ISSN 0023-1584, Kinetics and Catalysis, 2009, Vol. 50, No. 6, pp. 886–891. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © L.A. Isupova, E.Yu. Gerasimov, V.I. Zaikovskii, S.V. Tsybulya, N.A. Kulikovskaya, N.F. Saputina, 2009, published in Kinetika i Kataliz, 2009, Vol. 50, No. 6, pp. 922–928.

Synthesis of Homogeneous $La_{1-x}Ca_xMnO_3$ Solid Solutions by the Pechini Method and Their Activity in Methane Oxidation

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Received October 15, 2008

Abstract—Homogeneous $La_{1-x}Ca_xMnO_3$ solid solutions have been synthesized by the Pechini method (using polymer–solid compositions). Their microstructure, stability at high temperatures, and catalytic activity in methane oxidation are reported. A continuous series of solid solutions stable in air up to 1100°C forms in the system, and the particle surface is enriched with calcium. A distinctive microstructural feature of the particles is their microporosity. The catalytic activity of all calcium-containing samples (except for $x = 0.7$) below 700°C is lower than that of lanthanum manganite and decreases under the action of the reaction medium, which can be due to the decrease in the amount of weakly bound oxygen on the surface because of the enrichment of the surface with calcium and the formation of strongly bound surface carbonates. The higher activity and stability of the $La_{0.3}Ca_{0.7}MnO_3$ sample (calcined at 1100°C) above 500°C can be due to the formation of nanosized areas with an Mn_3O_4 structures on the perovskite particle surface in the reaction medium.

DOI: 10.1134/S0023158409060159

Perovskite $La_{1-x}Ca_xMnO_3$ solid solutions are widely known for their unusual magnetic and electronic properties. In particular, these compounds are characterized by colossal magnetic resistance and high catalytic activity and exhibit the charge ordering effect. Since these compounds are very stable, they are promising materials for a number of high-temperature processes, for instance, as high-temperature cathodic materials and oxidation catalysts [1, 2]. However, researchers have not come to a consensus as to the boundaries of the homogeneous solid solution fields in the system. Some authors [3] reported that there is a continuous series of solid solutions, while others believe that there are no solutions with intermediate x values [4] or that x cannot exceed 0.8 [5]. It cannot be ruled out that these discrepancies are due to different oxide preparation conditions. The properties of the perovskites (including catalytic properties) were shown [2] to depend substantially on the preparation conditions: temperature; oxygen pressure; and the method of synthesis, which determines the microstructure, the impurity composition, the concentration of defects in the oxide, and its phase composition.

There has been a comparative study of a series of perovskite-like $La_{1-x}Ca_xMnO_3$ oxides synthesized by ceramic and mechanochemical methods [6]. The samples prepared by ceramic sintering at 1100°C were single-phase solid solutions (according to X-ray data). The $x = 0.8$ sample was shown by high-resolution transmission electron microscopy (HRTEM) to have a modular structure, indicating its instability. The mechanochemical method gave only homogeneous solutions with $x \leq 0.4$, probably because of the instability of the solid solutions richer in calcium. The formation of microheterogeneous (nanocomposite) states characterized by a “shell” nanostructure was observed at $x \geq 0.4$: solid solutions with $x \leq 0.4$ form in the bulk of micron-sized particles, whereas the near-surface particle layers (down to 100 Å depth) are enriched with calcium. A study of CO oxidation as a model reaction demonstrated the lowered catalytic activity of all calcium-containing samples prepared by the ceramic and mechanochemical methods, which is due to calcium segregation on the surface. The data obtained suggest that either the $x > 0.4$ solid solutions are unstable and, therefore, do not form under the accelerated synthesis conditions or there are diffusion limitations for annealing, which retard the formation of homogeneous solid solutions.

The purposes of this work were to synthesize homogeneous $La_{1-x}Ca_xMnO_3$ solid solutions by the polymer–salt composition (Pechini) method [7, 8]), which makes it possible to obtain precursors with the most uniform cation distribution; to study the microstructure and phase composition of a series of samples at different substitution parameters x and thermal treatment conditions; to study the stability of the oxides in media with different partial oxygen pressures; and to analyze the influence of the substitution of calcium for lanthanum on the catalytic activity of the samples in the model reaction of methane oxidation.

EXPERIMENTAL

$La_{1-x}Ca_xMnO_3$ samples with stoichiometry varied in $x = 0.1$ steps were synthesized by dissolving metal nitrates in water, combining the solutions in appropriate ratios, and adding citric acid and ethylene glycol followed by evaporating the solution at 70–80°C to form a resin-like polymer (polymer–salt composition). After the oxidative destruction of the polymer, the product was calcined at 900 or 1100°C for 4 h.

X-ray diffraction analysis was carried out on a URD-63 diffractometer (Germany) using CuK_α radiation. Scanning was performed with $2\theta = 0.02°$ increments and a counting time of 5 s per point.

HRTEM images were obtained on a JEM-2010 microscope (Japan) with a resolution of 1.4 Å. Energy dispersive X-ray analyses (EDX) were carried out on an energy dispersive spectrometer with a Si(Li) detector and an energy resolution of 130 eV.

The catalytic activity of samples differing in composition and calcination temperature was determined in a flow reactor at 350 to 600°C using chromatographic analysis. A catalyst sample (1 g, size fraction of 0.25–0.5 mm) was placed in a tubular quartz reactor with an inner diameter of 4.5 mm. The flow rate of the reaction mixture ($0.9\%\ CH_4 + 9\%\ O_2 + 90.1\%\ N_2$) was 2.4 l/h, and the residence time was 1.5 s. Before each measurement, the sample was kept in the reaction mixture for ~30 min. In particular cases, the catalyst was kept at 600ºC for 1–4 h. The oxidation products were only CO_2 and water. The reaction rate constant was calculated under the assumption that the reactor operated in the plug flow regime using the formula

$$k = \ln(1-\alpha)/\tau m S_{BET},$$

where α is the methane conversion, τ is the residence time, m is the sample weight, and S_{BET} is the specific surface area of the fresh sample.

The specific surface area was determined by the BET method from thermal argon desorption data.

RESULTS AND DISCUSSION

Phase Composition and Microstructure of Samples

According to X-ray diffraction data (Fig. 1), all $La_{1-x}Ca_xMnO_3$ samples with $x = 0$–0.8 prepared by the Pechini method and calcined at 900 and 1100°C are single-phase and have a perovskite structure. Their diffraction peaks can be indexed in the orthorhombic system (space group *Pnma*). No reflections assignable to symmetry other than *Pnma* were observed. The $x = 0.8$ sample is characterized by a marked diffraction peak asymmetry, which likely indicates considerable compositional heterogeneity of this solid solution. The $x = 0.9$ and 1.0 samples are monoclinic (space group $P12_1/a$).

Table 1. Unit cell parameters of the $La_{1-x}Ca_xMnO_3$ samples synthesized by the Pechini method after their thermal treatment at 900°C

x (Ca content)	Unit cell parameter			
	a, Å	b, Å	c, Å	V, Å^3
0	5.491(8)	5.489(9)	7.774(4)	234.31
0.1	5.479(3)	5.481(1)	7.758(3)	232.98
0.2	5.483(4)	5.475(2)	7.750(4)	232.65
0.3	5.475(5)	5.466(2)	7.731(4)	231.36
0.4	5.458(3)	5.453(1)	7.719(4)	229.74
0.5	5.435(3)	5.430(1)	7.686(2)	226.83
0.6	5.402(5)	5.406(2)	7.643(3)	223.20
0.7	5.378(8)	5.376(2)	7.606(5)	219.91
0.8	5.353(9)	5.338(3)	7.551(7)	215.76
0.9*, $\beta = 90.3$	5.298(4)	5.310(3)	7.500(5)	211.00
1*, $\beta = 90.123$	5.270(3)	5.283(4)	7.466(7)	207.86

* Monoclinic phase; β is the monoclinic angle.

The unit cell parameters of the solid solutions calcined at 900°C are given in Table 1. The observed decrease in the unit cell volume (V) with an increase in x indicates an increase in the calcium content of the solid solution. The composition dependences of the pseudocubic cell parameter of perovskite (r), which is defined as the cubic root of the unit cell volume per formula unit ($r = \sqrt[3]{V/4}$), for the samples calcined at 900 and 1100°C are shown in Fig. 2. These two dependences are almost the same within the determination error, suggesting that the solid solutions are completely formed after calcination at 900°C.

On the whole, the unit cell parameters determined in this study are in good agreement with the data reported for single-phase solid solutions [3, 6, 9].

Note that the synthesized sample $La_{0.5}Ca_{0.5}MnO_3$ is a single-phase perovskite, although it would be expected to be two-phase, according to the literature [4]. Since some reflections, such as (222), are absent, the structure of this sample possibly has a higher, tetragonal symmetry. It cannot be ruled out that the synthesized single-phase sample is unstable and, on heating, undergoes decomposition in accordance with the phase diagram [4] or structural changes similar to those described in [10].

The diffraction peaks for this series of samples are somewhat broadened, which possibly indicates a size effect (small crystal blocks) or the existence of microdistortions (changes in the interplanar distances). Both effects reduce the effective size of the coherent scattering domain (CSD).

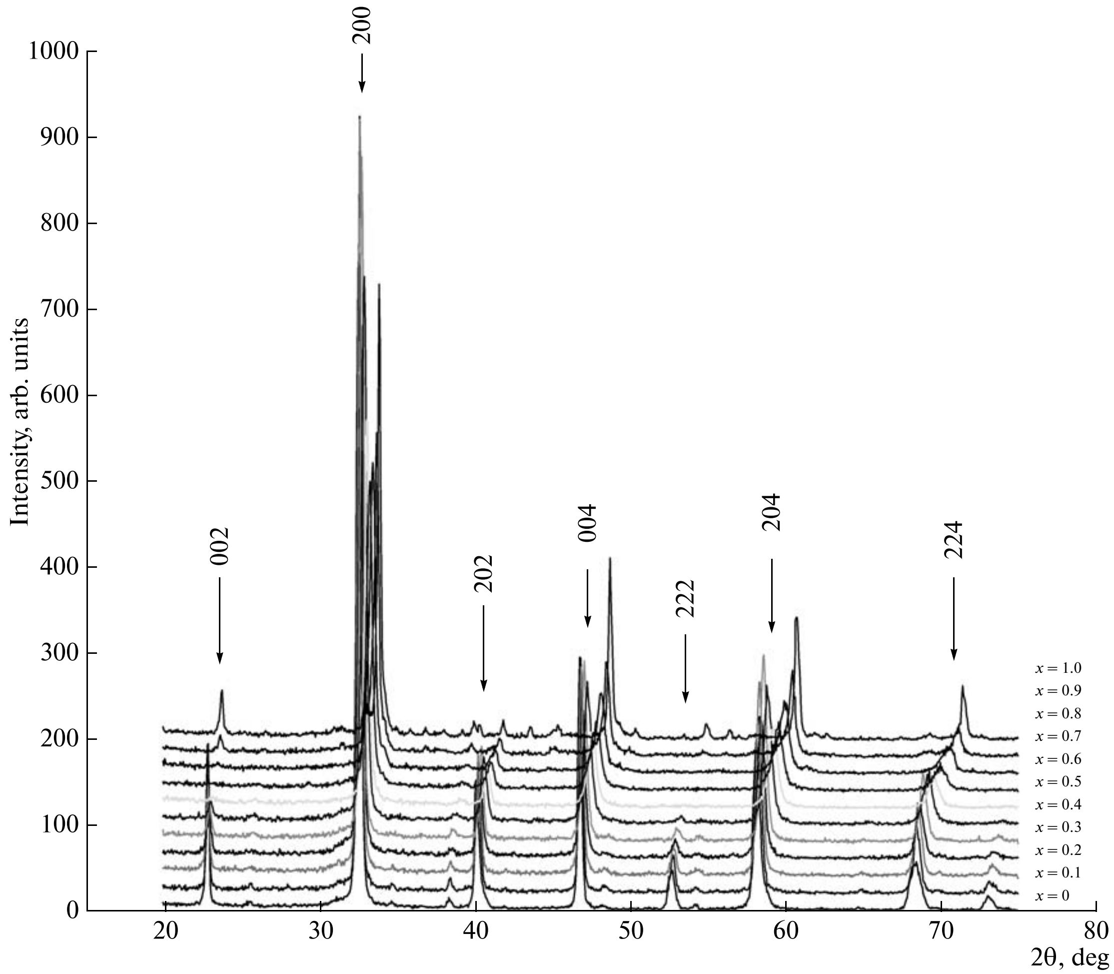

Fig. 1. X-ray diffraction patterns of the $La_{1-x}Ca_xMnO_3$ samples synthesized by the Pechini method after their thermal treatment at 900°C.

Table 2 lists the effective CSD sizes for all samples except the $x = 0.8$ one, whose CSD is difficult to estimate because of the strong anisotropy of the peak shape. As the calcium content increases to $x = 0.7$, the CSD size decreases, regardless of the calcination temperature, and then somewhat increases again at $x > 0.8$. The CSD size increases as the calcination temperature increases from 900 to 1100°C. This is possibly an indication of annealing and sintering processes occurring at the high heat-treatment temperatures. Evidently, an increase in the calcium content of the solid solution results in the buildup of structure distortions, and this is manifested as a decrease in the effective CSD size.

According to HRTEM data, $La_{0.5}Ca_{0.5}MnO_3$ consists largely of aggregates of massive round particles, whose size ranges between 100 and 500 nm (Fig. 3a). The EDX analysis showed that the chemical composition of this sample corresponds to the solid solution $La_{0.5}Ca_{0.5}MnO_3$. The crystal blocks contain extended planar defects (Fig. 3b), which are also indicated by the microdiffraction data. Another microstructural feature of the particles is the presence of pores, which likely result from the removal of residual functional groups upon sample calcination.

At the same time, the sample contains a minor amount of platelike particles about 500 nm in size, whose elemental composition is closer to $La_{0.4}Ca_{0.6}MnO_3$. It is most likely that the amount of the solid solution with this composition in the analyzed sample is small, because its presence exerts almost no effect on the X-ray diffraction pattern and the average unit cell parameter, which corresponds to $x = 0.5$.

According to HRTEM and EDX data, the $La_{0.3}Ca_{0.7}MnO_3$ sample is also a homogeneous single-phase solid solution. The size of its particles ranges between fractions of a micrometer to several micrometers. The particles consist largely of randomly oriented crystal blocks 100 to 500 nm in size. The micrograph of this sample (Fig. 4) shows the presence of pores, which result from the removal of residual functional groups during calcination.

A special high-temperature X-ray diffraction experiment was carried out to estimate the thermal stability of the $x = 0.5$ sample. Heating $La_{0.5}Ca_{0.5}MnO_3$ in air to 1350°C did not change the diffraction pattern, which remained nearly the same as was obtained at room temperature (leaving aside the thermal expansion effect). Therefore, the $La_{0.5}Ca_{0.5}MnO_3$ sample is thermally stable in air in the indicated temperature range.

The results obtained by us differ from published data [4, 10], according to which the samples of the nominal composition $La_{0.5}Ca_{0.5}MnO_3$ form no single-phase solid solution and consist of two phases—$La_{0.6}Ca_{0.4}MnO_3$ and $La_{0.4}Ca_{0.6}MnO_3$. In our case, we can claim the formation of the homogeneous solid solution $La_{0.5}Ca_{0.5}MnO_3$ as the main phase (in spite of a minor admixture of $La_{0.4}Ca_{0.6}MnO_3$) and its high thermal stability in air (up to 1350°C).

A comparison of the CSD sizes determined by X-ray diffraction (200–500 Å) with the particle sizes determined by HRTEM (micrometer level) and those derived from the S_{BET} values (Table 2) under the assumption that the particles are spherical (~1000 Å) suggests that the microporous particles have a mosaic (microblock) structure with a block size of 200–500 Å. This possibly indicates a high density of extended defects (interblock) boundaries) in the particles of the samples. In addition, the microdistortions indicate the existence of strains inside the blocks, and these strains increase with the degree of substitution of calcium for lanthanum.

Catalytic Activity

The results of tests of the samples calcined at 900°C in methane oxidation are presented in Fig. 5. Obviously, no linear dependence is observed between the catalytic activity of the samples and their calcium content. The starting lanthanum manganite shows the highest activity, and all substituted samples are inferior to it in this respect. The intermediate maxima at $x = 0.2$ and 0.4 are likely unstable, because longer exposure of the samples to the reaction mixture at a preset temperature decreases the methane conversion. For example, during the reaction on the $x = 0.2$ sample at 600°C, the methane conversion decreases from 74.8 to 51.5% within 1 h. If a run at 500°C (Fig. 5, curve *3*') is carried out after the test at 600°C, the calcium-containing sample will exhibit a somewhat lower, but more stable, activity. At the same time, the methane conversion at 600°C on calcium-free lanthanum manganite does not decrease over 4 h and the results obtained at 500°C after the tests at 600°C nearly coincide with the results of a standard experiment in which the temperature is raised to 500°C. Therefore, the introduction of calcium into lanthanum manganite up to $x = 0.3$ reduces the steady-state activity of the sample. At larger x values, the activity increases and stabilizes near the activity level of the extreme of the solid solution series (lanthanum-free calcium manganite). This also indicates that the surface is enriched with calcium cations, probably as a surface film of calcium manganite, whose activity is approximately half the activity of lanthanum manganite.

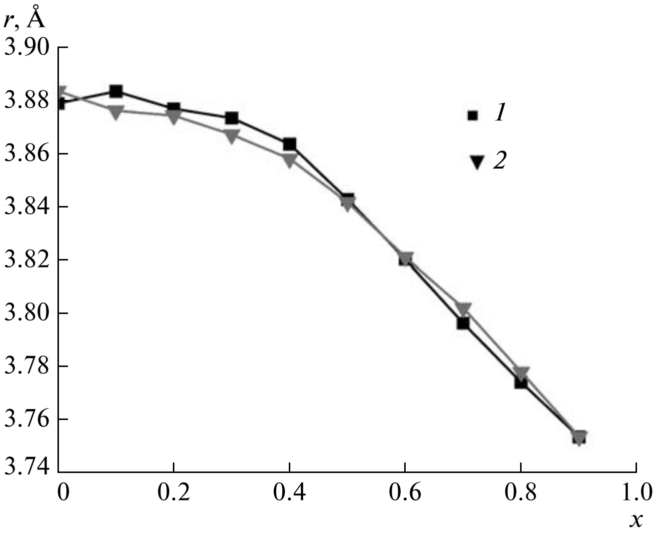

Fig. 2. Dependences of the pseudocubic cell parameter (r) of perovskite on the calcium content (x) of the samples calcined at (*1*) 900 and (*2*) 1100°C. r was calculated as the cubic root of the unit cell volume per formula unit $(r = \sqrt[3]{V/4})$.

The results of tests of the samples calcined at 1100°C are shown in Fig. 6. At 500°C and below, the activity of the $x = 0.1$–0.3 samples is substantially lower than that the activity of the starting lanthanum

Table 2. Specific surface areas and CSD sizes of $La_{1-x}Ca_xMnO_3$ samples calcined at different temperatures

x	CSD (Å), at calcination temperature, °C		S_{BET} (m^2/g)*, at calcination temperature, °C	
	900	1100	900	1100
0	480	470	2.8(4.5)	1(1.8)
0.1	480	530	–	–
0.2	390	520	4.6(4.8)	2.7(3.4)
0.3	300	470	4.9(6.2)	2.5(3.5)
0.4	350	420	3.5(4.7)	2.5(3.0)
0.5	300	390	4.3(4.6)	2.6(3.3)
0.6	270	360	4.4(5.8)	2.3(3.2)
0.7	230	300	5.5(7.7)	2.8(4.2)
0.8	–	–	6.1(6.6)	3.7(4.7)
0.9	360	430	5.3(8.3)	3.4(5.3)
1.0	430	530	3.1(5.0)	1.8(3.0)

* The S_{BET} values measured after catalytic tests are given in parentheses.

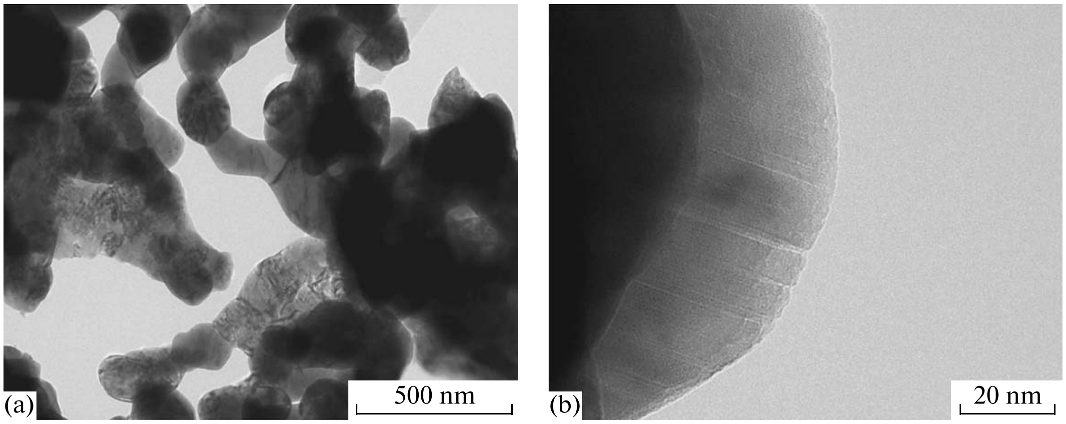

Fig. 3. HRTEM images of $La_{0.5}Ca_{0.5}MnO_3$.

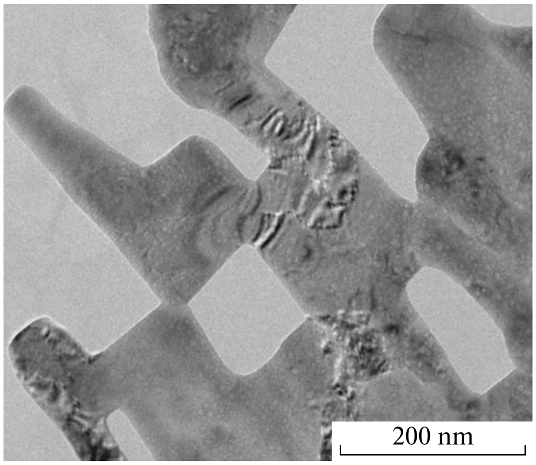

Fig. 4. HRTEM image of $La_{0.3}Ca_{0.7}MnO_3$.

manganite, whereas that the activity of the samples with $x > 0.3$ is almost independent of the composition and is at the activity level of the extreme member of the series. However, above 500°C, the $x = 0.7$ sample exhibits a higher activity than the other calcium-containing samples. If the temperature is decreased to 500°C after the tests at 600°C, the activity of this sample will be the same as in the standard experiment at 500°C, whereas the activity of the $x = 0.4$–0.6 and $x > 0.7$ samples will lower. This likely indicates a higher stability of the $x = 0.7$ sample.

Thus, the activity of all calcium-containing lanthanum manganites is lower than that of the unsubstituted sample, which can be explained (taking into account published data [11]) by a decrease in the amount of the least strongly bound surface oxygen. The results obtained indicate possible changes in the chemical and/or phase composition or the specific surface area of the catalysts under the action of the reaction medium.

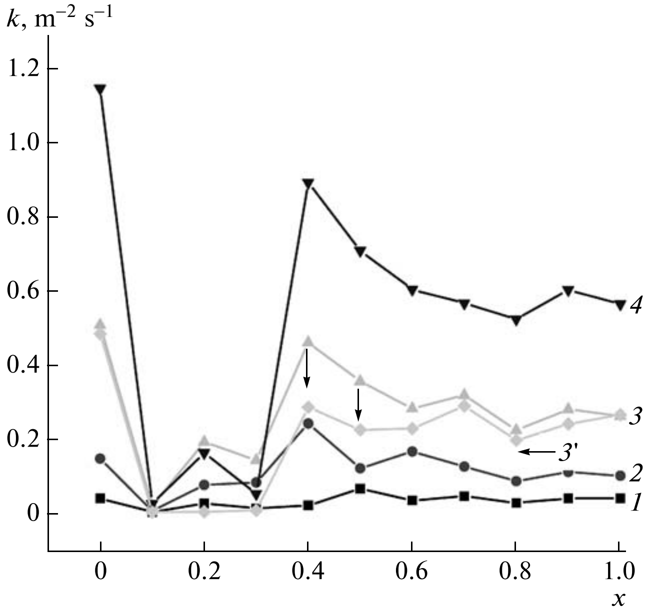

Fig. 5. Dependences of the methane oxidation rate constant (k) at (*1*) 400, (*2*) 450, (*3, 3'*) 500, and (*4*) 550°C on the calcium content (x) of the samples calcined at 900°C. Curve *3'* was obtained after tests at 600°C.

Since no decrease in the specific surface area of the samples under the action of the reaction medium was observed (Table 2) and, on the contrary, S_{BET} increased in most cases, the change in the activity is most likely due to the change in the chemical composition of the surface. The formation of strongly bound carbonate complexes on the calcium-enriched surface can be among the main causes of the deactivation of the samples in the reaction medium. The higher activity and stability of the $x = 0.7$ sample is likely due to other factors. For example, it can be assumed that the reaction medium, in which the partial oxygen pressure is lower than in air, affects the sample with the smallest effec-

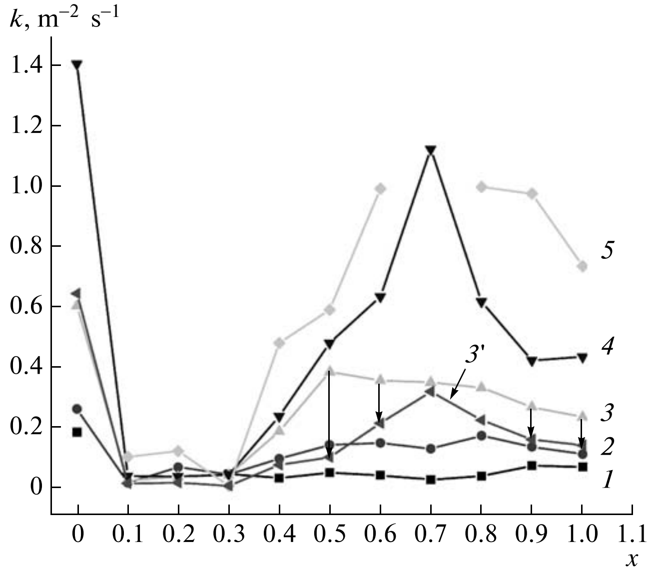

Fig. 6. Dependences of the methane oxidation rate constant (*k*) at (*1*) 400, (*2*) 450, (*3*, *3*') 500, (*4*) 550, and (*5*) 600°C on the calcium content (*x*) of the samples calcined at 1100°C. Curve *3*' was obtained after the tests at 600°C.

tive CSD size and, correspondingly, the most disordered structure and induces certain structural transformations. These transformations can be accompanied by the formation of the manganese oxide phase on the surface of nanosized particles, by analogy with the changes observed in the vacuum treatment of the sample with $x = 0.8$ [12]. This phenomenon requires further, more detailed investigation.

Thus, in the present work we studied $La_{1-x}Ca_xMnO_3$ samples ($x = 0$–1) synthesized by the polymer–salt composition (Pechini) method.

According to X-ray diffraction and HRTEM data, these samples are mainly single-phase solid solutions with a perovskite-type structure. No substantial structural changes occur on heating the samples with $x = 0.5$ to 1350°C, indicating that these samples are stable. Thus, single-phase homogeneous solid solutions thermally stable in air result from the Pechini synthesis. However, the HRTEM data for the $x > 0.3$ samples do not rule out the enrichment of the particle surface with calcium or the formation of some particles with an overstoichiometric calcium content (or both).

The activity of the calcium-containing samples with $x = 0$–0.3 is substantially lower than that of the starting lanthanum manganite, which is due to the decrease in the amount of weakly bound surface oxygen. It cannot be excluded that it is due to the enrichment of the particle surface with calcium in the form of calcium manganite that the samples with $x = 0.4$–1 are almost equally active at testing temperatures of 350–500°C.

Thus, although the Pechini method makes it possible to obtain almost single-phase homogeneous solid solutions in the $La_{1-x}Ca_xMnO_3$ system, all calcium-containing samples are less active than lanthanum manganite. This is most likely explained by the enrichment of the surface with calcium, which can lead to blocking of the surface with carbonate complexes. The fact that the $x = 0.7$ sample calcined at 1100°C is catalytically more active and is more stable in the reaction medium above 500°C can be due to the possible formation of nanosized areas with the Mn_3O_4 structure on the sample surface under the action of the reaction medium. This phenomenon requires further investigation.

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