Catalysts Based on Complex Oxides with Fluorite and Perovskite Structures for Soot Removal from the Exhaust Gas of Diesel Engines

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Abstract

Soot oxidation reactions are investigated in the mixture O_2 + helium and O_2 + NO_2 + helium in the presence of substituted perovskites based on lanthanum manganite and modified fluorites based on solid solution Ce–Zr–O, including those promoted with a small amount of platinum. It was shown that the efficiency of soot oxidation is higher in the mixture containing nitrogen dioxide. It was established that the presence of weakly bound surface oxygen is necessary to initiate soot oxidation, while the developed process of soot oxidation requires the mobility of lattice oxygen.

INTRODUCTION

Particulate matter which is present in the exhaust of diesel engines due to incomplete combustion of diesel fuel is among the most hazardous pollutants along with nitrogen oxides, CO and residual hydrocarbons [1]. The amount of particulates increases when sulphur-containing fuel is used; the composition of particulates is to a large extent determined by the composition of diesel fuel and includes soot, polyaromatic compounds and sulphates.

In order to remove soot from the exhaust, filters are used. Their regeneration can be performed during engine performance either in the continuous mode or periodically, depending on the type of diesel engine and its power. Soot oxidation proceeds efficiently at high temperature (600–700 °C) which can hardly be achieved under the conditions of a vehicle since the temperature of diesel engine exhaust is 200–400 °C. The use of efficient oxidation catalysts allows one to decrease soot oxidation temperature substantially. These catalysts include the catalysts of complete oxidation of hydrocarbons, based on the oxides of transition metals, platinum group metals deposited on various supports, and complex oxides with fluorite and perovskite structures [2–17]. The latter are of special interest for soot oxidation processes. Complex oxides with perovskite and fluorite structures containing transition metal cations and promoted with a small amount of platinum group metals exhibit noticeable activity in the reactions of CO and CH_4 oxidation within temperature range close to that of exhaust gas, and they are able to survive possible overheating to a high temperature [18–20]. High reactivity of the surface and lattice oxygen is characteristic of these systems. It is the presence of weakly bound chemisorbed oxygen (O^- being the surface form) and/or reactive surface oxygen in perovskite that is believed to be the reason of high activity of perovskite systems in soot oxidation reaction [4, 17]. For fluorite systems based on cerium dioxide promoted, for example, with lanthanum cations, an increase in the activity towards soot

oxidation is considered to be connected with an increase in the mobility of lattice oxygen due to the generation of anion vacancies when a trivalent promoter is introduced [21]. It is known that the efficiency of soot oxidation increases in the presence of nitrogen oxides due to the formation of a stronger oxidizer NO_2 as a result of the catalytic oxidation of NO with oxygen [5, 6, 8, 10, 13]. Oxidation of soot, a solid-phase substrate, in catalytic filters proceeds in the presence of a loose contact between the particulate matter and the solid catalyst [22]. The mobility of volume oxygen can indeed promote initiation of soot oxidation process due to the passing of weakly bound oxygen to the surface of soot particle having no contacts with gaseous oxidants like O_2 or NO_2. An increase in mobility should cause an increase in the efficiency of oxidative transformations of particulates.

The goal of the present work was to investigate the activity of soot oxidation with atmospheric oxygen and a mixture with nitrogen dioxide at the catalysts based on manganese manganite with perovskite structure and those with fluorite structure, based on a solid solution of cerium and zirconium dioxides modified with various additives. The activity of catalysts in soot oxidation reaction is compared with the reactivity and mobility of the surface and volume oxygen estimated according to the data of O_2 thermoprogrammed desorption (TPD) and H_2 thermoprogrammed reduction (TPR).

EXPERIMENTAL

Two types of materials were used in the investigation: those based on the Ce–Zr–O solid solution with fluorite structure having the composition $Ce_{0.6}Zr_{0.2}Ca_{0.2}$ (CeZrCa), $Ce_{0.5}Zr_{0.2}Ca_{0.1}Mn_{0.2}$ (CeZrCaMn), $Ce_{0.5}Zr_{0.2}Ca_{0.1}Co_{0.2}$ (CeZrCaCo), $Ce_{0.5}Zr_{0.2}Ca_{0.1}Bi_{0.2}$ (CeZrCaBi), $Ce_{0.3}Zr_{0.3}Mn_{0.4}$ (CeZrMn), $Ce_{0.5}Zr_{0.4}Nb_{0.1}$ (CeZrNb) and lanthanum manganite (LaMn) with perovskite structure in which up to 20 % of lanthanum and manganese were substituted with cerium (LaCeMn), Bi (LaBiMn) and Fe (LaFeMn), respectively. The samples were synthesized according to the procedure [17] providing homogeneous

distribution of the catalyst components. A principally important stage of the catalyst synthesis according to this procedure is the stage of formation of chelate compounds of esters of citric acid and ethylene glycol with metal cations from aqueous solutions of inorganic salts. The use of these organometallic precursors allows one to avoid or diminish the contribution from polymeric aggregates which are the products of hydrolysis of aqueous solutions of salts and thus to obtain the catalysts with homogeneous distribution of components. The final temperature of sample calcination was 500–700 °C. Platinum (mass concentration 0.2 %) was deposited by means of moisture capacity impregnation followed by calcination at 500–700 °C.

Soot oxidation was carried out in a flow IR cell with the mixtures of different composition: with atmospheric oxygen (volume fraction of O_2 in helium being 10 %) and with NO_2 added into the initial mixture (10.5 % O_2 + 0.5 % NO_2 in helium) with a load of 14 000 h^{-1} within temperature range 40–600 °C. Oxygen was analyzed by means of chromatography using a thermal conductivity detector. Analysis of nitrogen oxides and reaction products was carried out on the basis of the intensities of characteristic absorption bands of the compounds in IR spectra, cm^{-1}: H_2O 3730, CO_2 2360, NO 1900, NO_2 1630, N_2O 2210. Soot formed during the performance of an Ikarus bus was used in the experiments. Soot was deposited on the catalyst (mass concentration of soot: 10 %) by means of mechanical mixing of the powdered catalyst and soot in a closed vessel to provide loose contact. Mobility and reactivity of oxygen in complex oxides based on fluorite and perovskite structures was estimated using O_2 TPD and H_2 TPR within temperature range 40–900 °C according to the procedure described in [18]. The monolayer coating with respect to oxygen was accepted to be equal to 10^{19} O atoms/m^2.

RESULTS AND DISCUSSION

Catalytic properties of perovskites

The results of a detailed investigation of the properties and structural features of

substituted manganites were presented in our paper [18]. It was shown that for the perovskites synthesized according to this procedure it is characteristic to form extended defects with the elements of chalcolamprite or layered perovskite structure $A_{n+1}B_{n+1}O_{3n+5}$ within the framework of the pseudo-cubic perovskite structure based on lanthanum manganite. The formation of these defects during the synthesis according to this procedure is due to the high concentration of polyvalent cations Me^{4+} (Me = Mn, Fe, Ce). Concentrations and stability of defects vary in the following row: LaMn < LaBiMn < LaFeMn ≤ LaCeMn. Defect-bearing perovskites are characterized by higher mobility of volume oxygen (H_2 TPR and CO TPR) than that characteristic of the traditional synthesis methods (co-precipitation, oxalate method, or mechanochemical activation). The higher mobility of oxygen in the volume is exhibited at low temperatures (200−400 °C). The results of investigation of oxygen reactivity in perovskites according to the data of O_2 TPD and H_2 TPR are shown in Tables 1 and 2. These perovskites are characterized by the presence of weakly bound oxygen (E_{act} of desorption is about 40 kJ/mol) accounting for 1 to 30 % of the monolayer coating by oxygen, depending on the composition of substituted perovskite. Total amount of oxygen removed from perovskites (according to the data of O_2 TPD, it is 1−3 monolayers) is much larger than that

TABLE 1

Data on the reactivity of oxygen based on O_2 TPD spectra (oxygen monolayers) for substituted perovskites)

Sample	Oxygen form*			Total
	α	β	γ	
LaMn	0.3	1.3	0.4	2.0
LaCeMn	0.01	0.3	0.6	0.9
LaFeMn	0.3	1.5	1.1	2.9
LaBiMn	0.01	0.4	1.0	1.4
Pt/LaMn	0.3	2.1	−	2.4
Pt/LaCeMn	2.1	−	0.1	2.2
Pt/LaFeMn	0.3	2.8	0.4	3.5
Pt/LaBiMn	0.6	1.0	−	1.6

*α, β, γ are oxygen forms desorbing from perovskite surface during O_2 TPD with the activation energy of desorption/diffusion E_{act} which is approximately equal to 40, 80−120 and 160−400 kJ/mol, respectively.

TABLE 2

Amount of oxygen removed during H_2 TPR for substituted perovskites

Sample	H_2 TPR, 10^{-4} mol of O_2/g, at a temperature of, °C		Total
	<500	500−900	
LaMn	11.7	6.8	18.5
LaCeMn	14.2	4.6	18.8
LaFeMn	10.4	7.8	18.1
LaBiMn	15.1	8.5	23.6

for the oxides of transition metals. When a small amount of platinum is deposited, the amount of easily desorbed oxygen increases, and the peak of hydrogen absorption with H_2 TPR shifts to lower temperatures.

Typical temperature dependencies of the concentration of initial reagents and reaction products for soot oxidation with oxygen and with a mixture of oxygen with nitrogen dioxide on a perovskite catalyst are shown in Fig. 1.
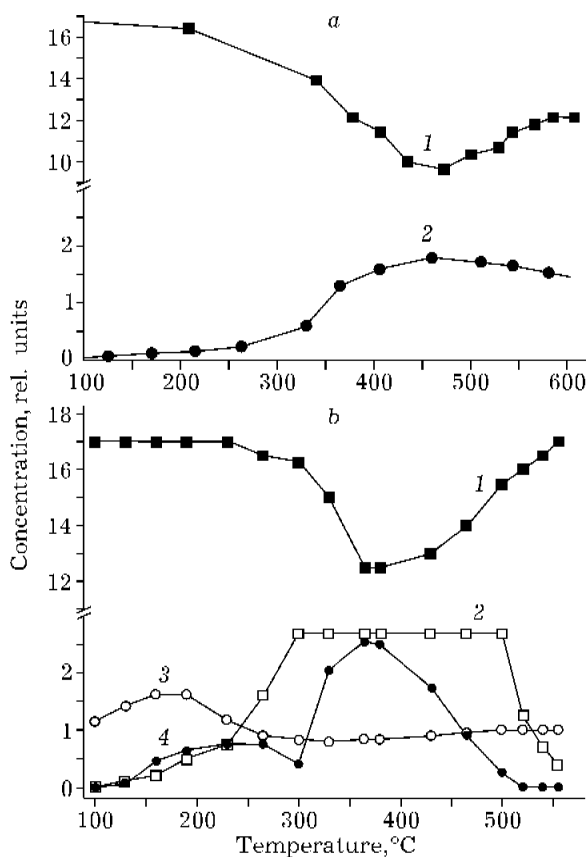

Fig. 1. Temperature dependence of the concentration of initial reagents and reaction products during soot oxidation on LaBiMn sample with oxygen (a) and a mixture of O_2 + NO_2 (b): 1 − O_2, 2 − CO_2, 3 − 10 × NO_2, 4 − 100 × N_2O.

One can see that the process of soot oxidation can be separated into two stages: initiation of oxidation, proceeding mainly without the participation of oxygen from the gas phase and resulting in the formation of CO_2, and a developed oxidation for which the oxygen from the gas phase starts to be consumed. In the presence of nitrogen dioxide in the mixture, both oxidation stages go on more actively due to the participation of a stronger oxidizer. Soot oxidation process starts at a lower temperature; according to the data on the final concentration of CO_2, oxidation degree is higher. Reaction products include also nitrogen (I) oxide; its amount only weakly depends on the catalyst composition. (We do not consider the features of nitrogen oxide transformations in the present work).
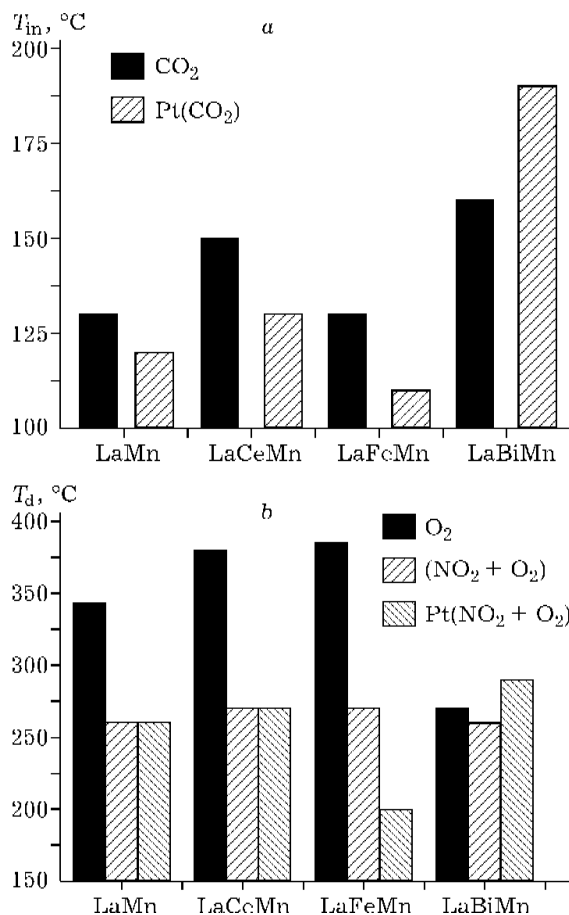

Fig. 3. O_2 TPD spectra of substituted perovskites and modified fluorites: LaMn (*1*), LaFeMn (*2*), Pt/LaFeMn (*3*), CeZrCa (*4*), CeZrCaMn (*5*) и CeZrCaCo (*6*).

The data on the temperature of soot oxidation initiation (estimated on the basis of the appearance of CO_2 in reaction products) without the participation of gas-phase oxygen (T_{in}) are shown in Fig. 2, *a*. At this stage, soot oxidation proceeds with the participation of nitrogen dioxide and oxygen of the catalyst. At the lowest temperature (about 130 °C) this process starts for the samples LaMn and LaFeMn, which are characterized by the highest fraction of the weakly bound α-form of oxygen (see Table 1 and Fig. 3). With platinum deposited, T_{in} decreases for all the perovskites except LaBiMn, though the fraction of the α-form of oxygen increases for this sample. However, total amount of removed oxygen as detected by the O_2 TPD spectra for this perovskite is the smallest in the row under investigation. The combination Pt + LaBiMn seems less favourable for the activation of nitrogen dioxide.

Changes in the temperature of the start of developed soot oxidation (T_d) by atmospheric oxygen and by a mixture of $NO_2 + O_2$ for substituted perovskites, including those promoted with platinum, are shown in Fig. 2, *b*. For LaBiMn, the developed soot oxidation starts at a higher temperature, perhaps due to the higher mobility of volume oxygen (see Table 2). For other perovskites T_d is higher by about 100 °C. With the addition of nitrogen dioxide into the initial mixture or with the deposition of platinum, T_d decreases by 100 °C, while the differences in perovskite composition are less

Fig. 2. Changes in the temperature of soot oxidation initiation in a mixture of $NO_2 + O_2$ (*a*) and in the temperature of the start of its developed oxidation in the mixtures of different composition on perovskite catalysts including those promoted with platinum (*b*). Initiation of soot oxidation was observed as the appearance of CO_2 in reaction products; the start of the developed oxidation was marked with the start of consumption of the gas-phase O_2.
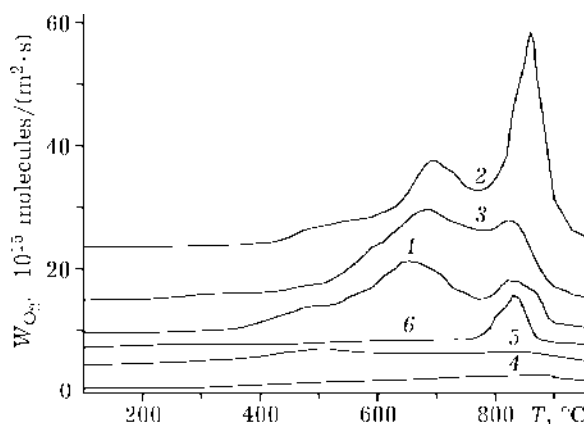
noticeable. However, the highest activity is exhibited by Pt/LaFeMn perovskite for which the process of developed soot oxidation starts at a temperature about 200 °C. Undoubtedly, the surface oxygen (β-form of oxygen) the fraction of which is maximal for this perovskite starts to make a contribution into this process (see Table 1 and Fig. 3).

So, a correlation between the activity and the amount of weakly bound oxygen in complex oxides based on perovskite structure is observed in soot oxidation reaction, unlike for the reaction of CO oxidation which is characterized by the structural sensitivity [18].

Catalytic properties of fluorites

The basis of the structure of Ce−Zr-containing samples with broadly varied concentrations of the additives is formed by a fluorite-like solid solution with a low content of unbound oxides of the promoter [20]. According to the data of H_2 TPR, the introduction of cations with variable valence not only leads to the low-temperature (200−500 °C) absorption of hydrogen due to their reduction but also promotes bulk reduction (Fig. 4 and Table 3). The modifying cations are characterized mainly by the highest oxidation degree. The data of O_2 TPD spectra of modified fluorites provide evidence of an increase in oxygen desorption in the low-temperature region in the presence of cations with variable valence (see Fig. 3, Table 4).
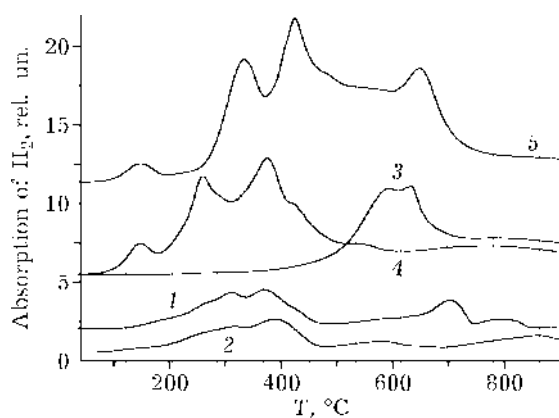
TABLE 3

Amount of oxygen removed during H_2 TPR for substituted fluorites

Sample	H_2 TPR, 10^{-4} mol O_2/g, at a temperature of, °C		Total
	<500	500−900	
CeZrCa	0.7	8.0	8.7
CeZrCaMn	8.5	3.8	12.3
CeZeCaCo	9.1	8.5	17.6
CeZrCaBi	11.6	3.7	15.3
CeZrMn	11.5	3.0	14.5
CeZrNb	1.8	9.9	11.7

So, Ce−Zr-containing composites are solid solutions based on fluorite in which the main part of the promoter is incorporated into the structure while the excess is stabilized is the form of surface/volume clusters. With such a combination, the reactivity of the surface and volume oxygen in modified fluorites increases in comparison with non-modified ones.

The data on the temperature of initiation and developed oxidation of soot by a mixture containing $NO_2 + O_2$ for modified fluorites and for the case of deposited platinum are shown in Fig. 5. The minimal temperature of soot

TABLE 4

Data on the reactivity of oxygen obtained on the basis of O_2 TPD spectra (oxygen monolayers) for substituted fluorites

Sample	Oxygen form*				Total
	α	$β_1$	$β_2$	γ	
CeZrCa	0.4	0.9	−	−	1.3
CeZrCaMn	0.3	0.9	0.5	−	1.7
CeZeCaCo	0.8	−	−	0.6	1.4
CeZrCaBi	0.8	0.4	−	−	1.2
CeZrMn	0.6	1.0	0.2	−	1.8
CeZrNb	1.3	−	−	0.7	2.0
Pt/CeZrCa	0.3	0.9	−		1.2
Pt/CeZrCaMn	0.2	0.7	0.7		1.6
Pt/CeZeCaCo	0.6	−	−	0.6	1.2
Pt/CeZrCaBi	0.1	1.0	0.6	−	1.7
Pt/CeZrMn	0.6	2.1	0.5	−	3.2
Pt/CeZrNb	1.0	1.0	−	0.3	2.3

Fig. 4. Hydrogen absorption, for substituted perovskites and modified fluorites: LaMn (1), LaFeMn (2), CeZrCa (3), CeZrCaMn (4) and CeZrCaCo (5).

*α, $β_1$, $β_2$ and γ are oxygen forms desorbing from perovskite surface during O_2 TPD with the activation energy of desorption/diffusion E_{act} approximately equal to 40, 60−80, 100−130 and 230−400 kJ/mol, respectively.
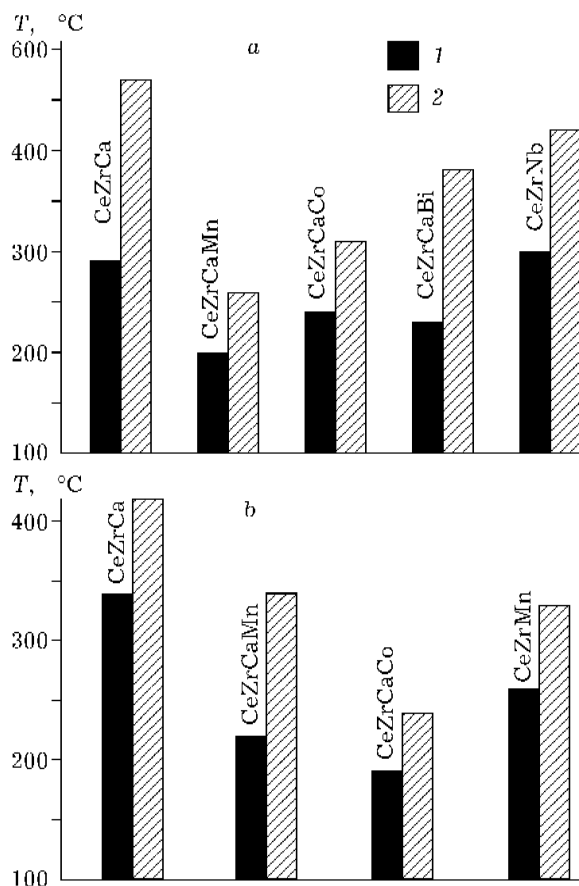
Fig. 5. Temperature of initiation (*1*) and developed oxidation of soot (*2*) for modified fluorites (*a*) and with platinum deposited (*b*) in a mixture containing $NO_2 + O_2$.

oxidation initiation (200–250 °C) is observed for fluorites containing easily reducible cations with variable valence Mn, Co and Bi, which is evidenced by the fact that at a temperature below 500 °C substantial hydrogen absorption occurs (see Table 3). For CeZrCa and CeZrNb samples, $T_{in} \approx 300$ °C, and hydrogen absorption is much lower at a temperature below 500 °C (see Table 3). Such a trend is conserved for developed soot oxidation in the presence of modified fluorites (see Fig. 5). Platinum deposition causes no substantial effect on the activity of fluorites. Similar trends for the initial and developed oxidation of soot are conserved also for supported catalysts. However, fluorite systems are less active in soot oxidation than perovskite ones, with is confirmed by higher T_{in} and T_d (by 50–80 °C).

As we have already mentioned above, particulates include not only soot (carbon) but also polyaromatic compounds for which, as a rule, the process of complete oxidation into CO_2 and H_2O includes a number of stages involving destruction followed by the oxidation of destructive fragments. Because of this, the concentration of CO_2 cannot be considered as an index of oxidation extent. The data on oxidation degree (oxidation extent) of soot in the mixtures O_2 + helium and $O_2 + NO_2 +$ helium are shown in Table 5. The extent of oxidation of the samples under investigation was determined on the basis of the amount of gaseous oxygen consumed for the process within the temperature range 50–550 °C. For oxidation in the mixture O_2 + helium, the chemical nature of the catalyst has no substantial effect on the extent of oxidation of particulates. At the same time, for the mixture $O_2 + NO_2 +$ helium the highest activity in destruction and oxidation of the particulates is exhibited by LaMn and Pt-containing catalysts LaFeMn, LaBiMn, CeZrCaCo, CeZrMn and CeZrNb.

TABLE 5

Oxidation extent of soot in mixtures: O_2 + helium (X_1) and $O_2 + NO_2 +$ helium (X_2) determined on the basis of the amount of gaseous oxygen consumed for the process within temperature range 50–550 °C on substituted perovskites and modified fluorites, %

Sample	X_1	X_2
LaMn	81	95
Pt/LaMn	40	64
LaCeMn	35	59
Pt/LaCeMn	35	44
LaFeMn	39	46
Pt/LaFeMn	39	95
LaBiMn	35	44
Pt/LaBiMn	39	82
CeZrCa	36	43
Pt/CeZrCa	40	76
CeZrCaMn	26	37
Pt/CeZrCaMn	28	40
CeZrCaCo	34	42
Pt/CeZrCaCo	29	94
CeZrCaBi	37	39
CeZrMn	38	64
Pt/CeZrMn	29	100
CeZrNb	53	100

CONCLUSIONS

The maximal activity in the catalytic oxidation of soot by atmospheric oxygen is exhibited by the most easily reducible composites with high mobility of volume oxygen (LaBiMn perovskite, Mn-containing fluorites) on which the efficient oxidation occurs at a temperature about 270 °C. When NO_2 is added into the initial mixture, for the entire series of perovskites and fluorites, modified with Mn and Co, efficient soot oxidation is observed at 260−280 °C. The differences in the nature of these catalysts are exhibited only at the initial stage of oxidation which is participated only by the oxygen of the catalyst: for perovskites, soot oxidation becomes noticeable at 120−150 °C, while for fluorites it becomes visible at 150−190 °C. The higher activity of perovskites in comparison with fluorites in the initiation of soot oxidation is connected with the larger fraction of weakly bound oxygen in the former. At the same time, the higher activity of fluorites in the process of complete oxidation of particulates is due to the contribution from the lattice oxygen. Deposition of Pt on these composites has no substantial effect on the oxidation of soot. For the entire row of catalysts investigated, no general correlation was observed between the activity and reactivity of the surface and lattice oxygen, which is due to the complex and multistage character of the process of soot/ particulate oxidation.

So, fine complex oxides based on perovskite and fluorite structures (even without Pr added) can be used for low-temperature oxidation of CO and soot. The high thermal stability of these oxides is an important advantage when they are used as regeneration catalytic filters.

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