $x > 0.5$) phases. In samples with $x < 0.5$ the MDPD data indicate the presence of a phase with Ca : Fe = 1 : 1 stoichiometry. This fact suggests that in the region of lower calcium concentrations $CaFeO_y$ phase is either crystallized in the perovskite-like structure or is X-ray amorphous. The analysis of MDPD stoichiograms suggests that the latter phase is deposited as a layer on the surface of perovskite particles. This suggestion agrees with SIMS data [16] indicating that the surface is enriched by calcium and depleted with lanthanum. As follows from the MDPD and XRD data, an increase of calcination temperature

TABLE 1

Phase composition of $La_{1-x}Ca_xFeO_{3-0.5x}$ samples (3 min MT, calcination temperature 700 °C, 4 h)

Sample[a] (S_{sp}, m^2/g)	La : Ca : Fe[b]	Phase composition (according to XRD)	Phase composition (according to MDPD), %
$LaFeO_3$ (3.5)	La_1Fe_1	$LaFeO_3$	La_1Fe_1 – 51.0
		Fe_2O_3	Fe – 3.0
		La_2O_3	La – 46.0
$La_{0.6}Ca_{0.4}FeO_{2.8}$ (4.4)	$La_{0.60}Ca_{0.40}Fe_1$	Fe_2O_3, CaO	–
$La_{0.4}Ca_{0.6}FeO_{2.7}$ (4.6)	$La_{0.44}Ca_{0.40}Fe_1$	Fe_2O_3	$La_{1.3}Ca_{1.0}Fe_{0.2}$ – 52.0
		CaO	Fe – 34.0
			La – 7.0
			Ca – 6.0
$La_{0.2}Ca_{0.8}FeO_{2.6}$ (3.3)	$La_{0.10}Ca_{0.63}Fe_1$	Fe_2O_3	$La_{0.19}Ca_{1.0}$ $Fe_{0.17}$ – 34.0
		CaO	Fe – 54.0
			La – 3.0
			Ca – 7.0
$Ca_2Fe_2O_5$ (3.8)	Ca_1Fe_1	$Ca_2Fe_2O_5$	CaFe – 69.4
			Fe – 16.5
			Ca – 14.0

Note. Here and in Tables 1–5:
[a]Nominal stoichiometry of the samples.
[b]Integral chemical composition.

TABLE 2

Phase composition of $La_{1-x}Ca_xFeO_{3-0.5x}$ samples (3 min MT, calcination temperature 900 °C, 4 h)

Sample[a] (S_{sp}, m^2/g)	La : Ca : Fe[b]	Phase composition (according to XRD)	Phase composition (according to MDPD), %
$LaFeO_3$ (1.7)	La_1Fe_1	$LaFeO_3$	La_1Fe_1 – 93.6
		Fe_2O_3	Fe – 0.8
		La_2O_3	La – 7.5
$La_{0.8}Ca_{0.2}FeO_{2.9}$ (4.4)	$La_{0.80}Ca_{0.19}Fe_1$	$LaFeO_3$	$La_{0.92}Ca_{0.08}Fe_1$ – 85.8
			Ca_1Fe_1 – 5.8
			Fe – 0.3
			La – 2.3
			Ca – 0.5
$La_{0.6}Ca_{0.4}FeO_{2.8}$ (4.5)	$La_{0.45}Ca_{0.39}Fe_1$	$LaFeO_3$	$La_{0.88}Ca_{0.14}Fe_1$ – 64.4
		$Ca_2Fe_2O_5$ (traces)	Ca_1Fe_1 – 27.4
			Fe – 0.6
			La – 0.4
			Ca – 1.4
$La_{0.4}Ca_{0.6}FeO_{2.7}$ (5.1)	$La_{0.49}Ca_{0.47}Fe_1$	$LaFeO_3$	$La_{0.88}Ca_{0.11}Fe_1$ – 67.1
		$Ca_2Fe_2O_5$	Ca_1Fe_1 – 30.0
			Fe – 0.7
			La – 0.7
			Ca – 1.2
$La_{0.2}Ca_{0.8}FeO_{2.6}$ (4.4)	$La_{0.20}Ca_{0.74}Fe_1$	$LaFeO_3$	$La_{0.67}Ca_{0.34}Fe_1$ – 60.1
		$Ca_2Fe_2O_5$	Ca_1Fe_1– 38.0
			Fe – 1.6
			Ca – 0.2
$Ca_2Fe_2O_5$ (1.1)	Ca_1Fe_1	$Ca_2Fe_2O_5$	Ca_1Fe_1– 96.0
			Fe – 1.1
			Ca – 2.8

[a, b] See Note to Table 1.

up to 900 °C leads to an increase of the total amount of interaction products to 90 % and results in formation of ternary oxides. With the increase of its amount in the initial mixture, the calcium content in the solid solution increases up to 0.4 (here and below: molar fractions per formula unit $La_{1-x}Ca_xFeO_{3-0.5x}$) (see Table 2).

In samples calcined at 1100 °C, the amount of the initial oxide phases decreases to 5 %, while the structure of perovskite and brownmillerite improves. Hence the phase composition of these samples does not change significantly as compared with that of samples calcined at 900 °C (Table 3). The MDPD data revealed that the synthesis products distributions is changed: the perovskite content in samples calcined at 1100 °C is lower than that in samples calcined at 900 °C, whereas the amount of brownmillerite is higher (Fig. 1, *a* and *b*). Therefore, an increase of the calcination temperature up to 1100 °C does not increase the amount of ternary perovskite, whereas the share of brownmillerite in the mixture increases. For all compositions, the quantity of calcium in perovskite is about $x = 0.2$ (see Table 3), which indicates that the amount of calcium decreases in samples calcined at 1100 °C as compared with samples calcined at 900 °C. The data received imply the instability of the solid calcium solutions in the perovskite structure (with calcium amount higher than $x = 0.2$) in the samples calcined at 900 °C.

As time of preliminary activation of oxides increases to 6 [16] and 10 min, the phase composition of samples does not significantly

TABLE 3

Phase composition of $La_{1-x}Ca_xFeO_{3-0.5x}$ samples (3 min MT, calcination temperature 1100 °C, 4 h)

Sample[a] (S_{sp}, m^2/g)	La : Ca : Fe[b]	Phase composition (according to XRD)	Phase composition (according to MDPD), %
$LaFeO_3$ (1.0)	La_1Fe_1	$LaFeO_3$	La_1Fe_1 – 94.0
			Fe – 0.5
		La_2O_3	La – 5.5
$La_{0.8}Ca_{0.2}FeO_{2.9}$ (3.3)	$La_{0.78}Ca_{0.23}Fe_1$	$LaFeO_3$	La_1Fe_1 (0.15 % Ca) – 73.0
		$Ca_2Fe_2O_5$ (traces)	Ca_1Fe_1 – 19.7
			Fe – 0.9
			La – 4.0
			Ca – 2.5
$La_{0.6}Ca_{0.4}FeO_{2.8}$ (2.6)	$La_{0.60}Ca_{0.37}Fe_1$	$LaFeO_3$	La_1Fe_1 (0.3 % Ca) – 74.0
		$Ca_2Fe_2O_5$	Ca_1Fe_1 – 24.0
			Fe – 0.3
			La – 1.1
			Ca – 0.7
$La_{0.4}Ca_{0.6}FeO_{2.7}$ (0.9)	$La_{0.50}Ca_{0.48}Fe_1$	$LaFeO_3$	$La_{0.75}Ca_{0.18}Fe_1$ – 59.6
		$Ca_2Fe_2O_5$	Ca_1Fe_1 – 39.0
			Fe_2O_3 – 0.4
			La_2O_3 – 0.3
			CaO – 0.7
$La_{0.2}Ca_{0.8}FeO_{2.6}$ (1.2)	$La_{0.20}Ca_{0.74}Fe_1$	$LaFeO_3$	$La_{0.68}Ca_{0.25}Fe_1$ – 44.4
		$Ca_2Fe_2O_5$	Ca_1Fe_1 – 52.1
			Fe_2O_3 – 1.5
$Ca_2Fe_2O_5$ (0.5)	Ca_1Fe_1	$Ca_2Fe_2O_5$	Ca_1Fe_1 – 96.6, CaO – 3.2

[a, b] See Note to Table 1.

change, the ratio between the amounts of product phases being only affected. MDPD data show (Fig. 2, *a*) that an increase in the time of MT from 3 to 6 min provides a slight decrease in the amount of perovskite phase in samples calcined at 900 °C. The only exception is observed for $x = 0.4$. For samples with $x > 0.5$ (see Fig. 2, *b*), the fraction of brownmillerite increases with the time of treatment. The total amount of products in samples activated for 6 min is also lower or at least not higher than that in samples treated for 3 min (see Fig. 2, *c*). These trends remain the same when the time of activation increases to 10 min (Table 4). Only if the time of the latter samples calcination is increased from 4 to 15 h, the amount of perovskite increases (Table 5).

For samples with $x < 0.5$ calcined at 1100 °C, an increase in the time of activation from 3 to 6 minutes (MDPD data) raises the content of the perovskite phase and decreases the content of brownmillerite (Fig. 3, *a* and *b*). If $x > 0.5$, the changes are insignificant being within the experimental error. This tendency remains as the time of activation rises to 10 min (see Fig. 3, *c*). It should be noted that the increase in the time of activation provides redistribution of the synthesis products in the samples with $x < 0.5$ calcined at 1100 °C: the content of perovskite and the total amout of products increase. For all samples, the concentration of calcium in perovskite (x) is 0.2. Hence, the concentration of calcium in samples calcined at 1100 °C is lower as compared to those calcined at 900 °C.

These results indicate that the increase in the MT time is not favorable for the samples series calcined at 900 °C and is advisable for samples calcined at 1100 °C. As regards the interaction beetween the solid reagents, the optimal MT time depends on the temperature of subsequent thermal treatment and is ~3 min

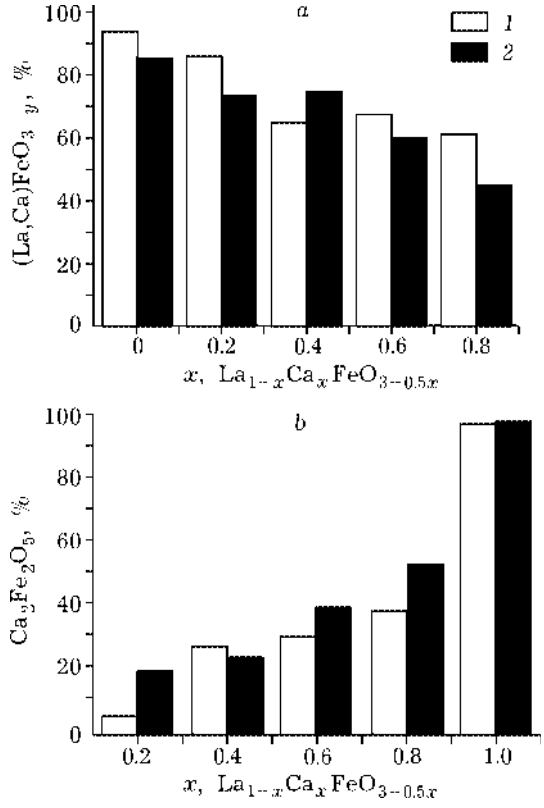

Fig. 1. Effect of the calcination temperature on the phase composition of samples treated for 3 min. *T*, °C: 900 (*1*), and 1100 (*2*).

for samples calcined at 900 °C and ~10 min for those calcined at 1100 °C. For the above temperatures, the difference in the optimal activation time can be associated, for example, with different rates of relaxation of the lattice strains in oxides calcined at different temperatures [19].

Hence, an application of MT for synthesis of ternary La–Ca–Fe–O systems does not significantly extend the region of homogeneous perovskite solid solutions existence. For ceramic synthesis, the maximal concentration of calcium in true homogeneous solid solution based on the perovskite structure does not exceed $x = 0.17$. For MT samples calcined at 1100 °C, the concentration of calcium is somewhat higher, but it does not exceed $x = 0.25$ irregardless of the activation time. Though the concentration of calcium in perovskite increases to $x = 0.4$ for MT samples calcined at 900 °C, the solutions are either unstable (since an increase in time or temperature of calcination provides a decrease in the calcium concentration) or are microheterogeneous. This conclusion agrees with

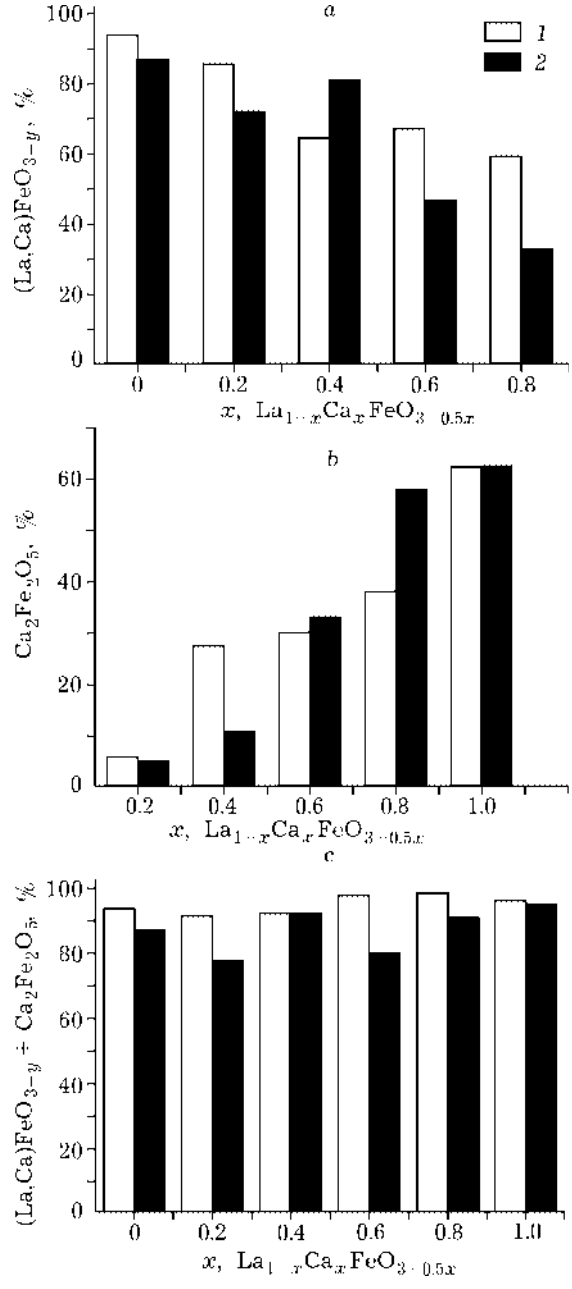

Fig. 2. Effect of the treatment time on the phase composition of samples calcined at 900 °C for 4 h. MT time, min: 3 (*1*), and 6 (*2*).

EM data obtained for samples subjected to mechanical treatment for 6 min.

Microstructure of samples

A sample of $La_{0.6}Ca_{0.4}FeO_{2.8}$ obtained by the mechanical treatment of reagents for 6 min and calcined at 900 °C for 4 h was found to be comprised of micron-sized particles. The outer shell of these particles is composed of random

TABLE 4

Phase composition of $La_{1-x}Ca_xFeO_{3-0.5x}$ samples (10 min MT, calcination temperature 700–1100 °C, 4 h)

T, °C	Sample[a] (S_{sp}, m^2/g)	La : Ca : Fe[b]	Phase composition (according to XRD)	Phase composition (according to MDPD), %
700	$La_{0.8}Ca_{0.2}FeO_{2.9}$ (10)	$La_{0.80}Ca_{0.20}Fe_1$	$LaFeO_3$ Fe_2O_3 La_2O_3	La_1Fe_1 – 33.4 Fe_2O_3 – 19.8 La_2O_3 – 41.9 Ca – 3.0 Ca_1Fe_1 – 19.0
	$La_{0.6}Ca_{0.4}FeO_{2.8}$ (6.4)	$La_{0.62}Ca_{0.36}Fe_1$	$(La,Ca)FeO_3$ Fe_2O_3 La_2O_3	La_1Fe_1 – 45.5 Fe_2O_3 – 21.1 La_2O_3 – 20.0 Ca_1Fe_1 – 7.7 Ca – 5.3
900	$La_{0.8}Ca_{0.2}FeO_{2.9}$ (5.7)	$La_{0.80}Ca_{0.19}Fe_1$	$(La,Ca)FeO_3$ La_2O_3	La_1Fe_1 – 71.2 Ca_1Fe_1 – 3.6 Fe – 5.9 La – 17.3 Ca – 2.0
	$La_{0.6}Ca_{0.4}FeO_{2.8}$ (5.4)	$La_{0.62}Ca_{0.36}Fe_1$	$(La,Ca)FeO_3$ La_2O_3	La_1Fe_1– 57.0 Ca_1Fe_1 – 7.8 Fe – 4.1 La – 25.1 Ca –5.3
1100	$La_{0.8}Ca_{0.2}FeO_{2.9}$ (2.1)	$La_{0.80}Ca_{0.19}Fe_1$	$LaFeO_3$	La_1Fe_1 – 40.2 $La_{0.8}Ca_{0.2}Fe_1$ – 55.9 La – 1.5 Ca – 1.3
	$La_{0.6}Ca_{0.4}FeO_{2.8}$ (1.3)	$La_{0.61}Ca_{0.37}Fe_1$	$(La,Ca)FeO_3$	$La_{0.8}Ca_{0.2}Fe_1$ – 85.5 Fe_2O_3 – 1.6 La_2O_3 – 1.3 Ca_1Fe_1 – 11.2

[a, b]See Note to Table 1.

TABLE 5

Phase composition of $La_{1-x}Ca_xFeO_{3-0.5x}$ samples (10 min MT, calcination temperature 900 °C, 15 h)

Sample[a]	La : Ca : Fe[b]	Phase composition (according to XRD)	Phase composition (according to MDPD), %
$La_{0.8}Ca_{0.2}FeO_{2.9}$	$La_{0.88}Ca_{0.18}Fe_1$	$LaFeO_3$	$La_1Ca_{0.08}Fe_1$ – 92.0 Ca_1Fe_1 – 5.2 La – 0.6 Ca – 2.2
$La_{0.6}Ca_{0.4}FeO_{2.8}$	$La_{0.65}Ca_{0.35}Fe_1$	$LaFeO_3$	$La_{0.86}Ca_{0.14}Fe_1$ – 85.3 Ca_1Fe_1 – 11.0 Ca – 3.6
$La_{0.4}Ca_{0.6}FeO_{2.7}$	$La_{0.50}Ca_{0.45}Fe_1$	$LaFeO_3$	$La_{0.83}Ca_{0.17}Fe_1$ – 71.0 Ca_1Fe_1 – 23.0 Ca_1Fe_2 – 3.5 Ca – 1.8
$La_{0.2}Ca_{0.8}FeO_{2.6}$	$La_{0.21}Ca_{0.73}Fe_1$	$LaFeO_3$ $Ca_2Fe_2O_5$	La_1Fe_1 – 28.9 Ca_1Fe_1 – 67.3 Ca – 3.1

[a, b]See Note to Table 1.

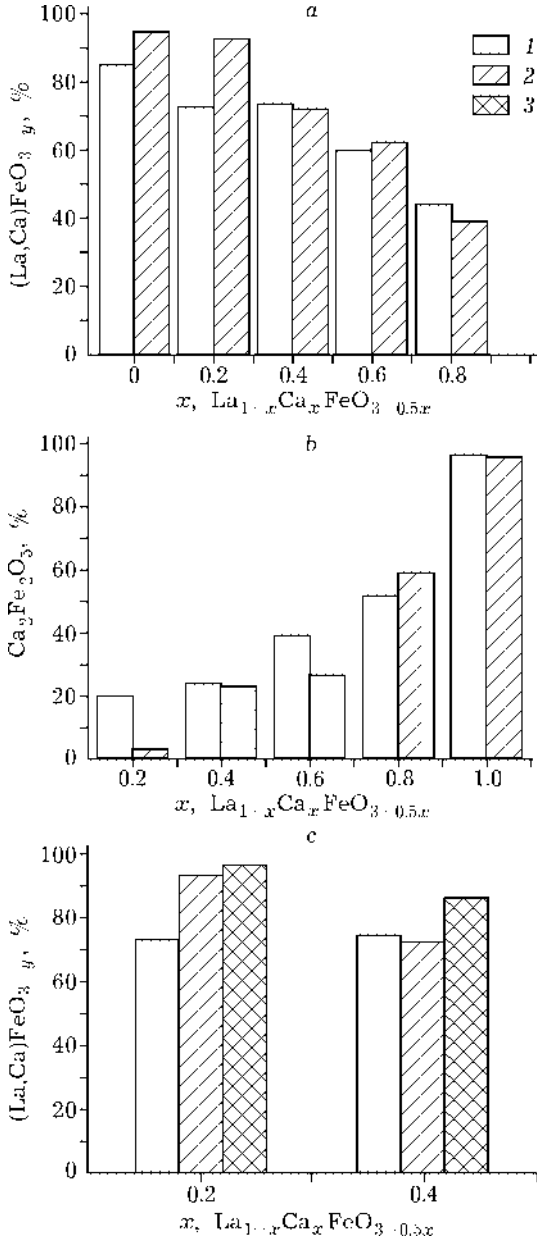

Fig. 3. Effect of the activation time on the phase composition of samples calcined at 1100 °C for 4 h: *a* and *b* – MT time, min: 3 (*1*), and 6 (*2*); *c* – MT time, min: 3 (*1*), 6 (*2*), and 10 (*3*).

stacked regions with the crystal structures of perovskite and brownmillerite, amorphous regions being observed as well (Fig. 4, *a*).

After calcination at 1100 °C for 4 h, this sample contains two types of particles with perovskite and brownmillerite structures (see Fig. 4, *b*). The microstructure of ceramic samples differs substantially from that of the MT samples (see Fig. 4, *c* and *d*). These data show that MT samples annealed at 900 °C are neither homogeneous solid solution nor ordered phases such as Grenier phase $La_{0.33}Ca_{0.67}FeO_{2.67}$ (see Fig. 4, *c*) or microheterogeneous solid solution $La_{0.5}Ca_{0.5}FeO_{2.75}$ (see Fig. 4, *d*), detected in ceramic samples. Instead, the MT samples annealed at 900 °C present a disordered stacking of perovskite and brownmillerite microphases which differs from ceramic series by their composition and nature of an intergrowth.

The differences in the phase composition and microstructure of the ceramic and MCA samples can be explained assuming that ternary homogeneous solid solution forms at temperatures not lower than 1100 °C and decomposes on cooling to yield microheterogeneous solid solutions. This assumption agrees with recent XRD studies [17] performed using a high-temperature chamber for $La_{1-x}Ca_xMnO_{3-x}$ system. At $T > 1100$ °C this system is a homogeneous perovskite-like solid solution, while on cooling it becomes a two-phase system. In the case considered in this work, the homogeneous solid solution is not formed *via* MT due to lower (900 °C) temperature of synthesis or inhomogeneity of the reaction mixture under synthesis conditions, which, in turn, may be associated with some kinetic restrictions (such as a short time of calcination) or formation of two-component perovskites with rather large particles at the stage of the mechanical treatment.

Catalytic activity of samples

As in the case of ceramic samples [13], the catalytic activity of perovskites in CO oxidation was found to change non-monotonously with Ca concentration, maximum being attained for the middle composition $La_{0.5}Ca_{0.5}FeO_{2.75}$ Since the surface of MT samples is not enriched by iron cations (SIMS data), the enhanced activity can be assigned to the sample microstructure (the presence of interphase and intergrain boundaries).

This assumption was supported by the SAXS data: the maximum integral intensity for ceramic sample ($x = 0.5$) was detected in the scattering region of size ~40 Å. Therefore, the enhanced catalytic activity of $La_{0.5}Ca_{0.5}FeO_{2.75}$ sample with intermediate degrees of Ca sub-

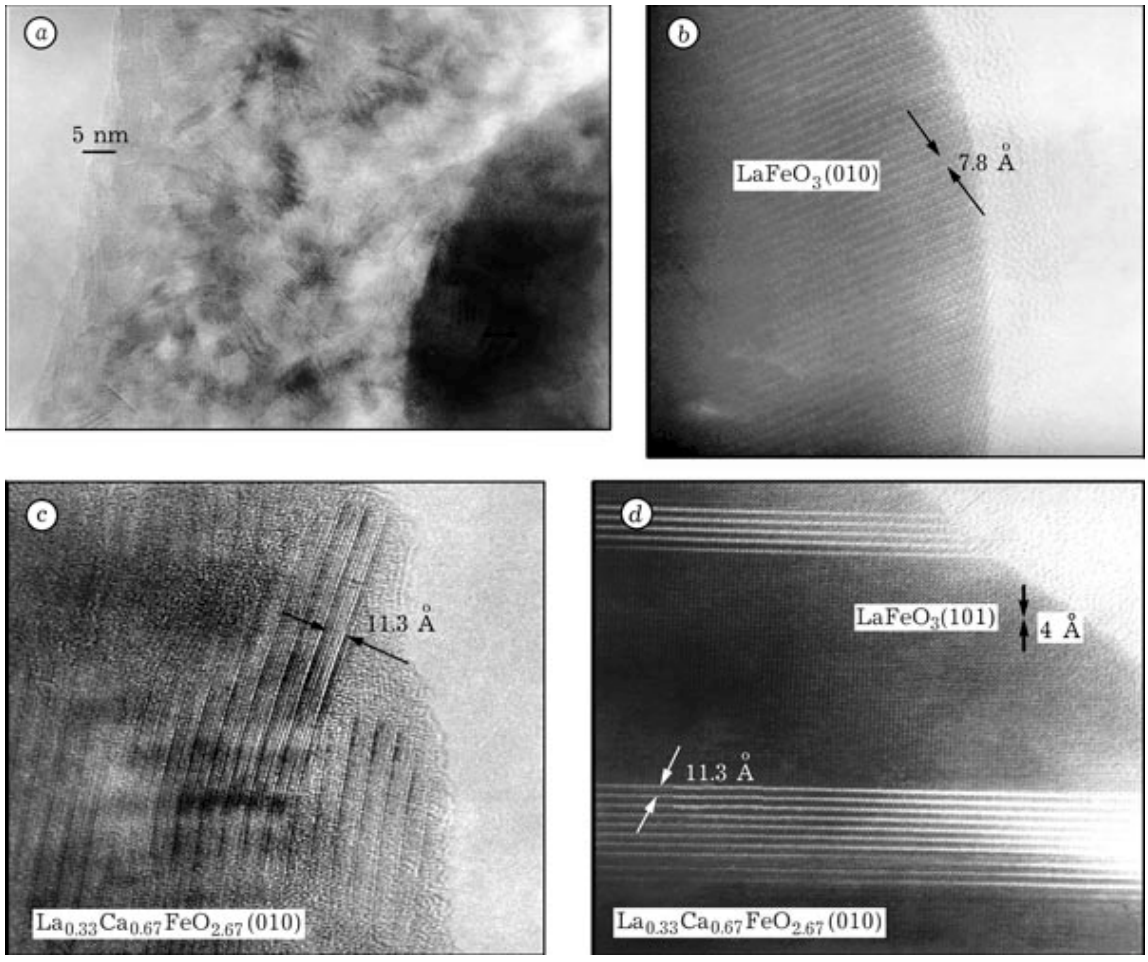

Fig. 4. TEM images of particles of $La_{1-x}Ca_xFeO_{3-0.5x}$ samples prepared *via* mechanical treatment (*a*, *b*) and by ceramic method (*c*, *d*) (magnification ~10^6): *a* – $La_{0.6}Ca_{0.4}FeO_{2.8}$: 6 min of MT, annealed at 900 ℃ for 4 h; *b* – $La_{0.6}Ca_{0.4}FeO_{2.8}$: 6 min of MT, annealed at 1100 ℃ for 4 h; *c* – $La_{0.2}Ca_{0.8}FeO_{2.6}$: annealed at 1100 ℃ for 150 h; *d* – $La_{0.4}Ca_{0.6}FeO_{2.7}$: annealed at 1100 ℃ for 150 h.

stitution is probably associated with formation of disordered microheterogeneous solid solution and its complex morphological structure.

For MT samples annealed at 900 ℃, irrespective of the time of reagents activation before sintering, the highest level of catalytic activity was similarly revealed at intermediate substitution degrees. In this case, enhanced activity correlates with developed interphase boundaries between perovskite and brownmillerite phases revealed here by TEM. The increase of activity after annealing at 1100 ℃ can be assigned to the increase in the density of intergrain boundaries caused by recrystallization of amorphous regions as was earlier studied in detail in [16].

Therefore, the maximum of catalytic activity at a middle degree of Ca substitution for all samples of La–Ca–Fe–O systems observed irrespectively of the preparation prosedure, can be explained by a maximum density of interphase and intergrain boundaries. It suggests that active sites are located at the surface outlets of those defects. The active centers could be assigned to coordinatively unsaturated clustered Fe^{2+} cations able to adsorb a weakly bound oxygen known to be the most active in reactions of deep oxidation [19]. The presence of weakly bound oxygen in samples of middle composition (x = 0.5) prepared either by ceramic or MT route are confirmed by TPR data (Fig. 5): for those samples there is a low temperature peak (T = 350–400 ℃ which is not observed for end compositions (x = 0 and 1).

Duration of mechanical treatment of the mixture of solid reagents was found to affect

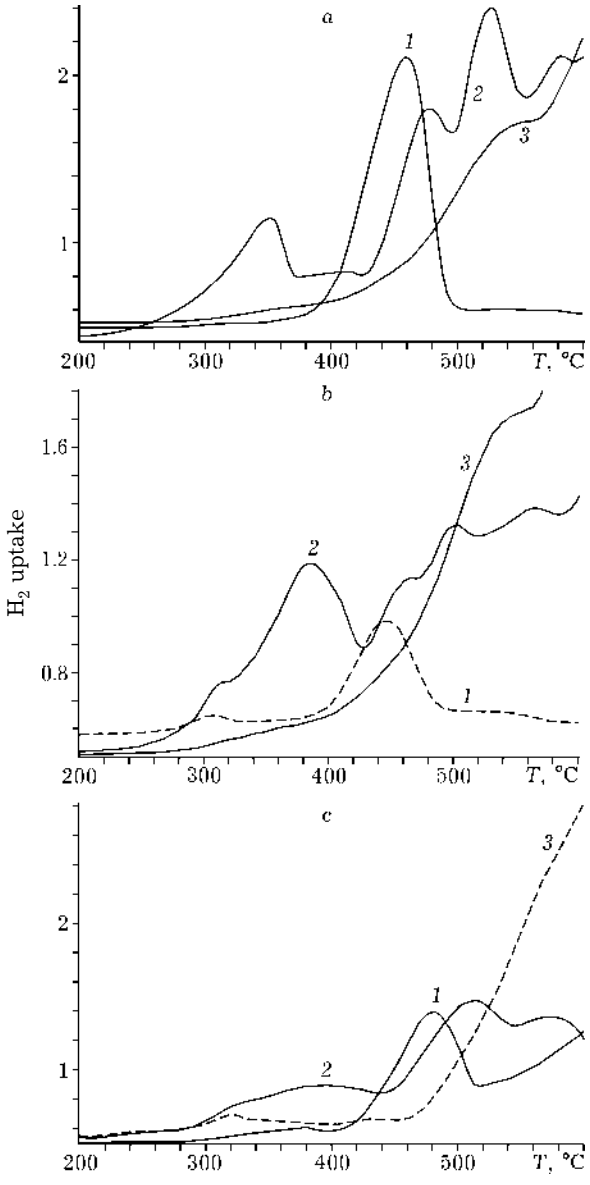

Fig. 5. TPR data for $La_{1-x}Ca_xFeO_{3-0.5x}$ samples prepared by mechanochemical (*a*, *b*) and ceramic (*c*) methods: *a* – 6 min of MT, calcination at 900 °C for 4 h; *b* – 6 min of MT, calcination at 1100 °C for 4 h; *c* – calcination at 1100 °C for 150 h; x = 0 (*1*), 0.6 (*2*), and 1.0 (*3*).

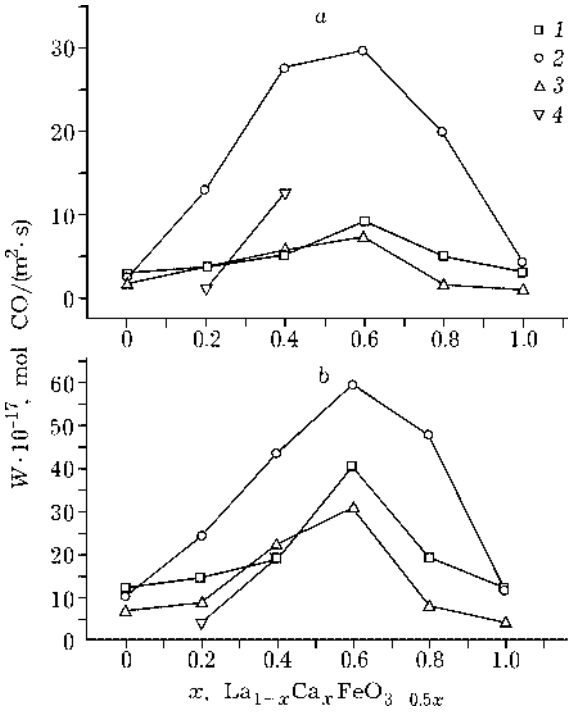

Fig. 6. The rate of CO catalytic oxidation at 400 (*a*) and 450 °C (*b*) *vs.* Ca content for $La_{1-x}Ca_xFeO_{3-0-05x}$ samples prepared by mechanochemical (1100 °C, 4 h) and ceramic (1100 °C, 150 h) methods: *1* – ceramics, *2–4* – MT time, min: 3 (*2*) 6 (*3*), and 10 (*4*).

the level of the catalytic activity of samples (Fig. 6). Thus, for samples with longer activation times (6 and 10 min), the activity is close to that of samples prepared via ceramic route. For samples with small (3 min) time of activation, catalytic activity is certainly higher than for ceramic samples, though the difference decreases with the increase of the reaction temperature.

Hence, MT permits to decrease the time of a catalyst synthesis of perovskites $La_{1-x}Ca_xFeO_{3-0.5x}$ and to obtain higher or close values of specific catalytic activity, as compared with samples of ceramic series. Though the real structure of samples prepared by different procedures varies considerably, in all cases active centers appear to be located at outlets of extended defects whatever is their nature. Another important advantage of the mechanochemical method of synthesis is a higher dispersion (specific surface area) of samples, which ensures a higher catalytic activity per the unit mass of those systems.

CONCLUSIONS

The phase composition and microstructure of $La_{1-x}Ca_xFeO_{3-0.5x}$ samples prepared by MT depend significantly on such parameters as calcium concentration, temperature and time of the activated mixture calcination as well as time of the MT.

If oxide mixtures are preliminarily mechanically activated before their calcination, the concentration of calcium in the perovskite structure rises to $x = 0.25$ compared to $x = 0.17$ for ceramic samples. This indicates that the region of formation of true solid solutions does not extend significantly. Hence, true perovskite-like solid solutions with a broad range of La substitution for Ca are not formed irrespective of the synthesis procedure.

The method of synthesis was found to affect significantly both the microstructure and phase composition of samples. In contrast to the ceramic samples, the MT samples do not contain Grenier phase $La_{0.33}Ca_{0.67}FeO_{2.67}$ and microheterogeneous solid solution $La_{0.5}Ca_{0.5}FeO_{2.75}$. The layered structures detected for ceramic samples are suggested to be the products of decomposition of the high-temperature homogeneous solid solution formed during the long-time calcination at temperatures exceeding 1100 °C. The differences in the phase composition and microstructure of the ceramic and MT samples appear to be caused by kinetic barriers of the high-temperature homogeneous solid solution $La_{1-x}Ca_xFeO_{3-0.5x}$ formation due to lower temperatures of synthesis or short time of annealing in the case of the mechanochemical method.

For the samples with an intermediate ($x \sim 0.5$) degree of La substitution, samples exhibit higher or close level of catalytic activity as compared with ceramic samples. The fact that the MT samples have higher values of S_{sp} permits one to conclude that the method of mechanical treatment is very promising for synthesis of $La_{1-x}Ca_xFeO_{3-y}$-based catalysts for deep oxidation processes.

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