Synthesis, Morphology, and Activity of $La_{1-x}Ag_{x}MnO_{3\pm v}$ Catalysts

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Abstract—La_{1 – x}Ag_xMnO_{3 ± y} (x = 0–0.3) mixed oxides have been synthesized by the pyrolysis of polymer– salt compositions using different organic compounds and different salt : organic compound ratios. The correlation between the reaction medium temperature during pyrolysis, the composition of the resulting oxide, and synthesis conditions has been investigated. The effect of these conditions on the character of the pyrolysis process, on the phase composition and microstructure of the resulting oxide particles and metallic silver, and on their mutual distribution is reported. The catalytic properties of the synthesized oxides in methane and soot oxidation are considered, and a correlation is established between the catalytic activity of the oxides and the synthesis conditions.

Keywords: lanthanum manganite, silver, catalytic oxidation of methane and soot, catalytic activity **DOI:** 10.1134/S0023158416050165

INTRODUCTION

Mixed oxide materials with a perovskite (ABO_3) structure are finding increasing application owing to the fact that their properties can be tuned by doping their A and B sublattices. In some cases, in perovskite and related structures there can be heterovalent substitution in the oxygen sublattice as well as a result of e.g., the introduction of fluoride ions therein [1, 2]. Perovskite-type materials (including lanthanum manganite-based ones [3, 4]) show a high catalytic activity in redox reactions involving oxygen or oxygen-containing compounds, have a high oxygen ion conductivity [5], and are capable of transporting protons [6, 7]. Manganites are employed as components of electrodes and solid-oxide membranes in fuel cells, electrochemical sources of oxygen, sensor elements, and catalysts protecting the atmosphere from toxic emissions [8]. In particular, these catalysts effectively accelerate the oxidation of carbon monoxide, hydrocarbons, and various organics and simultaneously reduce nitrogen oxides [9, 10]. In recent years, there has been extensive search for catalysts capable of oxidizing soot that is emitted by some industrial processes and diesel engines [11]. Promising catalysts in this area are perovskite-type mixed oxides. Depending on their purpose and operating conditions (temperature, gas medium composition, etc.), these systems are knowingly doped with certain metal ions. The catalytic characteristics of the doped systems depend significantly on the nature and quantity of these ions [12, 13]. It was discovered earlier [3, 14, 15] that the introduction of silver ions into the lanthanum sublattice of lanthanum manganite, as compared to the introduction of other metals, leads to a greater increase in the catalytic activity of the material in the oxidation of soot, organic compounds, and carbon monoxide, including for catalysts supported on nickel foam. It was found [3, 14, 15] that part of the silver in the catalyst is in the free metal state, additionally increasing the catalytic activity of the system. For this reason, we chose silverdoped lanthanum manganites with the general formula La_{1-x}Ag_xMnO_{3±y} to be an object of our further studies. These materials seem most promising from the standpoint of catalytic activity for developing thermocatalytic devices for exhaust gas treatment.

Along with optimizing the perovskite composition, it is essential to find methods and conditions for the synthesis of mixed oxide compositions possessing the best catalytic properties. Synthesis conditions have an effect on the phase composition, state of the surface, and particle size and morphology of mixed-oxide systems, on the mutual distribution of particles of the main and impurity phases, and on the possibility of synergistic effects arising from contact between different phases in heterogeneous mixed-oxide catalysts.

The base synthetic methods used in this study were the pyrolysis of polymer–salt compositions (PSCs) [16] and its variant involving glycerol as the organic component added to metal nitrates. Within these methods, it is possible to widely vary the synthesis conditions (e.g., the proportions of components in the reaction mixture) to tune the properties of the resulting material. One of the main purposes of this study was to establish a correlation between the synthesis conditions and the properties of the mixed oxides.

EXPERIMENTAL

The La_{1-x}Ag_xMnO_{3 \pm y} mixed oxides (x = 0-0.3, x = 0.1 steps) were synthesized by PSC pyrolysis or by the glycerol-nitrate method. The starting components were lanthanum(III) hexahydrate (La(NO₃)₃ \cdot 6H₂O, analytical grade), silver nitrate (AgNO₃, analytical grade), manganese(II) nitrate tetrahydrate $(Mn(NO_3)_2 \cdot 4H_2O, analytical grade), glycerol$ $(C_3H_5(OH)_3)$, analytical grade), and polyvinyl alcohol (PVA, USSR State Standard GOST 10779-78, brand 11/2). The synthesis of mixed oxides by PSC pyrolysis is based on the introduction of a water-soluble nonionic polymer into a solution of thermally decomposable metal salts followed by removing the solvent. The pyrolytic synthesis of the products is due to the redox interaction of nitrate ions with the polymer component. This reaction is exothermic, leading to a self-heating of the mixture and, in some cases, to a spontaneous process similar to self-propagating high-temperature synthesis. The resulting mixed oxide exerts an additional catalytic effect on redox reactions involved in the synthesis [10, 16, 17]. In order to investigate the effect of the synthesis method and conditions on the formation of catalytic compositions and their properties, we varied the proportions of the salt and polymer components of PSC. In addition, as was mentioned above, glycerol was used as the organic component of the reaction mixture for the sake of comparison.

The PSCs were prepared and pyrolyzed in the following way. Weighed samples of nitrates of appropriate metals were dissolved in distilled water in a water bath. A solution containing 5% PVA was separately prepared. Combining these solutions or adding glycerol to the nitrate solution yielded a PSC, which was then poured into a porcelain dish and heated on a hot plate. Initially, water removal took place, which was followed (in the case of PVA used as the organic component) by the formation of a film. After the film dried completely, it underwent pyrolysis. The resulting powder was finally heat-treated at 650°C for 48 h. The pyrolysis temperature was measured with a Testo 835-T2 (Testo, Germany) infrared high-temperature thermometer (pyrometer).

Identification of the synthesized mixed oxides and determination of their phase composition were carried out by X-ray powder diffraction (XRD) on a DRON-6 automated diffractometer (Russia, CuK_{α} radiation, $2\theta = 20^{\circ}-90^{\circ}$). Phases were identified using ICDD files [18]. Crystallographic parameters were calculated using the Fullprof software. Specific surface areas (S_{BET}) were measured on a TriStar 3020 (Micromeritics, United States) automated sorption analyzer using the volumetric variant of the BET method. S_{BET} values

were calculated from low-temperature nitrogen vapor sorption isotherms. The morphology of particles was studied using an AURIGA CrossBeam scanning electron microscope (Carl Zeiss NTS, Germany). In equipment operation and control and data processing, we used the Analysis Station software package (AURIGA series, Version 3.7).

The catalytic activity of the mixed oxides was estimated in methane and soot oxidation reactions. Methane oxidation was performed in a flow reactor operating in a near-plug-flow regime. A gas mixture consisting of 1% CH₄, 9% O₂, and helium was fed into the reactor. The concentration of the initial reactants (methane and oxygen) and reaction products (carbon oxides, oxygen, and unrelated methane) were determined on a Tsvet 500 gas chromatograph (Tsvet, Russia). Catalytic activity was measured on a 0.5-0.25 mm particle size fraction while elevating the reactor temperature from 300 to 650°C in steps. The fraction was prepared by pressing the catalyst powder followed by sieving it through sieves with opening diameters of 0.25 and 0.5 mm. catalytic tests were carried out on 1 cm³ samples, whose weight was 1.3-1.5 g.

Soot was oxidized in air in an open reactor while raising the reactor temperature from 200 to 600°C in 50°C steps. Weighed, thermally pretreated alumina boats containing a soot—catalyst mixture were placed in a preheated furnace and were heat-treated for 30 min. Thereafter, the boats were weighed again. The reaction zone temperature was controlled with an Oven TRM10 temperature regulator (Oven, Russia) and a KhA68 thermocouple. The model soot Printex (Degussa) was examined, which is commonly used to compare results obtained in different laboratories with different catalysts. A soot sample was combined with a fourfold weight excess of a powder catalyst, and the mixture was thoroughly ground in order to obtain tight contact between particles.

RESULTS AND DISCUSSION

The La_{1-x}Ag_xMnO_{3 $\pm v$} (x = 0-0.3) samples were black powders. Table 1 presents the pyrolysis temperature data obtained using the infrared pyrometer. Variation of the salt : polymer affects the course of pyrolysis. For the samples prepared from PSC at a stoichiometric polymer-to-nitrate ratio (reaction designed for the formation of water, carbon dioxide, and molecular nitrogen as gaseous products [10, 16]), pyrolysis has a specific stepwise character. The process does not take place simultaneously throughout the reaction mixture, but it occurs sequentially in different reaction zones of the polymer-salt film. The following pyrolysis stages are observed, irrespective of the composition of the mixed oxide being synthesized. As water is progressively removed from the PSC, a film forms, whose temperature is initially no higher than 100°C. Next, pyrolysis commences at the edges of the film at a tem-

Sample no.	Formula	Organic component	Salt : polymer	Temperature, °C				
				T_1	T_2	$T_{\rm max}$	$T_{\rm fin}$	
1	LaMnO _{3 $\pm y$}	PVA	1:1	108	100	314	145	
2	$La_{0.9}Ag_{0.1}MnO_{3 \pm y}$	PVA	1:1	102	93	395	243	
3	$La_{0.8}Ag_{0.2}MnO_{3 \pm y}$	PVA	1:1	110	96	446	310	
4	$La_{0.7}Ag_{0.3}MnO_{3 \pm y}$	PVA	1:1	300	190	516	330	
5	$La_{0.8}Ag_{0.2}MnO_{3 \pm y}$	Glycerol	1:1	*	*	482	190	
6	$La_{0.8}Ag_{0.2}MnO_{3 \pm y}$	PVA	1:2	146	*	406	210	
7	$La_{0.8}Ag_{0.2}MnO_{3\pm y}$	PVA	1:4	156	183	520	284	

 Table 1. Characteristics of mixed oxide synthesis

* No film formation takes place in this system.

perature T_1 , while the temperature of the film itself decreases to T_2 . Thereafter, the film gradually burns away, with its temperature exceeding T_1 . As the film burns, its temperature grows progressively, and the film residue burns at the highest temperature (T_{max}). The pyrolysis process yields a mixed oxide, whose final temperature (T_{fin}) at the combustion cessation point is below the maximum pyrolysis temperature. Note that increasing the amount of silver introduced into the manganite structure leads to a monotonic increase in T_{max} .

At smaller salt : polymer ratios, the process does not proceed stepwise. After the onset of pyrolysis at the film edges, a dramatic heating takes place, which is not observed in the pyrolysis of the stoichiometric composition, and then the entire surface burns out rapidly. With an increasing polymer content, the maximum pyrolysis temperature and the onset temperature of pyrolysis increase.

With glycerol in place of the polymer component $(La_{0.8}Ag_{0.2}MnO_{3\pm y}, sample 2)$, pyrolysis begins immediately after the removal of the liquid (no film formation is observed).

According to XRD data, all $La_{1-x}Ag_xMnO_{3\pm y}$ samples contain, aside from the perovskite phase, the metallic silver phase. The introduction of silver changes the shape of diffraction peaks from the perovskite phase, shifts them relative to the peaks of $LaMnO_{3\pm y}$, and changes the space group of the phase (Fig. 1).

Table 2 lists the silver-to-perovskite ratios in the samples. These data suggest that part of the silver in the La_{1-x}Ag_xMnO_{3±y} samples is incorporated in the perovskite structure. This finding is in agreement with our earlier data [19] and with data reported by other researchers [20, 21]. Kucharczyk and Tylus [20] believe that La_{0.9}Ag_{0.1}MnO_{3±y} is a single-phase material. This is possibly explained by the specific features of their synthetic procedure. Table 3 presents the calculated crystallographic parameters of La_{1-x}Ag_xMnO_{3±y} solid solutions (x = 0.1-0.3). The unit cell parameters of this phase depend nonlinearly

on the amount of silver introduced into the lanthanum sublattice. The incorporation of silver ions in the perovskite structure (Table 3, samples 2, 3) increases the unit cell parameters and volume, which can be explained by the difference between the ionic radii of La^{3+} and Ag^+ (1.03 and 1.15 Å, respectively). However, as the silver content is further increased (Table 3, samples 3, 4), the unit cell parameters decrease, which can be due to the fact that the introduction of the differently charged dopant generates an additional amount of Mn^{4+} , which has a smaller ionic radius. The nonlinear dependence of the unit cell parameters in the amount of silver introduced correlates well with our earlier results [22].

The effect of synthesis conditions on the morphology of $La_{0.8}Ag_{0.2}MnO_{3 \pm y}$ samples (Figs. 2, 3) was studied by scanning electron microscopy. Perovskite particles form large, stable, porous aggregates. Increasing the proportion of polymer in the initial PSC leads to an increase in the particle size of both phases—perovskite and metallic silver located on the surface of the aggregated particles (Fig. 3). This may be a consequence of the higher temperature reached in the pyrolysis process.

In $La_{0.8}Ag_{0.2}MnO_{3 \pm y}$ synthesized from the PSC with a stoichiometric salt : polymer ratio (Table 1, sample 3), the size of perovskite particles is 40 to 80 nm (Fig. 2a), which is in agreement with the particle size derived from the width of diffraction peaks from the perovskite phase (Table 2). These nanoparticles form high-porosity, branched, submicron- and micron-sized agglomerates. Figures 2b and 2c show formations typical of this mixed oxide synthesized by pyrolysis. The synthesis yields a porous, gas-permeable catalytic composition based on aggregated of mixed oxide nanoparticles that are in rather intimate contact (Figs. 2a, 2b). As a rule, the inter-aggregate space is filled by extensive particle ensembles with strong point contacts creating the specific cellular structure of the mixed oxide (Fig. 2c). In some cases, a denser matrix can form cells with a cavity accommodating the above-mentioned network of nanoparticles. It was possible to visualize metallic silver particles only using the backscattered electron technique. This technique provides information about the average atomic number of the elements constituting the material examined, thus making it possible to distinguish phases differing in their composition. Figures 2b and 2d show images of an area of the sample surface that were obtained at a fixed magnification but in different (secondary and backscattered electron imaging) modes. The metallic silver particles (Figs. 2d, 3a) are lighter colored and are more uniformly distributed in the surface of the agglomerates. Their size is approximately 50 nm and is comparable with the size of the primary perovskite particles in the agglomerates.

In the La_{0.8}Ag_{0.2}MnO_{3 ± y} sample prepared using a twofold excess of PVA in the initial PSC (Table 1, sample 6), the size of metallic silver particles is 300–500 nm. Electron micrographs allow the shape of separate silver crystals to be distibuished, which have a cubic structure (Fig. 3b). in this case, the silver particles are larger than the primary perovskite particles, whose size is at most 100 nm.

In the La_{0.8}Ag_{0.2}MnO_{3 ± y} obtained using a fourfold excess of PVA (Table 1, sample 7), the size of metallic silver particles is up to 1 μ m (Fig. 3c) and is comparable with the size of the perovskite particle aggregates. The primary particles of perovskite in this sample are also larger (100–200 nm). However, despite this particle coarsening, the micron-sized aggregates retain their high porosity.

Figure 3d presents an image of $La_{0.8}Ag_{0.2}MnO_{3 \pm y}$ synthesized using glycerol in place of PVA as the organic component (Table 1, sample 5). This sample also contains micron-sized porous aggregates of primary, 30- 40-nm perovskite particles. The size of metallic silver particles is 30–50 nm, and they can be distinguished only using the backscattered electron technique.

These data indicate that the size of the primary perovskite particles and silver particles depends on the polymer content of the PSC. It would be expected that the highest catalytic activity will be shown by $La_{0.8}Ag_{0.2}MnO_{3\pm y}$ samples synthesized at a stoichiometric salt : organic component ratio, since more finely dispersed heterogeneous nanosystems form in this case. As was mentioned above, in all samples the metallic silver phase is uniformly distributed with respect to the perovskite phase.

Variation of the salt : polymer ratio and the consequent variation of the temperature reached in the pyrolysis process have no significant effect on the specific surface area of the product. The resulting samples differ in S_{BET} by at most 1 m²/g (Table 4). This can be explained by the fact that, in spite of the coarsening of the perovskite and metallic silver particles, the porous structure of the agglomerates remains invariable.



Fig. 1. (a) XRD patterns of (*1*) LaMnO_{3±y}, (2) La_{0.9}Ag_{0.1}MnO_{3±y}, (3) La_{0.8}Ag_{0.2}MnO_{3±y}, and (4) La_{0.7}Ag_{0.3}MnO_{3±y} (b) XRD patterns of (*1*) LaMnO_{3±y} and (2–4) La_{0.8}Ag_{0.2}MnO_{3±y} samples prepared from PSCs with different salt : polymer ratios: (2) sample 3, (3) sample 6, and (4) sample 7.

Figures 4-6 plot the dependences of the methane and soot conversions (α) on the reaction temperature and on the amount of silver (x) in $La_{1-x}Ag_{x}MnO_{3+x}$ Table 4 presents data characterizing the specific catalytic activity of the mixed oxides in methane oxidation and data concerning soot conversion and soot ignition and complete oxidation temperatures. For all of the samples, 100% methane conversion is observed at 500°C (Fig. 4a); 100% soot conversion, at 700°C (Fig. 5a). The introduction of silver into lanthanum manganite generally enhances its catalytic activity at low temperatures (350–400°C in methane oxidation and 350–500°C in soot oxidation); however, in both reactions the increase in catalytic activity is not proportional to the amount of silver introduced (Figs. 4b, 5b). Among samples 1-4, which were prepared by the same method, sample 2 displays the highest catalytic

Table 2. Phase composition of $La_{1-x}Ag_{x}MnO_{3\pm y}$

Sample no.	Formula	Identified	Proportio m	ons of phases, 101 %	Total Ag content	Formula of perovskite from experimental data***	
		phases	LaMnO ₃	Ag	fractions**		
1	LaMnO _{3 $\pm y$}	LaMnO _{3 $\pm y$}	100	0	0	LaMnO _{3 $\pm y$}	
2	$La_{0.9}Ag_{0.1}MnO_{3 \pm y}$	LaMnO _{3 $\pm y^*$} , Ag	93	7	0.099	$La_{0.9}Ag_{0.029}Mn_{3 \pm y}$	
3	$La_{0.8}Ag_{0.2}MnO_{3 \pm y}$	LaMnO _{3 $\pm y^*$} , Ag	89	11	0.17	$La_{0.8}Ag_{0.07}Mn_{3 \pm y}$	
4	$La_{0.7}Ag_{0.3}MnO_{3 \pm y}$	LaMnO _{3 $\pm y^*$} , Ag	84	16	0.26	$La_{0.7}Ag_{0.1}Mn_{3 \pm y}$	

* Solid solution based on $LaMnO_{3 \pm y}$. ** Determined by atomic absorption spectroscopy and converted to the perovskite formula. *** Calculated from XRD atomic absorption spectroscopy data.

Unite cell parameters Identified Sample Space Formula phases no. group a**, Å b, Å *c*, Å $V, Å^3$ 1 $LaMnO_{3+v}$ LaMnO_{3 $\pm v$} 5.497 5.497 13.321 348.6 $R\overline{3}c$ $La_{0.9}Ag_{0.1}MnO_{3\pm y}$ LaMnO_{3 $\pm y^*$}, Ag 232.2 2 5.502 Pbnm 5.449 7.745 4.088 68.3 _ Fm3m La_{0.8}Ag_{0.2}MnO_{3 $\pm y$} LaMnO_{3 $\pm y$}*, Ag 3 Pbnm 5.450 231.7 5.452 7.728 4.085 68.2 Fm3m — _ La_{0.7}Ag_{0.3}MnO_{3 $\pm y$} LaMnO_{3 $\pm y$}*, Ag 4 Pbnm 5.494 231.8 5.450 7.742 4.089 68.4 _ _ Fm3m

Table 3. Unite cell parameters of $La_{1-x}Ag_{x}MnO_{3\pm y}$

* Solid solution based on LaMnO_{3 $\pm y$}. ** The measurement error is no larger than 0.005.

Table 4. Catalytic properties of $La_{1-x} Ag_x MnO_{3\pm y}$

Sample no.	Formula	S _{BET} , m ² /g	Methane oxidation rate, μmol m ⁻² s ⁻¹		Soot oxidation				
					conversion, %		T. °C	T of	
			300°C	400°C	300°C	500°C	T _{ign} , C	1 100%, C	
1	LaMnO _{3±y}	8.5	0.0011	0.0100	6.0	72	393	750	
2	$La_{0.9}Ag_{0.1}MnO_{3\pm y}$	7.8	0.0017	0.0153	1.8	100	365	500	
3	$La_{0.8}Ag_{0.2}MnO_{3 \pm y}$	13.2	0.0010	0.0149	1.7	95	324	600	
4	$La_{0.7}Ag_{0.3}MnO_{3 \pm y}$	14.9	0.0011	0.0112	6.3	97.7	325	550	
6	$La_{0.8}Ag_{0.2}MnO_{3 \pm y}$	12.7	0.003*	0.0104	5.6	100	311	450	
7	$La_{0.8}Ag_{0.2}MnO_{3 \pm y}$	12.2	0.0008	0.0029	15.5	100	265	400	

* 350°C.



Fig. 2. Electron micrographs of La_{0.8}Ag_{0.2}MnO_{3 $\pm y$} (sample 3): (a) ×76000, (b) ×31000, and (c) × 33000; (d) backscattered electron image of the same sample (×33000).

activity in methane oxidation (Table 4). With the same sample, 100% soot conversion is attained at the lowest temperature (500°C), although the ignition temperature for samples 3 and 4 is lower.

The catalytic activity of the oxides depends on the conditions under which they were prepared. $La_{0.8}Ag_{0.2}MnO_{3 \pm y}$ samples prepared using different organic components (PVA and glycerol) or different proportions of a given organic component (Table 4, samples 3, 5–7) show different activities in the methane and soot oxidation reactions (Figs. 6a, 6b, Table 4). Samples 3 and 5 (Table 4), synthesized using a stoichiometric mixture but different organic components and characterized by similar perovskite and silver particle sizes, differ insignificantly in their catalytic properties. Increasing the proportion of the polymer component in the initial PSC (Table 1, samples 3, 6, 7), which leads to an increase in the silver particle size, diminishes the catalytic activity of the material in

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methane oxidation relative to that of the sample prepared at a stoichiometric ratio of the components (Fig. 6a, Table 4). At the same time, catalytic activity in soot oxidation depends on the polymer content in the opposite way (Fig. 6b, Table 4): the maximum activity is exhibited by sample 7 (Table 4), which was prepared using an increased proportion of organic matter and contains the largest amount of silver with the largest particle size. This sample is characterized by the lowest ignition temperature ($265.5^{\circ}C$) and 100% conversion temperature ($400^{\circ}C$).

The data obtained for methane oxidation can be explained in terms of the compositions and morphology of the oxides. The highest activity is shown by the samples that are characterized by a developed texture, the largest amount of silver in the perovskite phase, the smallest size of silver and perovskite particles, and the presence of the metallic silver phase (samples 2 and 5). Apparently, these factors maximize the amount of



Fig. 3. Backscattered electron images of $La_{0.8}Ag_{0.2}MnO_{3 \pm y}$: (a) sample 3, ×33000; (b) sample 6, ×17000; (c) sample 7, ×9000; (d) sample 5, ×20000.

weakly bound oxygen on the surface (owing the microheterogeneity of the sample and the defectiveness of the perovskite phase), the species that determines the oxidizing activity of the catalysts [23, 24]. At the same time, the highest activity in the oxidation of soot, for which the inner surface of perovskite is inaccessible, is shown by the sample with the highest silver phase content and the largest silver particle size. It is not impossible that, in this case, catalytic activity is mainly due to the presence of silver particles. Apparently, the size effect associated with the formation of an oxide film on the surface of large silver particles (but not on the surface of small particles, which are more resistant to oxidation) is manifested here. This issue needs to be investigated in greater detail using specialized methods [25].

Thus, in the optimization of catalyst composition (with due regard for economic parameters) and synthesis conditions, it is necessary take into consideration the temperature regime under which the catalyst is to be operated. This study also demonstrates that, by varying the synthesis conditions, the resulting mixedoxide composition can be adapted to a particular catalytic reaction, namely, the oxidation of a gas or solid. For the efficient simultaneous catalytic oxidation of solids and gases, combined catalysts containing silver particles of different sized can be used in practice.

CONCLUSIONS

Perovskite-type mixed oxide with the general formula $\text{La}_{1-x}\text{Ag}_x\text{MnO}_{3\pm y}$ (x = 0-0.3) were synthesized by the pyrolysis of nitrate-containing compositions under various conditions (using glycerol or PVA as the organic component and different salt : polymer ratios in the initial composition). The dependence of the composition of the resulting mixed oxide on the above conditions and pyrolysis temperature was investigated. It was found that increasing the amount of silver introduced into the PSC increases the maximum temperature reached in pyrolysis. Increasing the polymer content of the initial PSC over the stoichiometric value changes the way pyrolysis proceeds and, in addition, raises the temperature maximum in the reaction



Fig. 4. Methane conversion as a function of (a) temperature and (b) the amount of Ag introduced into $\text{La}_{1-x}\text{Ag}_x\text{MnO}_{3\pm y}$: x = (1) 0, (2) 0.1, (3) 0.2, and (4) 0.3.



Fig. 5. Soot conversion as a function of (a) temperature and (b) the amount of Ag introduced into $\text{La}_{1-x}\text{Ag}_x\text{MnO}_{3\pm y}$: x = (1) 0, (2) 0.1, (3) 0.2, and (4) 0.3.

medium. The resulting $La_{1-x}Ag_xMnO_{3\pm y}$ (x = 0-0.3) samples are not single phases: they contain metallic silver as a minor phase. They show a high catalytic activity in methane and soot oxidation. Crystallographic parameters of these phases were calculated, and the average particle size of mixed oxide particles was estimated by XRD. The effect of synthesis conditions on the morphology of the phases was studied. The samples synthesized from PSCs containing excess polymer, contain larger particles of both perovskite and metallic silver phases. The specific surface area changes insignificantly on passing to polymer-rich compositions owing to the fact that the resulting aggregated, micron-sized perovskite particles retain high porosity. The metallic silver particles are uni-

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formly distributed on the surface of the perovskite phase. The introduction of silver into LaMnO_{3 ± y} enhances the catalytic activity of the oxide in methane and soot oxidation with oxygen; however, the dependence of the catalytic activity on the amount of silver introduced is nonlinear. The catalytic activity of La_{1-x}Ag_xMnO_{3 ± y} depends on the method of its synthesis. As the polymer content of the initial PSC is increased, the catalytic activity of the oxide in methane oxidation decreases and its catalytic activity in soot oxidation increases. Therefore, the catalyst preparation procedure should be chosen with regard for the conditions under which the catalyst is to be operated, namely, temperature and specific features of the catalytic process.



Fig. 6. Temperature dependences of (a) methane and (b) soot conversion over $La_{1-x}Ag_xMnO_{3\pm y}$ synthesized from PSCs at different salt : polymer ratios: (1) sample 3, (2) sample 6, and (3) sample 7.

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REFERENCES

- 1. Tarasova, N.A., Filinkova, Ya.V., and Animitsa, I.E., *Russ. J. Electrochem.*, 2013, vol. 49, no. 1, p. 45.
- 2. Tarasova, N.A., Filinkova, Ya.V., and Animitsa, I.E., *Russ. J. Phys. Chem. A*, 2012, vol. 86, no. 8, p. 1208.
- Ostroushko, A.A., Schubert, E., Zhuravleva, L.I., Isupova, L.A., Alikina, G.M., Bogdanov, S.G., Valiev, E.Z., Pirogov, A.N., Teplykh, A.E., Mogil'nikov, Yu.V., Udilov, A.E., and Ostroushko, I.P., *Russ. J. Appl. Chem.*, 2000, vol. 73, no. 8, p. 1383.
- 4. Buchneva, O., Rossetti, I., Biffi, C., Allieta, M., Kryukov, A., and Lebedeva, N., *Appl. Catal., A*, 2009, vol. 370, p. 24.
- Filonova, E.A., Russkikh, O.V., and Dmitriev, A.S., *Inorg. Mater.*, 2014, vol. 50, no. 7, p. 728.
- Tarasova, N.A., *Al'tern. Energetika Ekol.*, 2011, no. 6, p. 25.
- Animitsa, I., Tarasova, N., and Filinkova, Y., Solid State Ionics, 2012, vol. 207, p. 29.
- Ostroushko, A.A., Schubert, E., Makarov, A.M., Minyaev, V.I., Udilov, A.E., Elokhina, L.V., and Aksenova, V.I., *Russ. J. Appl. Chem.* 2003, vol. 76, no. 8, p. 1253.

- Antsiferov, V.N., Makarov, A.M., and Ostroushko, A.A., *Problemy poroshkovogo materialovedeniya* (Topics in Powder Materials Science), part VII: *Vysokoporistye pronitsaemye yacheistye materialy – perspektivnye nos- iteli katalizatorov* (High-Porosity Permeable Cellular Materials as Promising Catalyst Supports), Yekaterin-burg: Ural. Otd. Ross. Akad. Nauk, 2006.
- Antsiferov, V.N., Ostroushko, A.A., and Makarov, A.M., Sintez, svoistva i primenenie katalizatorov okisleniya sazhi na osnove modifitsirovannykh vysokoporistykh yacheistykh materialov (Soot Oxidation Catalysts Based on Modified High-Porosity Cellular Materials), Yekaterinburg: Ural. Otd. Ross. Akad. Nauk, 2007.
- Ostroushko, A.A., *Tekhnologiya izgotovleniya katalizatorov: Termokataliticheskaya ochistka otkhodyashchikh* gazov v promyshlennosti, energetike, na transporte (Catalyst Production Technology: Thermocatalytic Treatment of Exhaust Gases in Industry, Power Production, and Transport), Yekaterinburg: Ural. Gos. Univ., 2002.
- Pecchi, G., Campos, C.M., Jiliberto, M.G., Delgado, E.J., and Fierro, J.L.G., *Appl. Catal.*, *A*, 2009, vol. Ň. 371, no. 1, p. 78.
- 13. Song, K.S., Kang, S.K., and Kim, S.D., *Catal. Lett.*, 1997, vol. 49, nos. 1–2, p. 65.
- 14. Song, K.S., Cui, H.X., Kim, S.D., and Kang, S.K., *Catal. Today*, 1999, vol. 47, nos. 1–4, p. 155.
- 15. Lim, E., Kim, Y.J., Kim, J.H., Ryu, T., Lee, S., Cho, B.K., and Yoo, S., *J. Catal.*, 2014, vol. 319, p. 182.
- 16. Ostroushko, A.A., *Inorg. Mater.*, 2004, vol. 40, no. 3, p. 259.
- Ostroushko, A.A., *Mendeleev Chem. J.*, 1998, vol. 42, nos. 1–2, p. 153.
- 18. *PCPDFWiN v. 2.1*, Swarthmore, Penn.: International Centre for Diffraction Data, 2000.
- 19. Ostroushko, A.A., Russkikh, O.V., and Udilov, A.E., VI Ross. konf. "Nauchnye osnovy prigotovleniya i tekh-

nologii katalizatorov," V Ross. konf. "Problemy dezaktivatsii katalizatorov" (VI Russian Conf. on Scientific Foundations of Catalyst Preparation and Production Technology, V Russian Conf. on Catalyst Deactivation), Novosibirsk, 2008, vol. 1, p. 73.

- 20. Kucharczyk, B. and Tylus, W., *Appl. Catal., A*, 2008, vol. 335, no. 1, p. 28.
- Machocki, A., Ioannides, T., Stasinska, B., Gac, W., Avgouropoulos, G., Delimaris, D., and Pasieczna, S., *J. Catal.*, 2004, vol. 227, no. 2, p. 282.
- 22. Russkikh, O.V., Ostroushko, A.A., Udilov, A.E., Petrova, S.A., and Zaharov, R.G., XVII Int. Conf. on

Chemical Thermodynamics in Russia, Kazan, 2009, vol. 2, p. 307.

- 23. Isupova, L.A., Yakovleva, I.S., Alikina, G.M., Rogov, V.A., and Sadykov, V.A., *Kinet. Catal.*, 2005, vol. 46, no. 5, p. 729.
- 24. Yakovleva, I.S., Isupova, L.A., Rogov, V.A., and Sadykov, V.A., *Kinet. Catal.*, 2008, vol. 49, no. 2, p. 261.
- Kibis, L.S., Avdeev, V.I., Koscheev, S.V., and Boronin, A.I., *Surf. Sci.*, 2010, vol. 604, nos. 13–14, p. 1185.

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