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Reactivity of $La_{1-x}Sr_xFeO_{3-y}$ (x = 0–1) Perovskites in Oxidation Reactions

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Abstract—Oxygen species and their reactivity in $La_{1-x}Sr_xFeO_{3-y}$ perovskites prepared using mechanochemical activation were studied by temperature-programmed reduction (TPR) with hydrogen and methane. The experimental data were compared with data on the catalytic activity in oxidation reactions. It was found that the rates of CO and methane oxidation on the perovskites in the presence of gas-phase oxygen correlated (k = 0.8) with the amount of reactive surface oxygen species that were removed by TPR with hydrogen up to 250°C. Maximum amounts of this oxygen species were released from two-phase samples (x = 0.3, 0.4, and 0.8), which exhibited an enhanced activity in the reaction of CO oxidation. In the absence of oxygen in the gas phase, methane is oxidized by lattice oxygen. In this case, the process activity and selectivity depend on the mobility of lattice oxygen, which is determined by the temperature, the degree of substitution, the degree of reduction, and the microstructure of the oxide. Thus, the high mobility of oxygen, which is reached at high concentrations of point defects or interphase/domain boundaries, is of importance for the process of deep oxidation. However, the process of partial oxidation occurs in single-phase samples at low degrees of substitution (x = 0.1–0.2).

INTRODUCTION

The high activity and operational stability of oxides with perovskite structures (ABO_3) in various catalytic reactions have attracted the serious attention of researchers. It is commonly accepted that the activity of perovskites in deep oxidation reactions depends on the nature of the transition metal in the B sublattice and on the electronic state of this metal, which depends on substitutional cations in the A and B sublattices. Moreover, this activity depends on preparation conditions, which are responsible for the real oxide structure (microstructure) [1–4]. These factors ultimately determine the strength of the metal–oxygen bond on the oxide surface; the rates of deep oxidation reactions depend on this bond strength [5, 6].

Various oxygen species can occur on the surface of oxides. However, as found previously [7] for simple oxides, the most weakly bound species formed at the outlets of extended defects (for example, dislocations) are responsible for activity in deep oxidation reactions. An analogous result was obtained previously for $La_{1-x}Ca_xFeO_{3-y}$ perovskites [8]. This system does not form a continuous series of homogeneous solid solutions under conditions of ceramic and mechanochemical syntheses (at $0.17 < x < 1.00$, all of the samples are two-phase microheterogeneous solid solutions with various microstructures). In this system, we found a relationship between the microheterogeneity of samples or maximum concentrations of the most weakly bound surface oxygen species in these samples and the catalytic activity in deep oxidation reactions [8]. Moreover, published data [9] on the oxidation of methane on homogeneous solid solutions formed in the given system at x = 0–0.5, which were synthesized from nitrates (it was found that the activity of samples in the deep oxidation of methane was independent of the composition of these samples), should be taken into account. On this basis, we can hypothesize that a change in the density of point defects in perovskites due to substitution (the formation of vacancies or an increase in the charge of the 3*d*-metal cation in homogeneous solid solutions with perovskite structures) is insignificant for deep oxidation processes. Nevertheless, Li *et al.* [10] discussed the participation of perovskite lattice oxygen in the heterogeneous reactions of deep oxidation. On the other hand, because it is well known that the mobility of lattice oxygen depends on the concentration of vacancies, a change in the point defects has a considerable effect on the mobility of oxygen in the bulk oxide; this effect can be of importance for membrane oxidation processes.

Homogeneous solid solutions are formed in the $La_{1-x}Sr_xFeO_{3-y}$ system, and an increase in the strontium content results in the formation of Fe^{4+} cations [11]. Therefore, it is likely that a new oxygen species, which is a constituent of the coordination sphere of a highly charged cation, appears in this system, and this species can participate in deep oxidation reactions. In the series prepared by mechanochemical activation, the perovskite samples with x = 0.3, 0.4, and 0.8 were found to be non-single-phase [12]. According to TEM data, these samples were microheterogeneous solid solutions, which were formed in low-temperature polymorphic phase transitions upon cooling the samples in air (preliminary data). Consequently, by analogy with the $La_{1-x}Ca_xFeO_{3-y}$ system, these samples can additionally contain reactive oxygen species inserted into interphase boundaries.

Thus, various oxygen species can occur on the surface of perovskites in the $La_{1-x}Sr_xFeO_{3-y}$ system prepared with the use of mechanochemical activation. These are surface species, species inserted into interfaces, and lattice species, including those bound to Fe^{4+} and Fe^{3+} cations. Temperature-programmed reduction (TPR) is one of the techniques that can distinguish various oxygen species according to their reactivity. Therefore, the aim of this work was to study the reactivity of various oxygen species in perovskite oxides from the $La_{1-x}Sr_xFeO_{3-y}$ series by TPR and to relate these species to the activity of oxides in the reactions of CO and CH_4 oxidation.

EXPERIMENTAL

The samples of $La_{1-x}Sr_xFeO_{3-y}$ were synthesized by the calcination of the mechanically activated mixtures of parent oxides taken in required ratios at 1100°C for 4 h. The time of mechanical treatment was 3 min; the procedure of the mechanochemical synthesis and the results of phase analysis were described elsewhere [12]. With the use of X-ray diffraction analysis and differentiating phase dissolution, it was found that single-phase perovskites were formed in the system under the specified conditions of the synthesis except for samples with $x = 0.3$, 0.4, and 0.8, which consisted of two phases: orthorhombic and rhombohedral (or cubic) perovskites.

The catalytic activity of samples (particle size fractions of 0.5–1 and 1–2 mm) in the reaction of CO oxidation was determined in a circulation-flow reactor at 250–450°C with the use of chromatographic analysis. The sample weight was 1 g; the circulation rate was 1200 l/h; the flow rate of the reaction mixture (1% CO + 1% O_2 in He) was 10 l/h. The specific rate of reaction at a 1% concentration of CO was calculated from the equation

$$w,\ [\text{molecule CO m}^{-2}\ \text{s}^{-1}] = X/(1-X)(7.47\times10^{17}/S_{sp}), \quad (1)$$

where X is the conversion of CO. The error of the chromatographic determination of gas mixture components was no higher than 10%.

The catalytic activity of samples (particle size of 0.5–1 mm) in the reaction of CH_4 oxidation was determined in a flow reactor at 500–600°C using GC for the analysis of reactants and products. The sample weight was 1 g; the catalyst volume was 0.6 cm^3; the flow rate of the reaction mixture (0.5% CH_4 + 9% O_2 in He) was 2.4 l/h (i.e., 4000 h^{-1}). The rate of reaction was calculated from the equation

$$w,\ [\text{molecule CH}_4\ \text{m}^{-2}\ \text{s}^{-1}] = k_aC_0\times2.69\times10^{19}, \quad (2)$$

where k_a is the apparent rate constant of first-order reaction, which was calculated by the equation $k_a = -2.3\log(1-X)/(tmS_{sp})$ for a plug-flow reactor (X is the conversion of CH_4, m is the sample weight, t is the contact time, and $C_0 = 0.5$ is the initial concentration of methane). The error of the chromatographic determination of gas mixture components was no higher than 10%.

The TPR study of samples with hydrogen was performed in a flow system with a thermal-conductivity detector using a fraction of samples with a particle size of 0.25–0.5 mm. Before the reduction, the samples were pretreated in O_2 at 500°C for 0.5 h and cooled to room temperature. The sample weight was 50 mg; the flow rate of the reducing mixture (10% H_2 in Ar) was 40 cm^3/min. The samples were heated at a rate of 10 K/min to 900°C. The peak areas of the TPR of samples corresponding to hydrogen consumption (mmol/(g sample)) were calculated with the use of an asymmetric Gaussian function profile.

The TPR with methane was performed using a flow of 1% CH_4 + He (10 l/h) at a heating rate of 5 K/min. The sample weight (q) (particle size of 0.5–1 mm) was 0.2–0.3 g. After reaching a temperature of 880°C, the samples were additionally kept in a flow of the reaction mixture for 70 min. The reaction products (CO_2, CO, H_2, and H_2O) were analyzed using a PEM-2M gas analyzer. The amount of removed oxygen was found from the graphical representation of the amount of a product as a function of temperature (time). The rates of oxygen consumption were calculated from the rates of product formation using the equations

$$w_{CO_2},\ [\text{atom O m}^{-2}\ \text{s}^{-1}] = 29.876\times10^{17}[CO_2]/(qS_{sp}), \quad (3)$$

$$w_{CO},\ [\text{atom O m}^{-2}\ \text{s}^{-1}] = 7.469\times10^{17}[CO]/(qS_{sp}). \quad (4)$$

RESULTS AND DISCUSSION

Catalytic Activity of Substituted Perovskites from the $La_{1-x}Sr_xFeO_{3-y}$ Series in the Deep Oxidation Reactions of CO and Methane

The specific catalytic activity of perovskites from the $La_{1-x}Sr_xFeO_{3-y}$ series in the reaction of carbon monoxide oxidation nonmonotonically changed with x. Two activity maximums were observed at $x = 0.3$–0.4 and 0.8 (Fig. 1).

In the catalytic reaction of the deep oxidation of methane, which occurred at higher temperatures (500–600°C) (Fig. 2), the reaction selectivity for CO_2 was 100% for all of the samples regardless of test tempera-

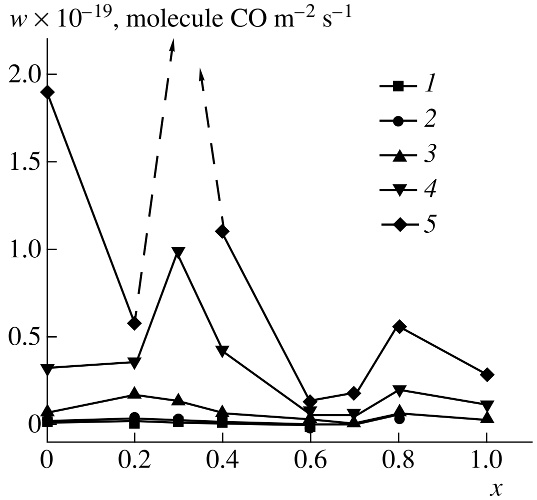

Fig. 1. Dependence of the rate of CO oxidation on the composition (x) of $La_{1-x}Sr_xFeO_{3-y}$ at (*1*) 250, (*2*) 300, (*3*) 350, (*4*) 400, and (*5*) 450°C.

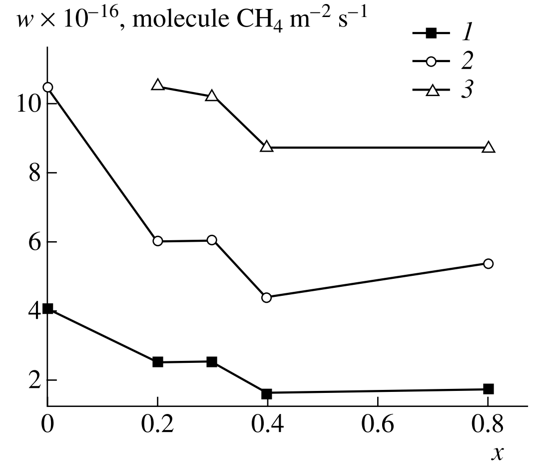

Fig. 2. Dependence of the rate of methane oxidation on the composition (x) of $La_{1-x}Sr_xFeO_{3-y}$ at (*1*) 500, (*2*) 550, and (*3*) 600°C.

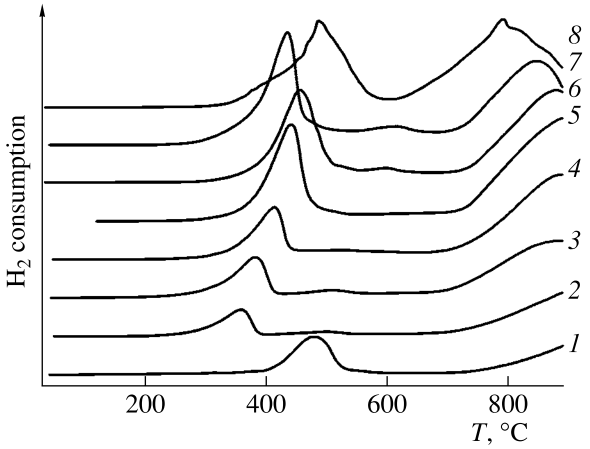

Fig. 3. Curves of the TPR of perovskites from the $La_{1-x}Sr_xFeO_{3-y}$ series with hydrogen: x = (*1*) 0, (*2*) 0.2, (*3*) 0.3, (*4*) 0.4, (*5*) 0.6, (*6*) 0.7, (*7*) 0.8, and (*8*) 1.

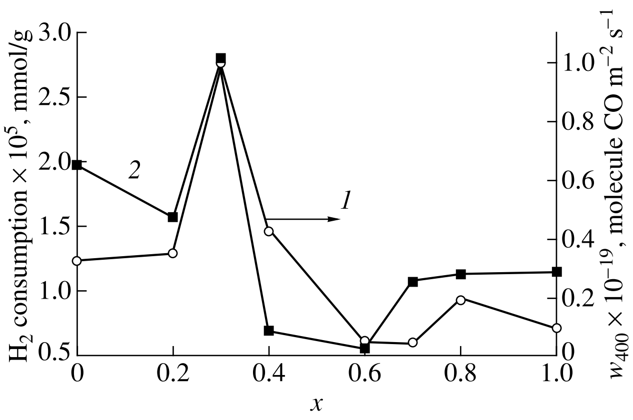

Fig. 4. Dependence of (*1*) the rate of CO oxidation at 400°C and (*2*) the amount of hydrogen consumed up to 250°C on the composition (x) of $La_{1-x}Sr_xFeO_{3-y}$.

ture. Close values of specific catalytic activity (no maximums) in methane oxidation were obtained for all samples. Thus, the behaviors of the $La_{1-x}Ca_xFeO_3$ and $La_{1-x}Sr_xFeO_{3-y}$ systems were different in CO and methane oxidation processes. In the Ca-containing system [8], the activity–composition relationship was the same in both of the deep oxidation reactions and exhibited maximums for samples with intermediate compositions (which also corresponded to a change in the amount of surface oxygen species). In the Sr-containing system there were maximums in CO oxidation and no maximums in methane oxidation [12]; this suggests the participation of different oxygen species in reactions that occur at different temperatures.

Temperature-Programmed Reduction of Samples from the $La_{1-x}Sr_xFeO_{3-y}$ Series with Hydrogen

As follows from the experimental data (Figs. 3–5, Table 1), the reduction of samples with hydrogen occurred in different temperature regions. This can be due to both a variety of surface and lattice oxygen species in perovskites and a non-single-phase character of samples from this series [12]. Three main peaks in the TPR curves of the samples can be recognized (Fig. 3): low-temperature hydrogen consumption, which quantitatively corresponds to the reduction of no more than a monolayer surface coverage with oxygen; consumption with maximums in the temperature region 400–600°C, which quantitatively corresponds to the reduction of Fe^{4+} cations to Fe^{3+} (or the removal of oxygen from the

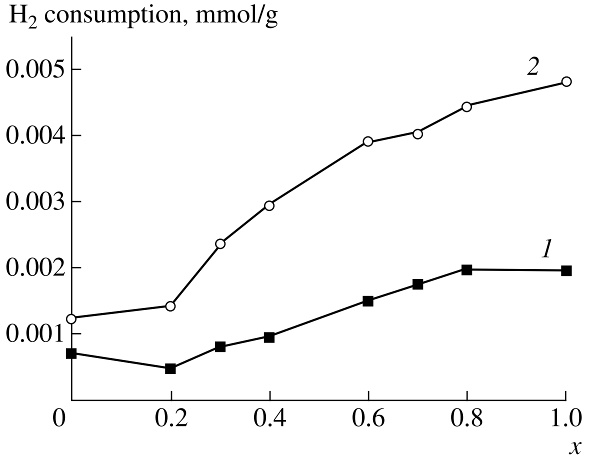

Fig. 5. Dependence of the amounts of hydrogen consumed to (*1*) 600 and (*2*) 900°C on the composition (*x*) of $La_{1-x}Sr_xFeO_{3-y}$.

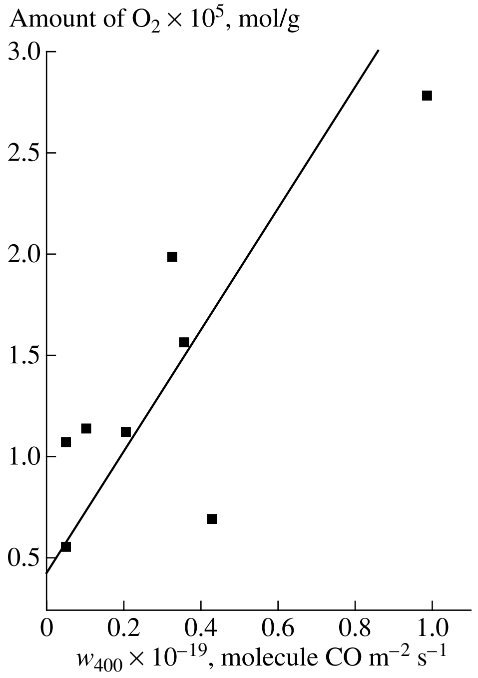

Fig. 6. Linear correlation (with a coefficient of 0.8) between the amount of weakly bound oxygen and the catalytic activity of $La_{1-x}Sr_xFeO_{3-y}$ in CO oxidation.

coordination sphere of highly charged cations with the formation of oxygen vacancies); and high-temperature consumption at temperatures higher than 600°C, which quantitatively corresponds to the deeper steps of the reduction of iron cations. It can be seen that the low-temperature consumption (to 250°C) nonmonotonically changed with increasing strontium content (Fig. 4), whereas the consumption in the region to 600°C and the total amount of oxygen removed in the course of TPR to 900°C (Fig. 5) or the reducibility of samples increased. Thus, the bulk reduction of lanthanum ferrite began at ~900°C, whereas the bulk reduction of strontium ferrite (Fe^{3+} to Fe^0) occurred by more than 80% at 900°C (Fig. 3). Let us consider the experimental data in accordance with the above subdivision into three groups and compare them with data on the catalytic activity.

(1) The lowest temperature (to 250°C) consumption of hydrogen quantitatively corresponded to the removal of no more than a monolayer of oxygen. Because the phase reduction of oxides does not occur in this temperature region, the consumption of hydrogen can characterize the most weakly bound reactive surface oxygen species (Table 1). We calculated the amount of hydrogen consumed in this temperature region as a function of sample composition. We found that this function exhibited maximums at $x = 0.3$ and 0.8 (Fig. 4, curve *1*); this is consistent with changes in the catalytic activity

Table 1. Amount of hydrogen consumed in the TPR of samples with hydrogen

Sample composition, *x*	H_2 consumption, mol/g			Amount of Fe^{4+}, %* (calculated from species 2)
	to 250°C (species 1) × 10^5	to 600°C (species 2) × 10^3	to 900°C (total) × 10^3	
0	1.98	0.71	1.24	–
0.2	1.57	0.49	1.44	22.7
0.3	2.77	0.82	2.37	37.2
0.4	0.69	0.96	2.94	42.6
0.6	0.56	1.5	3.90	63.6
0.7	1.07	1.75	4.04	76.2
0.8	1.13	1.97	4.44	79.5
1.0	1.14	1.96	4.82	74.4

* Percentage with respect to a theoretically possible value.

of samples in the reaction of CO oxidation (Fig. 4, curve *2*). Moreover, as follows from Fig. 6, a linear relation between the amount of oxygen removed in this temperature region, normalized to the unit surface area of samples, and the specific catalytic activity (per square meter) in the reaction of CO oxidation can be established with a correlation coefficient of 0.8. This relation indicates that the catalytic activity of perovskites in the reaction of CO oxidation depends on the amount of this oxygen species. By analogy with published data [8], it is likely that the observed maximums of activity are due to oxygen adsorbed at interfaces because these samples are non-single-phase, as found previously [12].

(2) The consumption of hydrogen at temperatures up to 600°C monotonically increased with strontium content. Moreover, the addition of strontium decreased the temperature of reduction. The amount of this oxygen species corresponds to the removal of one to a few tens of oxygen monolayers. This species can be associated with oxygen in the coordination sphere of the highly charged Fe^{4+} cation. These low temperatures of reduction (much lower than the reduction temperatures of α-Fe_2O_3) and the amount of removed oxygen suggest the removal of this oxygen species from perovskites in this temperature region. The amount of Fe^{4+} cations calculated from data on the consumption of hydrogen at temperatures lower than 600°C indicates that their concentration is close to the theoretically possible value (Table 1); this can also be indicative of the correct assignment of this peak. However, it can be seen that the amount of oxygen removed in this temperature region does not correlate with data on the catalytic activity of the samples in both of the catalytic oxidation reactions.

(3) The consumption of hydrogen at higher temperatures (up to 900°C) corresponds to the deeper reduction of oxides (Table 1). Therefore, it can be ascribed to the bulk reduction of perovskites, for example, the reduction of Fe^{3+} to Fe^{2+} and then to Fe^0 in the perovskite structure. The amount of hydrogen consumed in this region and the total consumption monotonically increased with x; this is inconsistent with the character of changes in the activity of the samples.

Thus, in the given system, which is electrically neutral because of the formation of highly charged Fe^{4+} cations, it is most likely that oxygen in the coordination sphere of these cations does not participate in the heterogeneous reactions of CO and CH_4 oxidation. It is likely that the correlation between the amount of surface oxygen species and the activity in the reaction of CO oxidation suggests that reactive surface oxygen species primarily participated in the reactions of deep oxidation. In our opinion, the absence of such a correlation for the reaction of methane oxidation can be explained by a change in the sample microstructure at the test temperatures specified due to a low-temperature polymorphic phase transition (by analogy with the $La_{1-x}Sr_xCoO_{3-y}$ system [13, 14]) and, consequently, the desorption of a portion of reactive surface species related to interfaces.

The experimental data allowed us to conclude that the lattice oxygen species of perovskites, including species in the coordination sphere of a highly charged cation, did not participate in the heterogeneous catalytic deep oxidation reactions of not only carbon monoxide but also methane.

The observed correlation between changes in the catalytic activity of samples and their surface reduction (to 250°C) is consistent with previous conclusions [1, 2, 4] on the stepwise reaction mechanism of CO oxidation on perovskites. The occurrence of reactive oxygen species on the surface near interfaces can be explained by the fact that clusters of coordinatively unsaturated Fe^{2+} cations can be formed at the sites of the outlets of these interfaces. These clusters can adsorb the most weakly bound oxygen species [15].

The independence of the activity of samples in the reaction of methane oxidation from the composition of samples could also be explained by a smaller degree of surface reduction in a methane-containing reaction atmosphere than that in an atmosphere containing CO. In addition, this could be explained by greater surface coverages with water formed in the course of reaction. It is well known that surface hydroxylation decreases the concentration of coordinatively unsaturated surface centers (in the case under consideration, iron cations). On the other hand, the microstructure of some samples could be changed with increasing test temperature because polymorphic phase transitions can occur in the system [16].

Thus, lattice oxygen did not participate in the deep oxidation reactions of methane and CO in an excess of oxygen. At the same time, the participation of lattice oxygen species is most important for membrane oxidation processes, the activity and selectivity of which depends on the mobility of oxygen [17, 18]. For this reason, we consider the effect of strontium substitution for lanthanum in perovskite on TPR with methane.

Temperature-Programmed Reduction of Samples from the $La_{1-x}Sr_xFeO_{3-y}$ Series with Methane

Methane was oxidized in the TPR of the specified catalysts with methane, and the products of deep and partial oxidation (CO_2, CO, H_2, and H_2O) were released into the gas phase. Moreover, samples with x = 0.8 and 1 released oxygen into the gas phase (Figs. 7, 8, Table 2). The experimental results suggest the occurrence of three lattice oxygen species. One of these species is responsible for the process of deep oxidation, whose products are CO_2 and H_2O. The second species is responsible for selective oxidation, which results in the formation of H_2 and CO. It is likely that the release

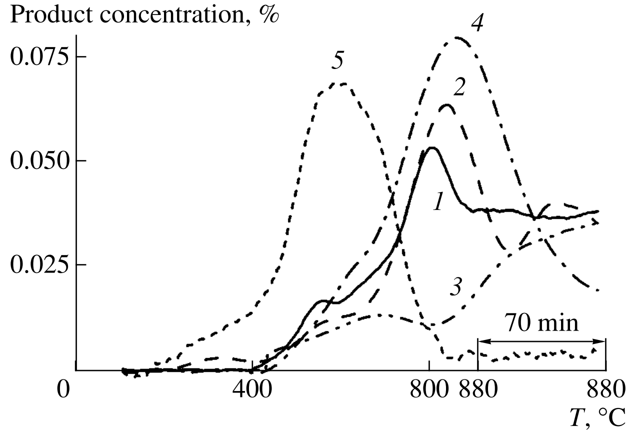

Fig. 7. Products released into a gas phase in the course of the TPR reduction of a $SrFeO_{3-y}$ sample with methane: (*1*) CO_2, (*2*) CO, (*3*) H_2, (*4*) H_2O, and (*5*) O_2.

of oxygen in the course of TPR with methane is due to the high mobility of oxygen at low temperatures, which are insufficient for methane activation. The overall degree of sample reduction at the end of the TPR process changed only slightly as the strontium content of the samples was increased (Table 2). However, the maximum rate of reduction increased; this fact suggests an increase in the mobility of oxygen in substituted samples. Moreover, the ratio between gaseous products of the reaction (process selectivity) and the temperature at which the rate of reduction reached a maximum changed. For example, note that the temperature and the maximum rate increased with strontium content. This reflects a relationship between the amount of vacancies formed and the mobility of oxygen. In the samples that released oxygen, the selectivity for hydrogen decreased without a decrease in the selectivity for CO; this may be indicative of the oxidation of the resulting hydrogen. The experimental data allowed us to recommend various perovskite compositions for deep or partial oxidation processes. Thus, samples with $x = 0.1$–0.2 can be used for the production of synthesis gas. Similar recommendations were made by Li Ranjia *et al.* [18], who also suggested a periodic (alternating-feed) process for producing synthesis gas. It is likely that single-phase samples with $x = 0.4$–0.8 can be used in the membrane or periodic processes of deep methane oxidation.

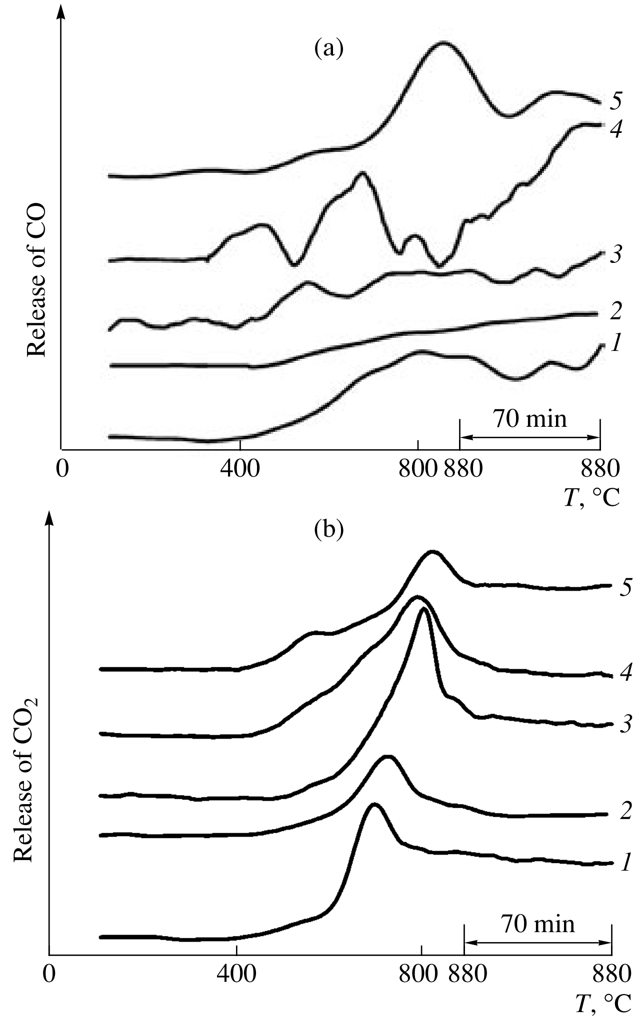

Fig. 8. Formation of (a) CO and (b) CO_2 in the TPR of perovskites from the $La_{1-x}Sr_xFeO_{3-y}$ series with methane: x = (*1*) 0.2, (*2*) 0.3, (*3*) 0.6, (*4*) 0.8, and (*5*) 1.

Table 2. Reactivity of perovskites according to data on TPR with methane

Sample composition, x	S_{sp}, m^2/g	Rates of reduction at 800°C, as calculated based on various products $\times 10^{16}$, atom O m^{-2} s^{-1}			Number of oxygen monolayers removed at temperatures (°C) to			Overall degree of reduction, %
		CO	CO_2	H_2	400	700	880	
0.2	3.1	2.38	10.56	2.84	0	14.84	71.6	61.9
0.3	2.6	2.79	4.03	–	0.96	17.72	64.0	45.3
0.6	1.3	4.53	19.13	6.60	8.20	29.67	204.1	66.3
0.8	0.9	10.37	18.15	0.90	1.20	49.64	224.2	58.2
1	0.1	74.10	289.6	33.13	8.50	362.64	2170	68.3

CONCLUSION

The reactivity of different oxygen species in $La_{1-x}Sr_xCoO_{3-y}$ perovskites prepared by mechanochemical activation has been studied by hydrogen and methane TPR methods.The data obtained have been compared with catalytic activity data for the deep oxidation of methane and carbon monoxide. The reduction of the perovskites with hydrogen proceeds in three temperature regions: the reactive surface oxygen is removed below 250°C, Fe^{4+} cations are reduced to Fe^{3+} up to 600°C, and the formation of iron metal occurs above 600°C. The reactivity of the perovskites in CO oxidation at 250–450°C depends linearly, with a correlation coefficient of 0.8, on the amount of the most reactive surface oxygen species, removable by hydrogen TPR below 250°C. The highest concentration of this oxygen is observed in the microheterogeneous specimens with $x = 0.3$–0.4, which result from low-temperature polymorphic transitions. The absence of a linear dependence between methane oxidation activity and the amount of surface oxygen species in the temperature range 500–600°C may be due to the fact that the low-temperature, orthorhombic modification transforms into the high-temperature, cubic modification between 450 and 500°C.

The reduction of the perovskites with methane yields both partial and deep oxidation products. Raising the strontium content of the system increases the yield of the deep oxidation products, the reduction rate, and, therefore, the mobility of lattice oxygen.

The most reactive surface oxygen species, localized at interphase boundary outlet sites, are involved in the deep oxidation, while lattice oxygen does not participate in this reaction. At the same time, in membrane processes, the catalytic activity and hydrocarbon oxidation selectivity depend on the nature and concentration of substitutional defects.

REFERENCES

1. Seiyama, T., *Catal. Rev.—Sci. Eng.*, 1991, vol. 34, no. 4, p. 281.
2. Yamazoe, N. and Teraoka, V., *Catal. Today*, 1990, vol. 8, no. 2, p. 175.
3. Tejuca, L.G., Fierro, J.L.G., and Tascon, J.M.D., *Adv. Catal.*, 1989, vol. 36, p. 237.
4. Baran, E.J., *Catal. Today*, 1990, vol. 8, p. 133.
5. Popovskii, V.V., *Teoreticheskie problemy kataliza* (Theoretical Problems of Catalysis), Novosibirsk: Inst. Kataliza, 1977.
6. Boreskov, G.K., *Geterogennyi kataliz* (Heterogeneous Catalysis), Moscow: Nauka, 1988.
7. Sadykov, V.A., Tikhov, S.F., Tsybulya, S.V., Kryukova, G.N., Veniaminov, S.A., Kolomiichuk, V.N., Bulgakov, N.N., Isupova, L.A., Paukshtis, E.A., Zaikovskii, V.I., Kustova, G.N., and Burgina, E.B., *Stud. Surf. Sci. Catal.*, 1997, vol. 110, p. 1155.
8. Isupova, L.A., Yakovleva, I.S., Rogov, V.V., Alikina, G.M., and Sadykov, V.A., *Kinet. Katal.*, 2004, vol. 45, no. 3.
9. Ciambelli, P., Cimino, S., Lisi, L., Faticanti, M., Minelli, G., Pettiti, I., and Porta, P., *Appl. Catal., B*, 2001, vol. 33, p. 193.
10. Li, R., Ma, J., Zhou, X., and Su, Zh., *React. Kinet. Catal. Lett.*, 2000, vol. 70, no. 2, p. 362.
11. Yue Wu, Tao Yu, and Bo-Sheng Dou, *J. Catal.*, 1989, vol. 120, p. 88.
12. Yakovleva, I.S., Isupova, L.A., Tsybulya, S.V., Chernysh, A.V., Boldyreva, N.N., Alikina, G.M., and Sadykov, V.A., *J. Mater. Sci.*, 2004, vol. 39, p. 5517.
13. Tsybulya, S.V., Kryukova, G.N., Isupova, L.A., Shmakov, A.I., Cherepanova, S.V., and Sadykov, V.A., *Strukt. Khim.*, 1998, vol. 31, no. 1, p. 92.
14. Petrov, A.N., Kononchuk, J.F., Andreev, A.V., Cherepanov, V.A., and Kofstad, P., *Solid State Ionics*, 1995, vol. 80, p. 189.
15. Isupova, L.A., Budneva, A.A., Paukshtis, E.A., and Sadykov, V.A., *J. Mol. Catal. A*, 2000, vol. 158, p. 275.
16. Dann, S.E., Currie, D.B., Weller, M.T., Thomas, M.F., and Al-Rawwas, A.D., *J. Solid State Chem.*, 1994, vol. 109, p. 134.
17. Anderson, H.U, Zhou Xiao-Dong, and Dogan, F., *Mixed Ionic Electronic Conducting Rerovskites for Advanced Energy Systems*, Orlovskaya, N. and Browning, N., Eds., Dordrecht: Kluwer, 2004, p. 303.
18. Li Ranjia, Yu Changchun, and Shen Shikong, *J. Nat. Gas Chem.*, 2002, vol. 11, p. 137.