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Catalytic combustion of soot over alkali doped $SrTiO_3$

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Abstract

The effect of introduction of alkalies (Me = Li, K, Cs) into $SrTiO_3$ on the physico-chemical properties of resulted materials and their catalytic activity in soot combustion was studied. Two groups of $SrTiO_3$ based perovskites were prepared: substituted in A-position of the structure ($Sr_{1-x}Me_xTiO_3$, $x = 0.05–0.2$) and impregnated with the same amount of alkali metals. Prepared materials exhibit low specific surface area and perovskite structure, only these ones impregnated with the highest amount of Cs (K) show weak XRD signals of Me_2O. TPD-O_2 experiments show bimodal profiles of O_2 desorption curves with maximums corresponding to individual step of alkali nitrates thermal decomposition. It is supposed that second peak of O_2 desorption from impregnated $SrTiO_3$ can be related to reversible decomposition of $MeNO_3$. XPS shows that surface of $SrTiO_3$ substituted with K (Cs) is much richer in these elements than the surface of impregnated one. Prepared materials lower the temperature of soot ignition from 530 (inert) to 470 °C for $SrTiO_3$ and to 302–303 °C for $Sr_{0.8}K_{0.2}TiO_3$ and $Sr_{0.8}K_{0.2}TiO_3$, respectively. Substituted materials are more active in soot combustion than impregnated ones. A mechanism explaining effect of alkali metals nitrate addition to $SrTiO_3$ on its catalytic activity in soot combustion is proposed.

Keywords: Perovskites; Alkalies; Surface structure; Soot combustion

1. Introduction

Particulate emissions from diesel engines are one of the most important air pollutants in urban areas. After treatment, systems are required within modern diesel engine designing to meet future emission regulations. One of the proposed methods of lowering particulates emission is a filtration on a porous trap followed by burning out the carbon particulates. In the absence of catalyst, filter must attain temperature at least 600–650 °C in order to auto-ignite deposited soot and sustain the combustion. Temperature of exhaust gases is usually much more lower and external heating is needed. This step may be assisted by catalytic combustion. Generally, there are two systems of catalytic combustion of particulate matter. First one employs the catalytic additives to the fuel-mixture of carbon deposites and catalyst particles accumulated on the filters is followed by oxidation of well-dispersed catalyst/carbon phases. Even this solution brings good results, a periodic regeneration is necessary to remove an ash of spent catalyst deposited on the filter walls [1]. The second system demands a filter walls washcoated with catalytically active material. The main problem of this kind of technique is providing enough contact between catalyst dispersed on filter walls and carbon phases [1,2]

Among catalytic systems reported for soot oxidation, platinum based ones exhibit activity, however they are active for soluble organic fraction (SOF) combustion but are less efficient for oxidation of carbonaceous fraction. Moreover, noble metals are sensitive to sulfur poisoning and very expensive [3,4]. Several others systems lowering down the ignition temperature of diesel soot has been proposed: oxides and chlorides of transition metals [5,6], alkali based materials [7,8] or combination of mentioned compounds [9]. Many other attempts have been made to develop catalyst for diesel soot combustion on the basis of simple metal oxides [1,10] and mixed oxides [11,12].

An important group of catalyst studied in diesel soot combustion are perovskite-type mixed oxides possessing general formula ABO_3 [13–17]. The lantanoid A-position based perovskites are mainly studied in the processes of NO_x

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Table 1
Composition of prepared catalysts

Li-doped		K-doped		Cs-doped	
A-position substituted $SrTiO_3$	Wt.% of Li in $Me/SrTiO_3$	A-position substituted $SrTiO_3$	Wt.% of K in $Me/SrTiO_3$	A-position substituted $SrTiO_3$	Wt.% of Cs in $Me/SrTiO_3$
$Sr_{0.95}Li_{0.05}TiO_3$	0.19	$Sr_{0.95}K_{0.05}TiO_3$	1.05	$Sr_{0.95}Cs_{0.05}TiO_3$	3.58
$Sr_{0.9}Li_{0.1}TiO_3$	0.39	$Sr_{0.9}K_{0.1}TiO_3$	2.19	$Sr_{0.9}Cs_{0.1}TiO_3$	7.08
$Sr_{0.8}Li_{0.2}TiO_3$	0.83	$Sr_{0.8}K_{0.2}TiO_3$	4.50	$Sr_{0.8}Cs_{0.2}TiO_3$	13.82

and particulates removal. Commonly studied perovskites posses position B filled with Co, Mn, Cr or Cu. Perovskite-type structure tolerates partial substitution of cations in both A- and B-position with other elements. This kind of distortion results in increasing activity of perovskites via creating oxygen vacancies, bonding extra oxygen or shifting some elements to abnormal oxidation state. Fino et al. reported that activity in soot combustion decreases in the following order of La based perovskites $LaCrO_3 > LaFeO_3 > LaMnO_3$; the best catalyst prepared in their work was the $LaCrO_3$ one with lanthanum partially substituted by K [15]. La–K–Mn–O system was suggested by Teraoka et al. for simultaneous removal of soot and NO_x [18].

The surface mobility of atoms (a good contact between soot and catalyst) is a key factor in oxidation of soot with oxygen [10]. This is a reason that molten salt based catalysts with compounds that melt at temperatures near to that ones of the soot oxidation are often studied [19]. A high activity of alkaline compounds in the oxidation reactions is well known, K is good promoter for coal gasification catalysts [20,24]. Therefore, various materials promoted with alkaline compounds have been tested in soot oxidation [21–26].

In this work, $SrTiO_3$ perovskites modified with variable content alkalies (Li, K and Cs) were studied in soot oxidation. Alkalies were introduced by impregnation of the $SrTiO_3$ with an aqueous solution of the respective nitrates or by substitution of Sr in $SrTiO_3$ structure by the same amount of Me. The aim of the work was to determine the effect of $MeNO_3$ on the soot combustion. To our best knowledge, this is the first report dealing with catalytic performance of alkalies modified $SrTiO_3$ in catalytic combustion of diesel soot.

2. Experimental

2.1. Catalyst preparation

Two groups of $SrTiO_3$ based materials containing alkalies (Li, K and Cs) were prepared: substituted in A-position of $SrTiO_3$ structure and doped with external alkalies. TiO_2 (POCh, p.a.), $Sr(NO_3)_2$, $CsNO_3$, KNO_3, $LiNO_3$ (Aldrich, p.a.) were used for catalysts preparation.

The $SrTiO_3$ was obtained by incipient wetness impregnation of TiO_2 with water solution of $Sr(NO_3)_2$. The impregnation followed by drying, grinding and intermediate calcination at 550 °C for 2 h and each step was repeated until Sr:Ti ratio was 1:1 and whole volume of impregnate solution ran out. Final calcination was carried out at 800 °C for 4 h. Alkali doped perovskites ($Sr_{1-x}Me_xTiO_3$; $x = 0.05, 0.1, 0.2$) were prepared by the impregnation of TiO_2 with water solution of Sr and Li, K or Cs nitrates in appropriate ratio. After each step of impregnation, samples were dried and calcined as in the case of pure $SrTiO_3$.

Impregnated counterparts of substituted $SrTiO_3$ were prepared by the impregnation of $SrTiO_3$ with water solution of appropriate nitrate followed by calcination at 550 °C for 2 h. The same (as in the $Sr_{1-x}Me_xTiO_3$ counterparts) amounts (wt%) of alkali elements were deposited. Composition of prepared materials is listed in Table 1.

For TG and some TPD-O_2 runs, alkali nitrates or nitrites supported over $SrTiO_3$ were prepared. The preparation route is the same as described above, without the calcination steps.

2.2. Characterization

XRD patterns were recorded with a DRON-3 diffractometer operating at 40 kV and 30 mA, using Cu Kα radiation. TG measurements were performed with using TGA 7 Series Perkin-Elmer apparatus under air atmosphere. TPD-MS measurements were performed in a flow apparatus using U-shaped quartz microreactor. A 100 mg of catalyst was pretreated at 823 K in oxygen flow for 1 h, then cooled to 303 K and changed in a He stream for 0.5 h. The catalyst was then ramped to 1203 K at a linear heating rate of 10 K/min in flow of He (30 ml/min). The analysis of concentration of O_2, CO_2, NO and NO_2 in the effluent gas was performed with a MS (OmniStar QMS 200, Pfeiffer Vacuum). XPS spectra were recorded with a SOECS PHOIBS-100 hemispherical analyzer operating at constant analyzer energy mode. The C 1s peak of the contamination carbon, at 284.6 eV, was taken as reference in calculating BE and accounting effects.

The specific surface area (S_{BET}) was determined by the BET method from N_2 adsorption data obtained at 77 K by standard volumetric method using an Autosorb-1 Quantochrome Instruments apparatus. Concentration of basic sites on investigated materials was determined by titration: weighted amount of catalysts (approximately 0.5 g) was preliminary treated with dry benzene 0.1 M solution of and benzoic acid. After 24 h treating a clear solution from above sediments was drawn and titrated with 0.05 M water solution of NaOH (bromothymol blue as Hammett indicator ($H_0 = 4.0$)) [27].

2.3. Catalytic activity in soot combustion

Catalytic activity of the prepared materials in the combustion of soot was determined using commercial amorphous

Table 2
Physico-chemical properties of studied materials

Sample	Substituted		Impregnated	
	S_{BET} (m^2/g)	Total basicity (mmol/g)	S_{BET} (m^2/g)	Total basicity (mmol/g)
$Sr_{0.95}$ $Li_{0.05}TiO_3$	2.8	0.010	2.5	–
$Sr_{0.9}$ $Li_{0.1}TiO_3$	3.6	0.028	2.4	–
$Sr_{0.8}$ $Li_{0.2}TiO_3$	3.3	0.035	1.8	0.070
$Sr_{0.95}$ $K_{0.05}TiO_3$	2.6	0.157	1.4	–
$Sr_{0.9}$ $K_{0.1}TiO_3$	2.5	0.215	1.2	–
$Sr_{0.8}$ $K_{0.2}TiO_3$	1.9	0.237	0.5	0.089
$Sr_{0.95}$ $Cs_{0.05}TiO_3$	2.4	0.078	1.1	–
$Sr_{0.9}$ $Cs_{0.1}TiO_3$	2.7	0.124	0.9	–
$Sr_{0.8}$ $Cs_{0.2}TiO_3$	1.9	0.176	0.9	0.101
$SrTiO_3$	S_{BET} = 3.6 m^2/g; total basicity = 0.022 mmol/g			

carbon particles (Printex-U from Degussa) as a model diesel soot. A 1 cm^3 of catalyst/soot mixture (5:1 weight ratio) prepared by addition of acetone and mixing both with spatula for 5 min. Then dry mass was crushed and fraction 0.20–0.35 mm was placed in tubular quartz reactor (d = 10 mm). Gas flow composition was adjusted at 10 vol.% of O_2, N_2 balance, GHSV: 20,000/h. Temperature of soot ignition was determined as the point of CO appearance in the outlet gas at concentration higher than 0.005 vol.% measured with Multor 610 gas analyzer.

3. Results and discussion

3.1. Overall characteristics of the catalysts

The phase composition of the prepared materials was determined by XRD (Fig. 1). In pure $SrTiO_3$, small amounts of TiO_2 (anatase) and Sr_2TiO_4 were observed. The patterns of the $SrTiO_3$, as well as Li substituted one, show sharp and intense peaks corresponding to crystalline phase of perovskites. There is no markedly difference between Li-substituted and external Li-doped $SrTiO_3$ spectra. This phenomenon confirms good solubility and possibility of migration of Li cations in $SrTiO_3$ lattice. Migration of Li atoms in the $SrTiO_3$ material as well as in other alkali earth titanates is recognized phenomenon [28]. In the case of K and especially Cs containing perovsiktes, peaks corresponding to Me_2O coexist in addition to the major perovskite phase. It can be concluded that as much as 0.2 mol of K (and especially Cs) cannot be completely substituted in A-position of $SrTiO_3$ crystal structure.

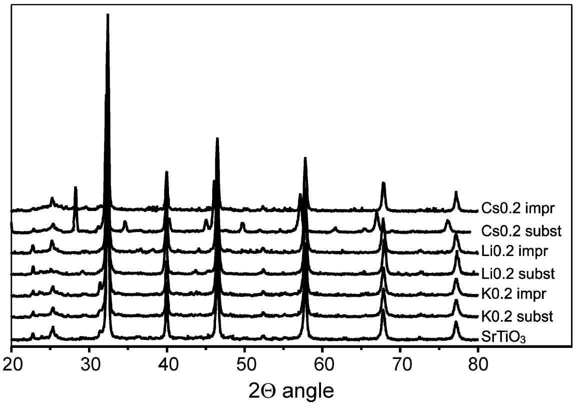


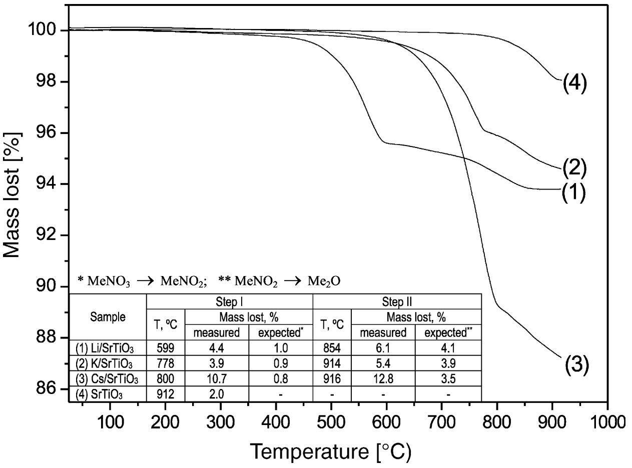
Fig. 1. XRD spectra of strontium titanates substituted (impregnated) with 0.2 mol of alkali metals.

All prepared materials exhibit low specific surface area—S_{BET} varies in the range 1–3.6 m^2/g (Table 2). Specific surface area of these materials lowers after substitution of Sr with alkalies. Deposition of alkalies on the surface of $SrTiO_3$ lowers specific surface area much more strongly than substitution of Sr with the same amount of alkalies despite of the fact, that substituted materials were calcined at higher temperature than the impregnated ones. Increase of alkalies content decreases the specific surface area of studied materials.

Total basicity of studied materials increases with the amount of introduced alkalies (Table 2) but the impregnated materials show lower basicity than substituted ones (except of lithium ones). Development of the basic properties of strontium titanate after substitution with alkali metals can be interpreted considering that the ABO_3 perovskite-like structure is created only if the A cation is sufficiently big. Oxide anions in such structure have only two coordinations with the small and strongly polarizing B cations and they are only weakly polarized by the big cation in A-position. On the surface, these oxide ions are coordinatively unsaturated, their coordination with B cations is lower than two. Substitution of Sr^{2+} with cation of alkali at +1 oxidation state additionally lowers unsaturation of oxide anions coordination and in this way the surface anions on perovskite surfaces become more nucleophilic.

The TEM images of $SrTiO_3$ and $Sr_{0.8}K_{0.2}TiO_3$ (not presented here), reveal that alkali doped material (several times treated at high temperature), is built from large, well-crystallized particles. TEM images of undoped $SrTiO_3$ show smaller particles with less regular shape.

Fig. 2 shows diagrams of TG measurements. It can be seen that alkali nitrates supported on $SrTiO_3$ decompose in two steps, which could be assigned to decomposition of: (1) $MeNO_3$ to $MeNO_2$ and (2) $MeNO_2$ to Me_2O. The temperatures of the each step of decomposition for particular salts are shifted to region of higher temperature in comparison to the data summarized in Table 4. The mass lost of Li/$SrTiO_3$ after first stage of decomposition (599 °C) corresponds to the total



* $MeNO_3 \rightarrow MeNO_2$; ** $MeNO_2 \rightarrow Me_2O$

Sample	Step I			Step II		
	T, ºC	Mass lost, %		T, ºC	Mass lost, %	
		measured	expected*		measured	expected**
(1) $Li/SrTiO_3$	599	4.4	1.0	854	6.1	4.1
(2) $K/SrTiO_3$	778	3.9	0.9	914	5.4	3.9
(3) $Cs/SrTiO_3$	800	10.7	0.8	916	12.8	3.5
(4) $SrTiO_3$	912	2.0	-	-	-	-

Fig. 2. TG spectra of $SrTiO_3$ and impregnated catalysts: (1) 0.83 wt.% $Li/SrTiO_3$, (2) 4.5 wt.% $K/SrTiO_3$, (3) 13.8 wt.% $Cs/SrTiO_3$ and (4) $SrTiO_3$.

decomposition of $LiNO_3$ (Fig. 2). It means that only above this temperature lithium can evaporate from the surface of strontium titanate. In the case of sample impregnated with KNO_3, the mass loss at 778 °C can be related with accuracy with total decomposition of this salt to K_2O. It can be concluded that below this temperature potassium nitrite is present at the surface of $SrTiO_3$. Only for material impregnated with $CsNO_3$, the mass lost is higher than this one calculated. Nevertheless, it should be noticed that this sample starts to loss the mass at temperature above 550 °C. The mass lost can be partially explained by decomposition of carbonate form of Cs (ca. at 600 °C), which is easy formed during the exposition to atmosphere.

3.2. TPD-MS experiments

TPD profiles of O_2, CO_2 and NO evolved from $Me/SrTiO_3$ materials with the highest content of alkali (calcined at 550 °C) as well as from $Sr_{0.8}Me_{0.2}TiO_3$ (calcined at 800 °C) are shown in Fig. 3. Data concerning amounts of released oxygen are gathered in Table 3.

For pure $SrTiO_{3\pm\delta}$ sample a single very small α-type O_2 desorption peak centered at ca. 477 °C (Fig. 3) is observed. Only under the highly reducing atmosphere, intrinsic oxygen vacancies may form in the original $SrTiO_3$ lattice (β-type desorption peak from bulk oxygen). Amount of evolved oxygen is about 2 μmol/g, which is characteristic to nearly stochiometric $SrTiO_3$ [29]. Materials impregnated with alkali metals nitrates ($MeNO_3/SrTiO_3$) and calcined at 550 °C evolve quite high amount of O_2 (Table 3) in comparison to both pure and substituted $SrTiO_3$. It should be noticed, that in the case of Cs- and especially K-doped $SrTiO_3$ two peaks (main peak at 620 °C with shoulders at about 700 °C) of oxygen desorption were registered, where the second one corresponds also to additional NO desorption with maximum desorption rate at 720 °C (Fig. 3). As NO desorption ends at about 750 °C, the CO_2 desorption begins originating from bulk cesium or potassium carbonates decomposition. For $Li/SrTiO_3$, the O_2 desorption temperature is shifted to lower temperature (515 °C), which is close to that of pure $SrTiO_3$ (477 °C) and NO desorption temperature is shifted to 525 °C.

In the case of substituted materials ($Sr_{0.8}Me_{0.2}TiO_3$) calcined at 800 °C considerable desorption of both O_2 and NO was observed only for K-doped $SrTiO_3$ (Table 3). These results could be explained by the formation of layers of

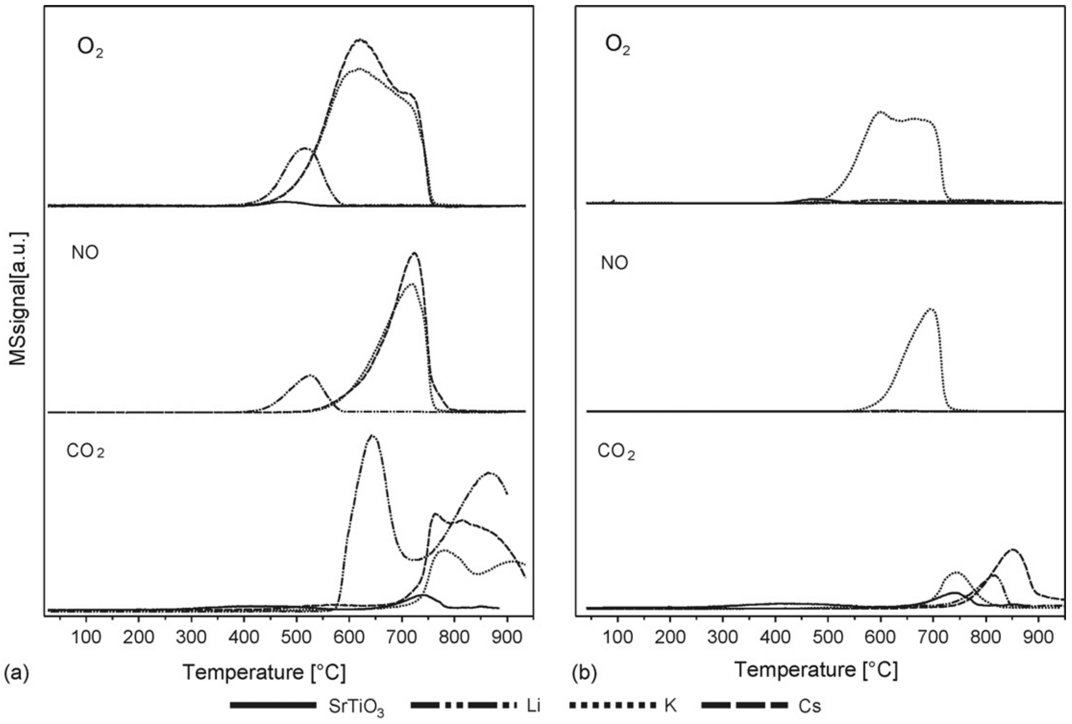


Fig. 3. TPD profiles of O_2, NO and CO_2 from studied materials: (a) $Me/SrTiO_3$ calcined at 550 °C and (b) $Sr_{0.8}Me_{0.2}TiO_3$ calcined at 800 °C.

Table 3
Amount of evolved O_2 from $SrTiO_3$[a]-doped with alkalies (μmol/g)

Temperature of final calcination (°C)	Li-doped (μmol/g)		K-doped (μmol/g)		Cs-doped (μmol/g)	
800	$Sr_{0.8}Li_{0.2}TiO_3$	1.7	$Sr_{0.8}K_{0.2}TiO_3$	87	$Sr_{0.8}Cs_{0.2}TiO_3$	6
550	0.83 wt.% Li/$SrTiO_3$	30	4.5 wt.% K/$SrTiO_3$	149	13.8 wt.% Cs/$SrTiO_3$	167

[a] $SrTiO_3$: O_2 desorption = 2 μmol/g.

thermally stable potassium nitrate compounds on the $SrTiO_3$ surface or it might indicate that even at such high temperature potassium salt does not decompose completely. However, the exact origin of these thermally stable phases is not known.

Table 4 shows values of the melting point (decomposition temperatures) of the pure nitrates used in this work and corresponding carbonates. Alkali metal nitrates melts easily at low temperatures (250–414 °C)—carbonates are more stable [30].

At low alkali metal nitrate loading, the metal cations are incorporated into surface vacant sites of the support, while their accompanying anions are positioned on the top for extra charge compensation or penetrate into the surface layer (or the bulk phase) with the increase of loading. In dependence on the support's dispersion capacity, well-dispersed surface nitrate or nitrite species strongly interacting with the support and then the bulk-like phases were observed [31]. It is known that bulk $MeNO_3$ is an active oxidizing agent, releasing additional oxygen during fluxing reactions [32]. The decomposition of $MeNO_3$ to $MeNO_2$ and then to metal oxides was coursed with the following reactions:

$$2MeNO_3 \rightleftarrows 2MeNO_2 + O_2 \qquad (1)$$

$$4MeNO_2 \rightarrow 2Me_2O + 4NO + O_2 \qquad (2)$$

Second O_2 desorption peak of K-substituted $SrTiO_3$ does not indicate as high oxygen release as for K-impregnated one. Cs-substitution gives also in this case lower desorption of O_2 than impregnation does. TPD-O_2 profile of Li-substituted material is quite similar to this one of unmodified $SrTiO_3$—no oxygen and very small NO_x desorption is observed.

Table 4
Melting point and decomposition temperature of some alkali metals salts [30]

Alkali metal	Melting points, decomposition temperature (°C)	
	Nitrate	Carbonate
Lithium	254 (>600)	723 (1310)$_{b.p.}$
Potassium	334 (400)	891 (>891)
Cesium	414 (849)	610 (610)

On the basis of the relation between O_2/NO_x peaks, it can be supposed that second peak of O_2 desorption from Me-impregnated $SrTiO_3$ can be related to reversible reaction of alkaline metal nitrates decomposition (Eqs. (1) and (2)). This explanation of the results of TPD-O_2 measurements was confirmed by additional experiments: TPD-O_2 profile of the material impregnated with KNO_2 consist only single oxygen peak, due to nitrite decomposition to NO and O_2 molecule (Fig. 4). Comparison of corresponding temperatures of both mass loss in TG experiments (Fig. 2) and oxygen desorption in TPD-O_2 measurements (Fig. 3) shows convergence of temperature of KNO_3 to KNO_2 decomposition determined by both methods.

3.3. XPS

Results of XPS measurements enable one to estimate surface composition of potassium- and cesium-doped $SrTiO_3$. Due to low sensitivity of lithium XPS signal, materials containing this element were not analyzed. Table 5 summarizes results of this determination, data expected for stochiometric compounds are also presented.

The surface layers of studied materials exhibit different atomic concentrations with respect to the bulk. Small excess of Sr in comparison to Ti was found for undoped $SrTiO_3$. In the case of substituted $SrTiO_3$, the Sr:Ti ratio is quite close to this one expected for Cs substituted $SrTiO_3$; this material shows a little bit higher excess of Sr in relation to Ti. All alkali containing materials present high excess of alkali in relation to Sr and Ti. Impregnated materials show higher excess of Sr in relation to Ti than substituted counterparts. For K-impregnated $SrTiO_3$, the ratios K:Sr and K:Ti are lower than for substituted one (nevertheless higher than those expected). In the case of Cs-impregnated materials, values of Cs:Sr and Cs:Ti are close to

Table 5
Composition of the surface of studied materials—results of the XPS analysis and theoretical values

	Sr:Ti		Me:Sr		Me:Ti	
	Nominal	Experimental	Nominal	Experimental	Nominal	Experimental
$SrTiO_3$	1	1.15	–	–	–	–
4.5 wt.% K/$SrTiO_3$	1	1.19	0.2	0.41	0.2	0.50
$Sr_{0.8}K_{0.2}TiO_3$	0.8	0.86	0.25	0.77	0.2	0.66
13.8 wt.% Cs/$SrTiO_3$	1	1.4	0.2	0.15	0.2	0.21
$Sr_{0.8}Cs_{0.2}TiO_3$	0.8	0.82	0.25	1.09	0.2	0.89

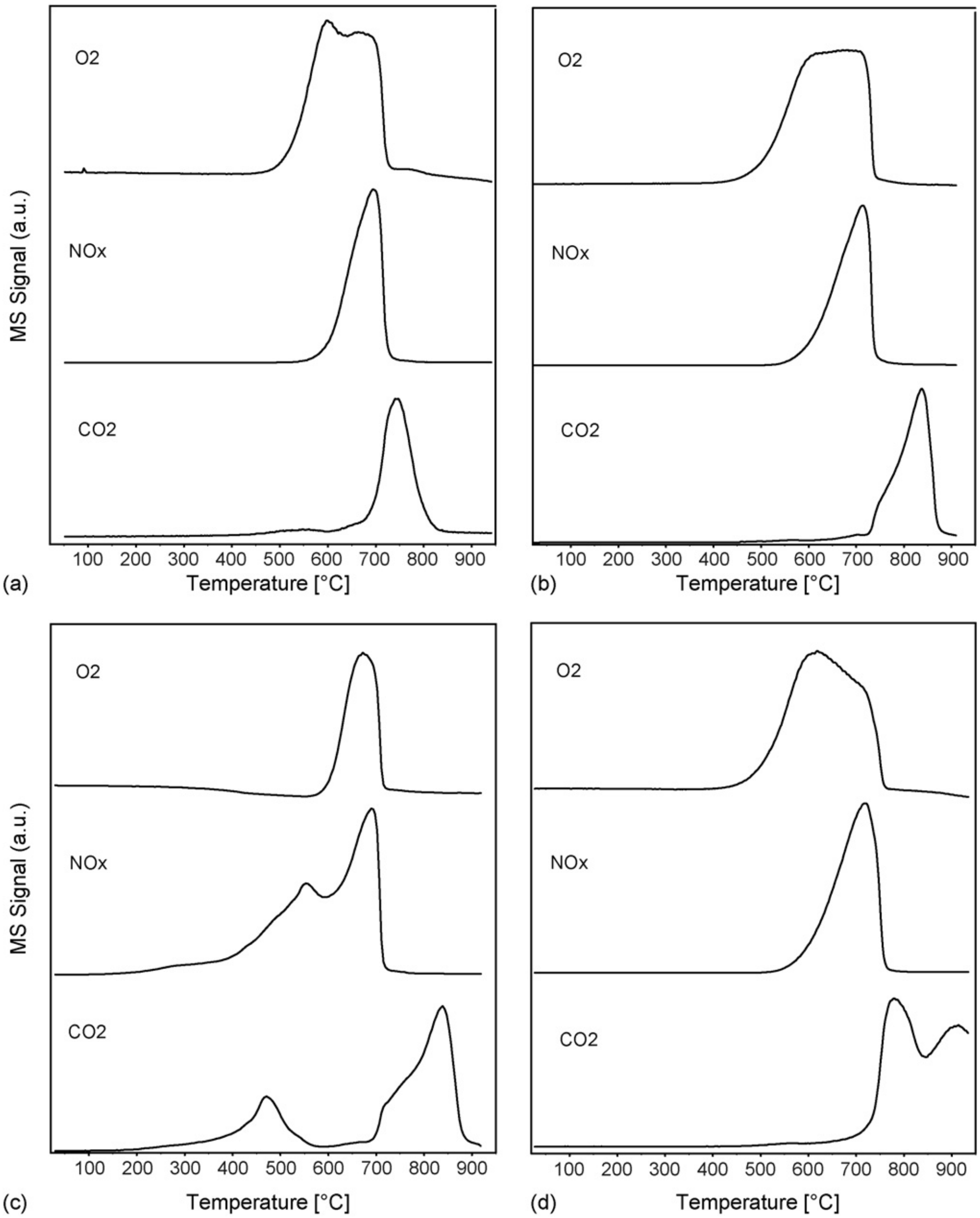


Fig. 4. TPD profiles of O_2, NO and CO_2 of: (a) $Sr_{0.8}K_{0.2}TiO_3$, (b) 4.5 wt.% K/$SrTiO_3$, (c) $KNO_2/SrTiO_3$ and (d) $KNO_2/SrTiO_3$ after treatment in oxidative atmosphere at 600 °C.

expected ones. These results suggest that the amount of K (Cs) on the surface of impregnated $SrTiO_3$ is lower than on the surface of corresponding substituted material. Surface of K (Cs) substituted $SrTiO_3$ is much richer in these elements than surface of impregnated materials. It seems that insertion of alkali in perovskite lattice stabilizes alkali on outer layer of surface. Addition of alkali to $SrTiO_3$ leads to lowering the amount of Ti on the surface (Ti is pushed into perovskite bulk) and in this way the surface is enriched in Sr.

Table 6 lists the corresponding values of binding energies of Sr $3d_{5/2}$, Cs $3d_{5/2}$, K $3p_{3/2}$ and Ti $2p_{3/2}$. The BE of Sr $3d_{5/2}$ and Ti $2p_{3/2}$ for the undoped $SrTiO_3$ are 132.47 eV and 458.04 eV, respectively, what is close to those ones in $SrTiO_3$ and TiO_2. Addition of alkali to $SrTiO_3$ results in decreasing of BE of Sr $3d_{5/2}$ and Ti $2p_{3/2}$ of corresponding materials. Differences in BE of Sr $3d_{5/2}$ and Ti $2p_{3/2}$ between $SrTiO_3$ and alkali doped samples are lower in the case of impregnated material than for substituted one. BE of TiO is reported to be equal 455 and ~457 eV for Ti_2O_3. These data suggest that titanium cations in

Table 6
Deconvoluted data of binding energies of studied materials (eV)

	BE (eV)			
	Sr $3d_{5/2}$	Cs $3d_{5/2}$	K $3p_{3/2}$	Ti $2p_{3/2}$
$SrTiO_3$	132.47			458.04
4.5 wt.% K/$SrTiO_3$	132.04		292.38	457.59
$Sr_{0.8}K_{0.2}TiO_3$	131.71		292.13	457.33
13.8 wt.% Cs/$SrTiO_3$	132.26	724.17		457.7
$Sr_{0.8}Cs_{0.2}TiO_3$	131.63	723.55		457.19

Table 7
Temperature of soot ignition over prepared materials (°C)

Catalyst	Substituted	Impregnated	Catalyst	Substituted	Impregnated	Catalyst	Substituted	Impregnated
$Sr_{0.95}Li_{0.05}TiO_3$	468	430	$Sr_{0.95}K_{0.05}TiO_3$	344	340	$Sr_{0.95}Cs_{0.05}TiO_3$	308	346
$Sr_{0.9}Li_{0.1}TiO_3$	467	426	$Sr_{0.9}K_{0.1}TiO_3$	328	330	$Sr_{0.9}Cs_{0.1}TiO_3$	306	344
$Sr_{0.8}Li_{0.2}TiO_3$	462	–	$Sr_{0.8}K_{0.2}TiO_3$	302	326	$Sr_{0.8}Cs_{0.2}TiO_3$	303	325
$SrTiO_3$	470		$Sr_{0.8}K_{0.2}TiO_3$[a]	–	385	Corundum	530	

[a] Prepared by impregnation $SrTiO_3$ with KCl.

the alkalies modified $SrTiO_3$ are present in the lower oxidation state than in the pure $SrTiO_3$. Oxidic vacancies can be created. Peaks of Ti $2p_{3/2}$ are narrow and symmetric, what could indicate that titanium phase is homogenous. In the case of Sr $3d_{5/2}$ differences in BE are not as large as these found for Ti $2p_{3/2}$.

Binding energy of Cs $3d_{5/2}$ for substituted sample is lower than for impregnated ones. This result suggests that chemical state of cesium is different for impregnated and substituted material. In the case of potassium containing $SrTiO_3$, difference of BE of K $3p_{3/2}$ between impregnated and substituted samples are rather low.

3.4. Soot combustion

The temperatures of soot ignition over studied materials are shown in Table 7. One can conclude that all studied perovskites exhibit catalytic activity in soot combustion. They lower the temperature of soot ignition from 530 °C (over corundum) to 470 °C in the case of $SrTiO_3$ and 302 and 303 °C for $Sr_{0.8}K_{0.2}TiO_3$ and $Sr_{0.8}K_{0.2}TiO_3$, respectively. Printex-U is often used in studies of soot combustion and various temperatures of this material ignition are reported. The temperature of soot ignition depends strongly on type of contact between soot and catalyst and on the way of soot–catalyst mixture preparation. Neeft et al. reported as high temperature as 621 °C as a point of Printex-U ignition (soot without any additives) [10] and in opposition Liu et al. reported that it is as low as 489 °C when this material is mixed with alumina [33]. An et al. used methanol for preparation of catalyst–Printex-U sample and found that it starts to combust in oxygen at ca. 450 °C [34]. We use acetone for preparation of mixture of soot–corrundum and it could be a reason of CO appearance in low temperature. Additionally, it should be taken into account that space velocity was not very high in the discussed experiments.

The K- (Cs-) added materials much more lower the ignition temperature than these ones containing Li. In general, the temperature of soot ignition decreases when alkalies content increases. Substitution leads to materials more active in lowering of soot ignition temperature than impregnation does. It seems that substitution decreases the activation energy, probably because of extra oxygen bonded to positive holes in the crystal lattice of perovskites. It can be supposed that Li atoms migration into the lattice decreases its access to the catalyst surface lowering in this way amount of active sites. During the test of K-doped materials abnormal presence of NO_x in the outlet gas stream was observed. It may be caused by decomposition of nitrates, which are stable over the $SrTiO_3$ surface. Presence of nitrate groups still adsorbed on the surface of alkali doped catalyst after calcinations at 800 °C reveal its strong basic nature. This phenomenon is in agreement with results of TPD experiments described above. It is also worth to notice, that $SrTiO_3$ impregnated with using KCl instead of KNO_3 shows distinctly higher temperature of soot ignition than this one containing nitrates. These results once more confirm an important effect of nitrates on soot combustion over studied materials. On the basis of the presented results, existence of the relationship between basicity of the studied materials and their catalytic activity in soot oxidation can be suggested. Substitution of $SrTiO_3$ with K (Cs) leads to enriching of its surface in alkali metal cations, which create basic sites. These sites can adsorb nitrogen oxides then produce active oxygen for soot combustion (Eqs. (1) and (2)). This supposition is now studied more detailed. Carrascull et al. have stated that addition of KNO_3 to ZrO_2 enhances its activity due to the increased contact between soot and catalyst and also because the KNO_3 act as catalyst: $2KNO_3 + C \rightarrow 2KNO_2 + CO_2$. Then nitrite is oxidized to nitrate by oxygen or the nitrogen oxide [8].

4. Conclusions

- $SrTiO_3$ doped with alkalies is active in soot combustion. Activity increases in the following order of alkali metals: $SrTiO_3 < Li/SrTiO_3 < Cs/SrTiO_3 < K/SrTiO_3$. Substitution produces catalysts with higher activity than impregnation does.
- Different routes of alkali introduction to $SrTiO_3$ in various way affect on the surface properties of resulted materials (the basicity, desorption of oxygen and surface structure).
- Relation between both surface composition and basicity of alkali modified $SrTiO_3$ and catalytic activity of these materials in soot combustion is suggested.

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