THE INFLUENCE OF THE CATALYTIC OXIDATION OF METHANE ON THE $La_{0.5}Ca_{0.5}Mn_{1-x}Fe_xO_3$ PEROVSKITE STRUCTURE

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Abstract

Solid solutions $La_{0.5}Ca_{0.5}Mn_{1-x}Fe_xO_3$ synthesized by the method of polymer-salt compositions at a temperature of 900 °C with the perovskite structure were tested in the methane oxidation reaction. It was shown that at 600 °C, complete conversion of methane occurs for all compositions, however, the nature of the dependence of the degree of conversion for lower temperatures is not linear and depends on the chemical composition. The formation of planar defects in the direction of crystallographic planes (101) in the perovskite structure at the stage of the synthesis of solid solutions and the appearance of nanoparticles of Ca-Mn oxides on the surface of perovskite after participation after reaction were shown by the HRTEM method.

Keywords: Perovskite, methane combustion, nanoparticles, planar defects, HRTEM

1. INTRODUCTION

The most common catalysts for the total oxidation reactions are the systems based on noble metals (Pt, Pd, Au) [1]. Despite the high activity, this class of catalysts has a number of disadvantages, namely, the high cost and limited reserves of the active component, low thermal stability, the possibility of poisoning with chlorine and sulfur-containing compounds. The actual problem is the search for alternative compounds having a low cost and high catalytic activity. These requirements are satisfied with solid solutions with the structure of perovskite based on alkaline earth metals and 3-d elements that have a low cost compared to noble metals, high thermal stability (up to 1200 °C), the possibility of regeneration, resistance to chlorine and sulfur - containing compounds and sufficiently broad possibilities of varying the chemical composition [2]. Catalytic activity in high-temperature oxidation reactions in solid solutions with perovskite structure demonstrated by compounds in which the high transport capacity of oxygen from the catalyst volume to the surface is realized [3]. Currently, a large number of publications are devoted to the optimization of the structure, synthesis methods and subsequent treatments to improve the reactivity of solid solutions with perovskite structure. The increase in catalytic activity in high-temperature reactions of complete oxidation is achieved by introducing promotional additives into the catalyst, doping solid solutions, surface treatment with various acids, partial reduction of the surface of perovskite. The use of different synthesis techniques allows obtaining solid solutions with homogeneous and heterogeneous structure, to vary the morphology and size of the obtained particles. The main purpose of these studies is to obtain a material in which high thermal stability, the ability to quickly change the charging state and the high transport capacity of oxygen will be realized and makes this problem actual for basic research of high-temperature oxidation catalysts [4].

Because of adjustment (adaptation) of the structure to the change of stoichiometry, it may be possible as continuous changes in oxygen compositions, and the formation of a number of discrete ordered phases. In the latter case, samples with variable integral oxygen content are divided into alternating nanoscale domains of stable phases. Such heterophase states may be interesting due to their unusual magnetic and electron transport properties (such as colossal magnetoresistance) and/or due to high catalytic activity. New aspects of the problem of partial decomposition of solid solutions with the perovskite structure appeared in connection with the discovered by us phenomenon of the formation of nanoparticles of simple oxides on the surface of the particles of the initial phases of the perovskite [5]. This effect seems to be directly related to the processes of activation and deactivation of perovskites in the conditions of catalytic reactions (in the case of manganites), the reduction stage of synthesis (in the case of ferrites) and requires a more detailed study.

In this work, the study of perovskites with the structural formula $La_{0.5}Ca_{0.5}Mn_{1-x}Fe_xO_3$ ($0.8 \geq x \geq 0.2$) in the field of morphotropic phase transitions is carried out. The influence of the degree of Mn cation substitution on the catalytic activity and stability of perovskites in the reaction of high-temperature oxidation of methane is shown.

2. MATERIALS AND METHODS

$La_{0.5}Ca_{0.5}Mn_{1-x}Fe_xO_3$ ($0.8 \geq x \geq 0.4$) samples were synthesized by the polymerizable precursor (Pechini) method. For this purpose, appropriate amounts of aqueous solutions of lanthanum, calcium, manganese and iron nitrates were combined, citric acid and ethylene glycol were added, and the mixture was evaporated at 70 - 80 °C until the formation of a resinous polymer (polymer-salt stock). The polymer was subjected to oxidative destruction. The precursor was calcined at 900 °C for four hours with a rise in temperature of 100 °C/h.

The catalytic activity of the samples in a reaction of methane oxidation was determined in a flow system at temperatures of 350 - 600 °C. A 1-g portion of a catalyst fraction of 0.25 - 0.5 mm was mixed with 1 cm^3 of quartz and placed in a U-shaped quartz reactor with an inside diameter of 4.5 mm. The feed rate of a reaction mixture of 0.9% CH_4 + 9% O_2 (and the balance N_2) was 2.4 L/h. Before the measurements, the sample was kept in the reaction mixture for ~30 min at a specified temperature. After testing at 600 °C, the sample was cooled in the reaction mixture to 500 °C and its activity was determined once again. Only carbon dioxide and water were the oxidation products of methane. The reaction products were determined by chromatography.

Electron microscopy investigation (HRTEM) was performed using a JEM-2200FS (JEOL Ltd., Tokyo, Japan) electron microscope operated at 200 kV with a lattice resolution 0.1 nm for obtaining HRTEM images.

XRD patterns were obtained on the Bruker AXS D8 Advance diffractometer (Karlsruhe, Germany) equipped with a high-temperature and supplying of various gas mixtures and the use of CuKα radiation on scanning with a step of $2\theta = 0.05°$ point by point and an accumulation time of 3 s at each point in a range of the angles $2\theta = 15° - 80°$.

Thermal analysis of the sample was performed using a synchronous thermal analysis device STA 449C Jupiter company NETZSCH (Germany). This device combines the methods of differential thermal analysis (DTA) and thermogravimetry analysis (TGA) in one dimension. The weight of the sample was approximately 50 mg. The furnace temperature was increased from 50 °C to 980 °C at a rate of 10 °C/min with He flux of 30 mL/min. The sample weight was monitored continuously as a function of temperature.

3. RESULTS

3.1. Characterization of initial samples

The ICP MS data is presented in **Table 1**. The compounds obtained by the composition of cations are close to the values of the chemical formula. The specific surface area values are also presented in **Table 1**. All the obtained values are in the range from 6.8 to 9.3 m^2/g, which is a fairly average value for perovskites synthesized at a temperature of 900 °C. As can be seen from the data presented, the observed surface values depend nonlinearly on the chemical composition.

Table 1 ICP MS and thermal desorption of argon data

Compound	ICP MS data	S., m²/g	Name
$La_{0.5}Ca_{0.5}Mn_{0.8}Fe_{0.2}O_3$	La0.53Ca0.47Mn0.80Fe0.20	6.8	5582
$La_{0.5}Ca_{0.5}Mn_{0.7}Fe_{0.3}O_3$	La0.51Ca0.49Mn0.72Fe0.28	8.3	5573
$La_{0.5}Ca_{0.5}Mn_{0.6}Fe_{0.4}O_3$	La0.52Ca0.48Mn0.60Fe0.40	9.3	5564
$La_{0.5}Ca_{0.5}Mn_{0.5}Fe_{0.5}O_3$	La0.52Ca0.48Mn0.50Fe0.50	7.1	5555
$La_{0.5}Ca_{0.5}Mn_{0.4}Fe_{0.6}O_3$	La0.51Ca0.49Mn0.40Fe0.60	8.4	5546

According to XRD data, perovskites synthesized by Pechini method were single-phase solid solutions of rhombic modification. **Figure 1** shows that with increasing Mn content, the observed reflexes shift to the region of small angles, which indicates an increase in the unit cell parameters. The coherent scattering regions calculated by the Selyakov-Scherrer formula were from 230 to 280 Å range. The obtained values of the unit cell parameters correspond to the literature data given in the work [6]. The unit cell parameters for perovskites in the initial state are presented in **Table 2**.

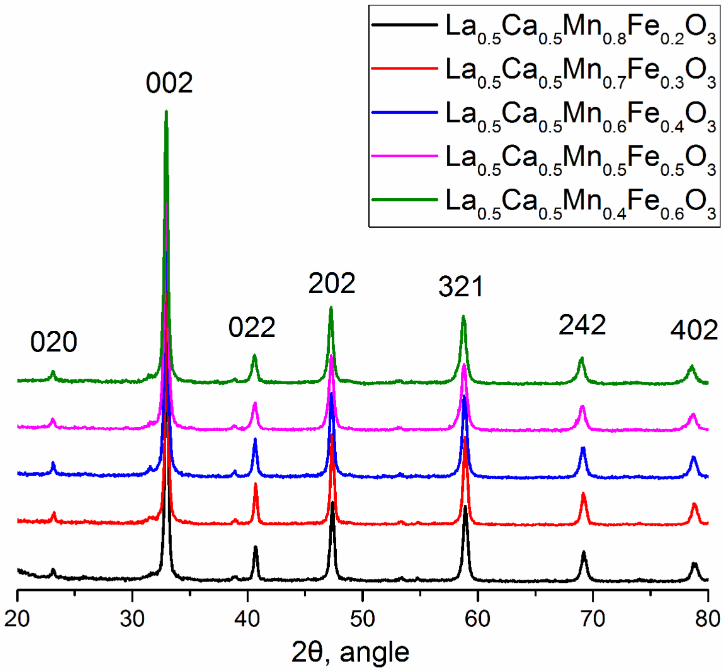

Figure 1 XRD patterns of initial $La_{0.5}Ca_{0.5}Mn_{1-x}Fe_xO_3$ samples

3.2. Catalytic activity in CH_4 oxidation

The degree of CH4 conversion on temperature and composition is represented in a **Figure 2**. At 350o C activity of catalyst varies from 4 to 21 % and nonlinear increases up to 600 °C. the most active catalyst in the temperature range from 350° to 450 °C is $La_{0.5}Ca_{0.5}Mn_{0.4}Fe_{0.6}O_3$. At higher temperatures, the catalytic activity of compounds with a degree of substitution x = 0.4 - 0.8 is compared and reaches 100% conversion to 600 °C. As can be seen from the **Figure 2**, at a temperature of 550 °C the order of activity depending on the degree of substitution looks like 5555>5546>5564>5573>5582. That is, it practically depends on the degree of substitution of iron cations in the manganese sublattice.

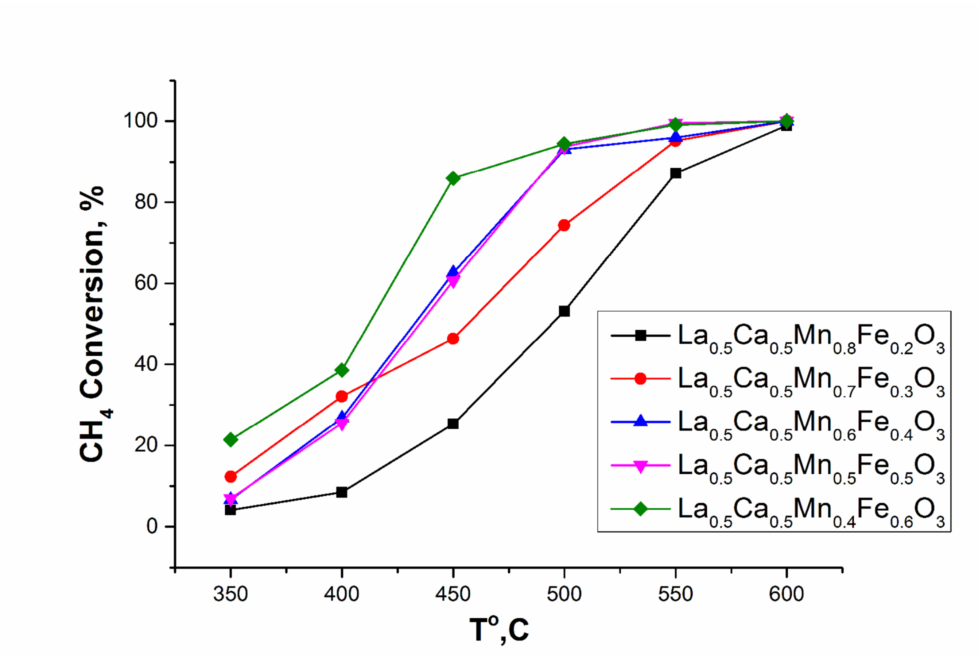

Figure 2 Dependence of methane conversion on temperature and composition of perovskites $La_{0.5}Ca_{0.5}Mn_{1-x}Fe_xO_3$

3.3. Characterization of the samples after reaction of methane oxidation

After testing at 600 °C, the samples $La_{0.5}Ca_{0.5}Mn_{1-x}Fe_xO_3$ were cooled in the reaction mixture to 500 °C and catalysts activity was determined once again. In all cases, there is a decrease in activity by several percent compared to the activity with gradual heating. Taking into account the nonlinear dependence of activity on temperature, studies of catalysts after participation in the oxidation of methane were carried out. The study of the solid solution after catalytic tests by XRD revealed no significant changes in the structure of the samples. There were slight increases in the volume of the unit cell. It can be seen from the data in **Table 2**.

Table 2 Unit cell parameters for initial and after reaction $La_{0.5}Ca_{0.5}Mn_{1-x}Fe_xO_3$ samples

Compound	Initial				After reaction			
	a, Å	b, Å	c, Å	V, Å^3	a, Å	b, Å	c, Å	V, Å^3
5546	5.45	7.69	5.44	227.77	5.45	7.70	5.45	228.80
5555	5.44	7.68	5.44	227.20	5.43	7.71	5.43	227.48
5564	5.44	7.67	5.44	226.88	5.44	7.69	5.43	227.29
5573	5.43	7.69	5.43	226.70	5.41	7.68	5.47	227.12
5582	5.43	7.68	5.43	226.50	5.43	7.68	5.43	226.47

However, comparison of the morphology of the samples before and after the reaction by HRTEM showed significant changes in the morphology and structure of the samples. Initial samples (**Figure 3a**) consists of rounded lamellar particles with an average diameter of about 30 nm (consistent with the coherent scattering region calculated from the XRD data). Particles form agglomerates with sizes from 20 nm to several microns. In the crystal lattice, planar defects in (101) directions are observed, which are visible on the HRTEM images as contrast lines and marked by arrows (**Figure 3b**).According to HRTEM, the result of the reaction on the perovskite structure is the appearance of Ca-Mn-O particles on the surface of the initial phase (**Figure 3c**). Depending on the substitution parameter, the number and size of these particles vary. Morphologically, these particles form agglomerates with a size of 10 to 50 nm and consist of crystallites with sizes about 5 nm. The measured interplanar distances observed by HRTEM allow this compound to be attributed to the Ca-Mn-O (**Figure 3d**) as observed in the work [6].

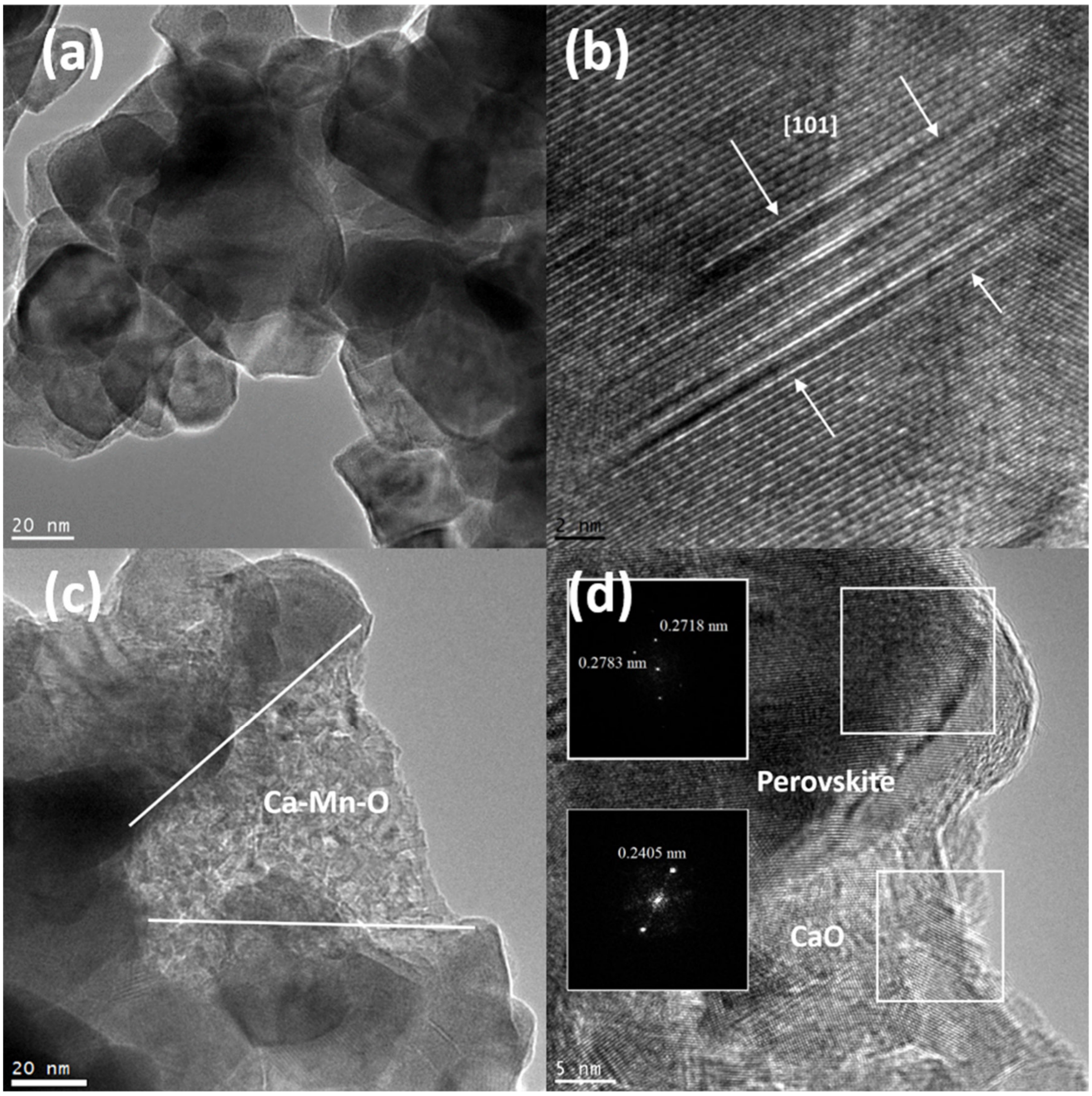

Figure 3 HRTEM images of $La_{0.5}Ca_{0.5}Mn_{0.4}Fe_{0.6}O_3$: (a) - morphology of initial sample, (b) -crystal structure of initial sample with planar defects in (101) direction, (c) - Ca-Mn-O agglomerates on perovskite surface after reaction, (d) Enlarged area of image cwith the interplanar distances of perovskite and Ca-Mn-O.

According to TGA (**Figure 4**) samples lost from 1 % to 1.5 % of the mass when heated in He up in the temperature range from 50° to 200 °C which can be associated with the removal of water, CO, -OH groups and adsorbed oxygen from the surface of the sample. For convenience of comparison, the dependence is given starting at a temperature of 50 °C (**Table 3**). From the above data, it is seen that samples with a low iron content lose significantly less mass, compared with samples containing a large amount of iron. In addition, an important detail is the sharp fall in mass loss observed in the range of 580° - 720 °C for perovskite with the high content of iron cations. No such drop was observed for the samples 5582 and 5573.

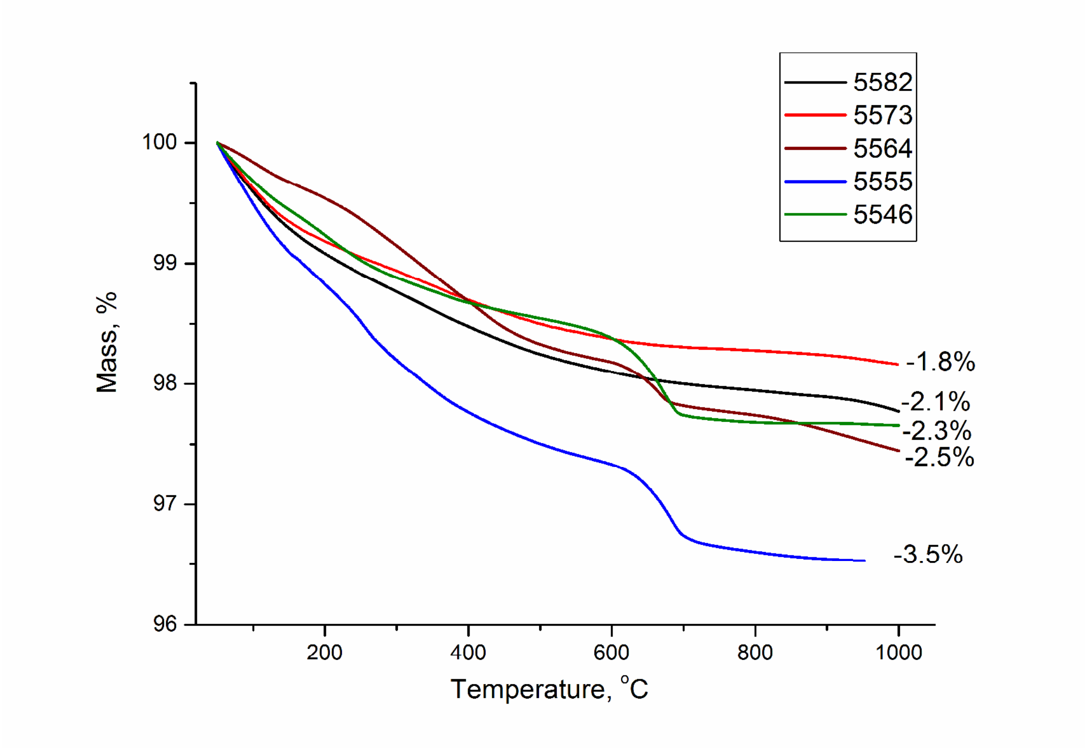

Figure 4 Dependence of perovskite weight loss on temperature in a helium flow

Table 3 Thermoanalytical data obtained in the heating of $La_{0.5}Ca_{0.5}Mn_{1-x}Fe_xO_3$ in He flow

Name	**m, %(50° - 980 °C)**	**m, %(580° - 720 °C)**
5582	2.1	0.1
5573	1.8	0.1
5564	2.5	0.4
5555	3.5	0.7
5546	2.3	0.7

4. CONCLUSION

Solid solutions $La_{0.5}Ca_{0.5}Mn_{1-x}Fe_xO_3$ synthesized by Pechini method at a temperature of 900 °C with the perovskite structure were tested in the methane oxidation reaction. It is shown that at 550 °C, complete conversion of methane occurs for all compositions, however, the nature of the dependence of the degree of conversion for lower temperatures is not linear and depends on the chemical composition.

The formation of planar defects in the direction of crystallographic planes (101) in the perovskite structure at the stage of the synthesis of solid solutions is shown by the HRTEM method. The appearance of nanoparticles of Ca-Mn oxides on the surface of perovskite was detected by transmission electron microscopy. This effect resulted from the influence of the reaction medium on the perovskite structure. The size of these particles does not exceed 10 nm, and the degree of coverage of the perovskite surface depends on the degree of substitution with Mn cations.

Thermogravimetric experiments on calcining the initial samples in the He current showed similar formation of Ca-Mn-O particles on the surface of the perovskite phase. Thus, under conditions of oxygen deficiency at high temperatures in solid solutions with the perovskite structure $La_{0.5}Ca_{0.5}Mn_{1-x}Fe_xO_3$, the microheterogeneous structure CaMnO - $La_{0.5}Ca_{0.5}Mn_{1-x}Fe_xO_3$ is formed.

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