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# Nanostructured Perovskites for Catalytic Combustion

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## Abstract

Until recently, for reducing the environment pollution, the combustion catalysts based on noble metals was considered the most active, practically irreplaceable. Their high cost, high thermal instability, high sensitivity to deactivation and to the attack of some harmful elements or compounds determine the intensification of studies to replace them with new cheaper and stable catalysts. Numerous experimental data from literature indicate that the semiconductive oxidic compounds can compete with combustion catalysts based on noble metals from catalytic activity standpoint. Recent studies led to the realization of remarkable catalytic activity at moderate (350–600°C) and high (over 600°C) temperatures at some oxidic perovskite compounds, which contain transition metals. In this study are presented a series of nanostructured oxidic compounds with perovskite structure, based on transition metals and synthesized by the precursor method of self-combustion, using polyvinyl alcohol as colloidal medium, for catalytic combustion of some volatile organic compounds at low (50–350°C) and moderate temperatures. The catalytic activity of the perovskite compounds in the total oxidation reactions of the gases is largely determined by the amount of weakly bound surface oxygen species which in turn depends on the presence of oxygen vacancies.

**Keywords:** perovskites, nanostructures, oxidation, self-combustion, catalytic combustion

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## 1. Introduction

Until recently, for reducing the environment pollution, the combustion catalysts based on noble metals were considered the most active, practically irreplaceable. Their high cost, high thermal instability, high sensitivity to deactivation and to the attack of some harmful elements or compounds determine the intensification of studies to replace them with new cheaper and stabler catalysts.

Catalysis is a procedure through which the kinetic of a chemical reaction is positively or negatively influenced by the presence of another substance, called catalyst. The catalyst is a substance, which participates in reaction, but is found unchanged at the end of reaction. The catalyst does not appear in the equation of the chemical reaction, nor is it in an apparent stoichiometric ratio with the reacting substances.

Catalyst important property consists of that it can reduce the reaction activation energy. In this way, the reactions can be triggered and developed in such conditions of temperature, pressure or concentration at which the reaction could not occur without catalysis. The catalyst can only accelerate or trigger the thermodynamically possible reactions, namely spontaneous reactions running freely toward the equilibrium, therefore reactions with negative free enthalpy.

Catalysts can be metals, oxides, bases, salts, and so on, which once introduced in the reaction medium in small or very small amounts, take part in a certain stage of chemical reaction, but at the end of the reaction, they can be found in the initial quantity without suffering any chemical transformation.

Catalysis can be of two types:

- Homogeneous catalysis in which both the catalyst and the reacting substances are miscible and form a homogeneous system consisting of a single phase, gaseous or liquid, for instance an acid added in an aqueous solution of reagents. Catalyst intervention is exclusively chemical.
- Heterogeneous catalysis, in which the catalysts and the reagents form a heterogeneous system consisting of several phases. The catalyst is usually under solid state, while the reagents are in solid or gaseous state. Catalyst intervention is both chemical and physical.

Heterogeneous catalysis occurs in three successive stages:

- adsorption of reagents molecules on catalyst surface;
- reaction between adsorbed molecules, with the participation of catalyst active centers;
- desorption of reaction products, that is, the substances resulted from reaction pass into the environmental medium.

Adsorption can be of two kinds: adsorption through van der Waals forces, and activated adsorption (chemisorption). Adsorption through van der Waals forces occurs rapidly and at low temperatures, and the van der Waals heats are small. Activated adsorption (chemisorption) is slow and accompanied by a bigger heat elimination than in the previous case because bonds of chemical nature are also established, as the result of the interaction between reagents molecules and the atoms of the catalyst active centers.

Combustion (burning) of a gas in air is a homogeneous reaction at high temperature and occurs in certain conditions [1]. The air/gas ratio has a minimum value and a maximum value (defining the flammability interval) within which the combustion can occur, interval specific to each flammable gas. Flammability interval increases with the increase of temperature and decrease of activation energy.

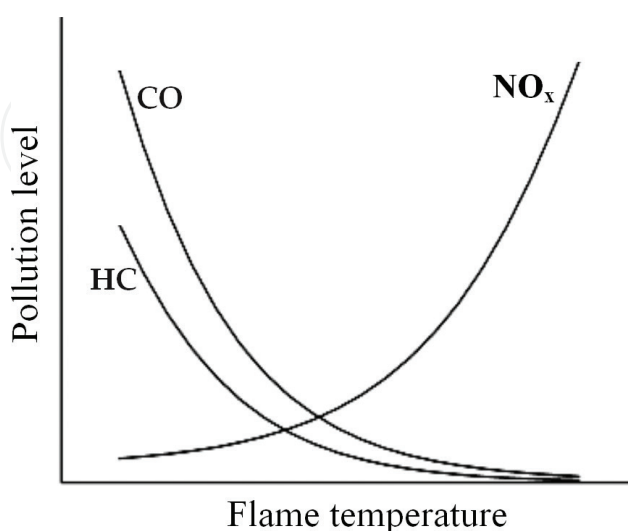
At a high enough temperature or at a small enough activation energy, combustion can occur for any air/gas ratio. Burning in the air the most usual combustibles, hydrocarbons, is accompanied by the release of polluting gases, especially carbon monoxide (CO), nitrogen oxides ( $\text{NO}_x$ ) and various unburnt hydrocarbons (HC). **Figure 1** shows the variation of polluting gas concentration (pollution level) with temperature during hydrocarbons burning in air. At higher burning temperatures, the concentration of nitrogen oxides increases. With the decrease of burning temperature, the amount of carbon monoxide and unburnt hydrocarbon increases. One can state that burning any combustible in air is unavoidably accompanied by polluting gases generation.

Catalytic combustion is the reaction of combustible gas oxidation in the presence of a catalyst. In almost all the cases, it is an heterogeneous reaction, the catalyst being a solid substance. Depending on catalyst, the reaction can occur at low, medium or high temperature, at very small concentrations of gas in air, and can be complete without generating polluting gases.

Unlike the noncatalytic combustion, at which the reaction thermally propagates throughout the available volume, in the case of catalytic combustion, the reaction only occurs at the catalyst surface. The model of the catalytic combustion describes a flux of reagents molecules toward the catalyst surface, and a reverse flux of reaction products molecules, as well as a heat flux. Catalytic combustion can be amplified by increasing the catalyst surface or the gas velocity at catalyst surface.

Usually, the catalyst consists of a substrate (metallic or ceramic) which provides the catalyst its form and mechanical strength, a ceramic support (alumina, zirconia, magnesia, silica, ceria, hexa-aluminates, etc.) with high specific surface area (aria/mass), and an active substance impregnated in support or deposited on it [2–4]. Sometimes, the active atoms are also introduced in the oxide composition support [5].

Catalytic combustion can occur at low (between 50 and 350°C), medium (between 350 and 600°C), or high (above 600°C) temperature.



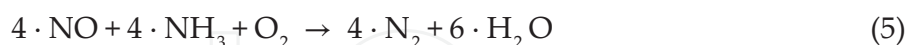
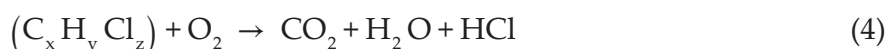
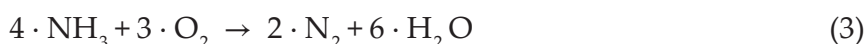
**Figure 1.** Variation of the pollution level with temperature during hydrocarbons burning in air.

Catalytic combustion at low and medium temperature is used to eliminate from air the polluting gases, volatile organic compounds (VOC), such as solvents vapors, mine gases, combustible gases released from industrial installations, and so on. Combustion occurs according to usual reactions, such as:



Generally, it is used when the concentration of combustible gases in air is very reduced and unable to keep the fire alive [6]. Still another possible utilization now studied is at combustible cells that can work at such temperatures. In this case, catalysts efficient at low and medium temperature which significantly reduces the activation energy of combustion reactions are used.

High-temperature catalytic combustion pursues complete burning and diminution of polluting gas emission. It is generally used in the installations which generate heat and energy. The concentration of combustible gases is high enough for a homogeneous combustion, but the purpose is a complete burning and diminution of polluting gases. The diminution of activation energy results in catalytic combustion of combustible polluting gases, while the decrease of the burning temperature decreases the concentration of nitrogen oxides. Through this type of catalysis, one can produce stable burning of combustible gases with small caloric power, different types of biogases, as well as of some gases considered as noncombustible, such as ammonia, chlorinated hydrocarbons or nitrogen monoxide, like in the reactions below:



The utilized catalysts in this case are from the category of those stable at high temperature, which yet are not the most active. For this reason, usually a number of catalysts are used in several stages of the combustion device temperature.

A special category of catalytic combustion is that used to reduce the pollutants from burnt gases evacuated by gas turbine and car motors (catalytic post combustion). The reactions occur in difficult conditions: moderate temperature, reduced oxygen amount, big number of polluting compounds in small concentration. A combination of catalysts is used, having both a reducing character to reduce the nitrogen oxides, and oxidizing character, for unburnt hydrocarbons oxidation [7]. There is also a mechanism of nitrogen oxides catalytic reduction by the combustible gases (unburnt hydrocarbons and carbon monoxide).

Until the recent years, aiming to reduce the environment pollutants, catalysts based on noble metals (platinum, gold, palladium, rhodium, iridium), as well as their alloys with other metals have been considered the most active, practically irreplaceable. Yet, their high cost, high temperature instability, high sensitivity to deactivation and to noxious elements or compounds, determined

an intensification of the studies meant to replace them with cheaper and more stable catalysts [2, 8, 9]. Due to the high cost of the noble metals, the utilization of these catalysts is restricted to industrial processes where the noble metals from used catalysts are recovered. The literature indicates that the oxide compounds can enter in competition with catalysts based on noble metals in terms of catalytic activity. Remarkable catalytic properties have been discovered to a number of oxide compounds: oxides of some metals, ferrites, perovskites, and so on. Recent researches resulted in the realization of remarkable catalytic activities at medium and low temperatures at some oxide compounds with perovskite structure. The first practical results were reported more than two decades ago, but most of the researches were performed in the last years.

Simple perovskites have the general formula  $ABO_3$ , the same as the natural mineral "perovskite" ( $CaTiO_3$ ) with face centered cubic crystalline structure, but the perovskites can also have other crystalline structure [10]. The elementary cell of a simple perovskite with cubic structure consists of a single molecule. In the peaks of the cube there are the A type ions with big ionic radius, which can be, for instance,  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $La^{3+}$ ,  $Pr^{3+}$ ,  $Nd^{3+}$ ,  $Gd^{3+}$ ,  $Y^{3+}$ . In the cube center, there are B-type ions with smaller radius, for example  $Fe^{3+}$ ,  $Mn^{3+}$ ,  $Cr^{3+}$ ,  $Al^{3+}$ ,  $Ti^{4+}$ ,  $Mn^{4+}$ . The oxygen ions are located in the cube face centers. The sample surface properties (surface composition and specific area) are also important in the case of catalytic combustion that uses perovskites.

Porous nanocrystalline compounds have a quite large surface area. Nanocrystalline particles can have a normal crystalline core and a shell with altered crystalline structure, their composition being different from that of the core. Their properties can be controlled through substitutions at A and B positions or by modifying the oxygen quantity. Through a slight modification of the initial composition of perovskite material, following a heat treatment, the dopant ions are concentrated at particles surface and influence to a great extent the physical surface properties.

A catalyst good for catalytic combustion of gases or vapors must satisfy four major conditions:

- reduce the combustible gas concentration to minimum;
- activate at minimum values of gas concentration;
- manifest catalytic conversion at minimum temperature;
- have a maximum utilization duration until deactivation (poisoning).

Since the heterogeneous catalysis is a surface phenomenon, its efficiency is determined by both chemical composition and catalyst surface structure. Generally, nanostructured oxide compounds are used [2, 11–13] obtained by various procedures [11, 12, 14, 15]. The nanostructure is the one which provides a large specific surface area and a superior catalyst reactivity [15]. Generally, a nanoparticle possesses a single phase crystalline core and a shell with altered crystalline structure and with several secondary phases, having a composition different from that of the core. When the material composition is non-stoichiometric, the atoms in excess are concentrated into the phases which form the particle shell that takes effective part in catalysis. Particles shape, dimension and superficial structure are determined by their preparation procedure. If the oxide nanoparticles are obtained through special synthesis and growth procedures, they have special catalytic properties which depend on the preparation procedure and the used support [11, 16].



There are numerous procedures to produce nanoparticles of oxide compounds, some general and other specific to catalysts. A procedure specific for catalysts preparation is support impregnation. The support is realized under the form of a ceramic microporous material and is impregnated with salts solutions [4, 7]. By assembly calcination, oxide compounds with nanostructure are formed inside the pores. The catalytic reaction occurs inside the pores and is intensified by a forced gas circulation through the catalyst. Preparation procedures for nanoparticles with catalytic properties represent the object of numerous researches and invention patents. The composition of combustion oxide catalysts is very diversified. The substances are stable oxide compounds and contain various active metal ions. Utilization of nontoxic compounds, easy to prepare, with high thermal and chemical stability and a low cost is preferred.

## 2. Reports from the specialized literature on a series of perovskites used for catalysts realization

Systematic studies of a big number of oxide compounds have proved that the catalytic activity represents a common phenomenon for the oxide compounds, perovskites included [17–30]. Recent specialized literature reports on a series of perovskites used for catalysts realization.

One of the first studied oxide catalysts [17] was simple perovskite  $\text{CuCoO}_3$  on  $\gamma\text{-Al}_2\text{O}_3$  support. This has been analyzed in comparison with a classical catalyst with platinum, in propylene elimination from the gases released in polypropylene preparation installations. It was found that this catalyst can successfully replace the classical catalyst with platinum.

Milt et al. have prepared perovskites  $\text{LaCoO}_3$  and  $\text{LaFeO}_3$  by the explosion method obtaining methane catalytic conversion over  $650^\circ\text{C}$  [18].

Hammami et al. obtain simple lanthanum  $\text{LaMnO}_{3+y}$  prepared by citric acid gel process and heating at  $700^\circ\text{C}$  obtaining methane catalytic conversion over  $600^\circ\text{C}$  [19].

The complex perovskite with oxygen deficit  $\text{La}_{1-x}\text{A}_x\text{FeO}_{3-\delta'}$  (where  $\text{A} = \text{Ca}, \text{Sr}$ , and  $x = 0.1\text{--}0.2$ ) prepared through the method of complexing with citric acid was studied for catalytic combustion of ammonia at temperatures of  $700\text{--}1000^\circ\text{C}$ . A good catalyst selectivity to the reaction of nitrogen oxide formation was found [20].

Batis et al. obtain good catalytic properties in methane combustion over  $800^\circ\text{C}$  using manganite  $\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_{3.03}$  prepared by thermal decomposition of a liquid precursor of lanthanum and calcium nitrates and manganese acetate, followed by calcination [21]. Ponce et al. found that the stability of  $\text{Mn}^{4+}$  ions seems to be the crucial factor determining the catalytic activity of manganites in the oxidation of methane in the temperature range  $200\text{--}800^\circ\text{C}$  [22].

Alifanti et al. synthesized  $\text{LaCoO}_3$  perovskite on  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  ( $x = 0\text{--}0.3$ ), for which the support was prepared by complexation with citric acid and calcined at  $700^\circ\text{C}$  for 6 h. The support was successfully impregnated with excess aqueous solution of La and Co nitrates (La/Co ratio 1/1) and citric acid, and the surface area achieved was between  $23.6$  and  $22.7\text{ m}^2\text{ g}^{-1}$  for the 10 and 20 wt% supported catalysts, respectively, and  $11.3\text{ m}^2\text{ g}^{-1}$  for the unsupported perovskite. The same study reported that  $\text{LaCoO}_3/\text{Ce}_{0.9}\text{Zr}_{0.1}\text{O}_2$  (20 wt%) achieved the best performances completely oxidizing 1700 ppm of benzene and toluene (air flow  $100\text{ mL/min}$ ) at around  $450$  and  $350^\circ\text{C}$ , respectively. It

also found that the bulk perovskite achieved a total conversion of benzene at a similar temperature while a higher temperature of 450°C was needed to fully oxidize toluene [23, 24].

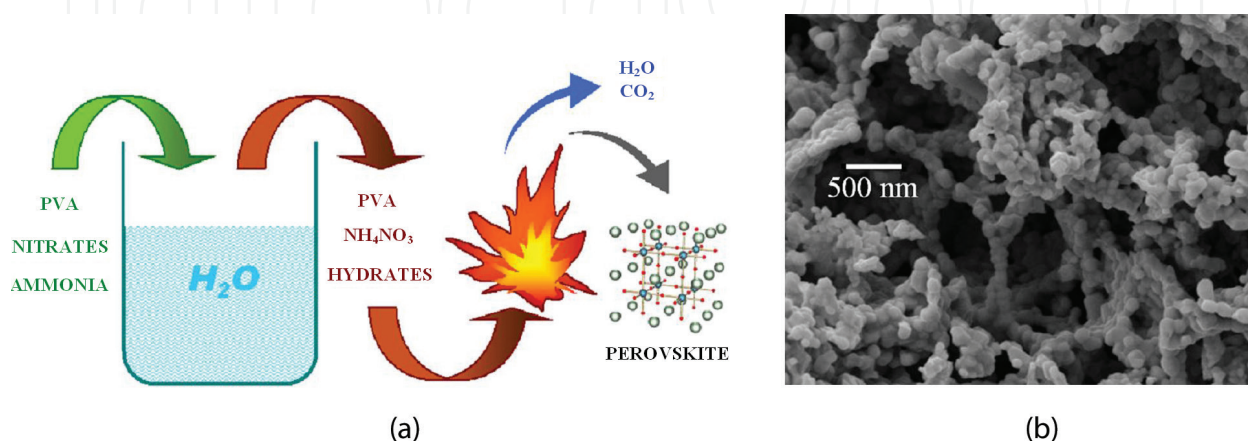
Zhang et al. realized a study on some perovskites type La–Sr–Co–O, being able to obtain in the case of the compound  $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$  the catalytic combustion of CO over 125°C [25].

Huang et al. prepared  $\text{La}_{0.8}\text{Cu}_{0.2}\text{MnO}_3$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  for the removal of toluene (6000 ppm GHSV 5000 h<sup>-1</sup>) in the presence of dodecyl mercaptan and both catalysts lost activity over time due to the formation of  $\text{CuSO}_4$  or  $\text{SrSO}_4$ . The activity decreased with the increase of  $\text{SO}_2$  concentration and dropped to around 30 and 20% of toluene conversion over 150 h operations with  $\text{SO}_2$  of 60 ppm for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  and  $\text{La}_{0.8}\text{Cu}_{0.2}\text{MnO}_3$ , respectively [23, 26].

### 3. Obtaining nanomaterials with perovskite structure by the precursor method of self-combustion

A recent method of nanoparticles preparation, including those with perovskite structure is the precursor method of self-combustion [31–38], which uses as colloidal precipitation medium the polyvinyl alcohol in various mass ratios with the metals. This method permits to obtain oxide compounds with homogeneous nanograined porous highly pure structure and reproducible properties. It is superior to other known conventional methods.

In essence, the precursor method of self-combustion consists of the co-precipitation with ammonia of the hydroxides from a mixture of nitrates solutions in a colloidal medium of polyvinyl alcohol. The dried precipitate contains an intimate and very homogeneous mixture of hydroxides, ammonium nitrate and polyvinyl alcohol. Microstructure of the precipitate and the final product can be modified by changing the ratio between the mass of polyvinyl alcohol and the mass of metal ions [32]. As in the case of a pyrotechnical mixture, the dry precipitate is enflamed at a point and suffers a rapid autonomous combustion which results, due to the very short reaction time, an oxide compound with nanometer structure, under the shape of powder (**Figure 2(a)**). A subsequent heat treatment will result in a controlled increase



**Figure 2.** Getting perovskites by the precursor method of self-combustion (a); SEM micrography for a perovskite obtained by this method (b).



of crystallites to the size necessary for applications, with single phase core and a possible poly-phase superficial layer.

In the SEM micrography of a sample of LPMO perovskite (**Figure 2(b)**), one can notice agglomerations of sub-micron grains of irregular shape, with inter-grains pores and large tubular pores (under 1  $\mu\text{m}$ ), favorable to gas access into the samples. This open-pores system appeared during the self-combustion reaction, through which a large amount of gases was eliminated. This porous structure appears at all the oxidic compounds prepared through this method.

## 4. Nanostructured perovskites for catalytic combustion of gases and of some volatile organic compounds

In this subsection are presented and characterized a series of perovskites ( $\text{SrMnO}_3$ ,  $\text{SrCoO}_3$ ,  $\text{MnFeO}_3$  and  $\text{GdAlO}_3$ ) obtained by the precursor method of self-combustion use for catalytic combustion of some volatile organic compounds (acetone, benzene, propane and Pb free gasoline).

### 4.1. Catalysts preparation and characterization

Nanograined perovskite powders of nominal compositions:  $\text{SrMnO}_3$  (P1),  $\text{SrCoO}_3$  (P2),  $\text{MnFeO}_3$  (P3) and  $\text{GdAlO}_3$  (P4) were prepared by the precursor method of self-combustion followed by heat treatment. It was used metal nitrates, ammonium hydroxide and polyvinyl alcohol (PVA) as starting materials. A solution containing metal nitrates was mixed with an aqueous solution (10% concentration) of polyvinyl alcohol. A small amount of  $\text{NH}_4\text{OH}$  solution (10% concentration) was dropped to adjust the pH value to about 8. This produced a sol of metal hydroxides and ammonium nitrate. By drying at  $100^\circ\text{C}$  for 12 h, the sol was turned into a dried gel. The dried gel was ignited in a corner and a combustion reaction spontaneously propagated through the whole gel. The obtained powders were calcinated at  $500^\circ\text{C}$  to eliminate the residual organic compounds. Finally, the calcined powders were annealed in air at  $1000^\circ\text{C}$ , 7 h.

The structure and surface properties of the heat-treated samples were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and Brunauer-Emmett-Teller (BET) analysis.

The catalytic testing of the perovskite catalysts in the flameless combustion of some selected gases was carried out at atmospheric pressure in a flow-type set-up (flow rate of  $100\text{ cm}^3/\text{min}$  and VOC concentration in air of 1–2%). The catalyst powder (0.3–0.5 g) was sandwiched between two layers of quartz wool in a quartz tubular microreactor (diameter of 7 mm) placed in an electrical furnace. The increase of the temperature was made in steps of  $50^\circ\text{C}$ , from 50 to  $550^\circ\text{C}$ . At every predetermined temperature, as a result of catalytic combustion, the gas concentration at the exit of reactor will be smaller than the inlet gas concentration. The catalytic activity of the perovskite catalysts under study was evaluated in terms of the conversion degree of gases over catalysts calculated as [28, 29, 39]:

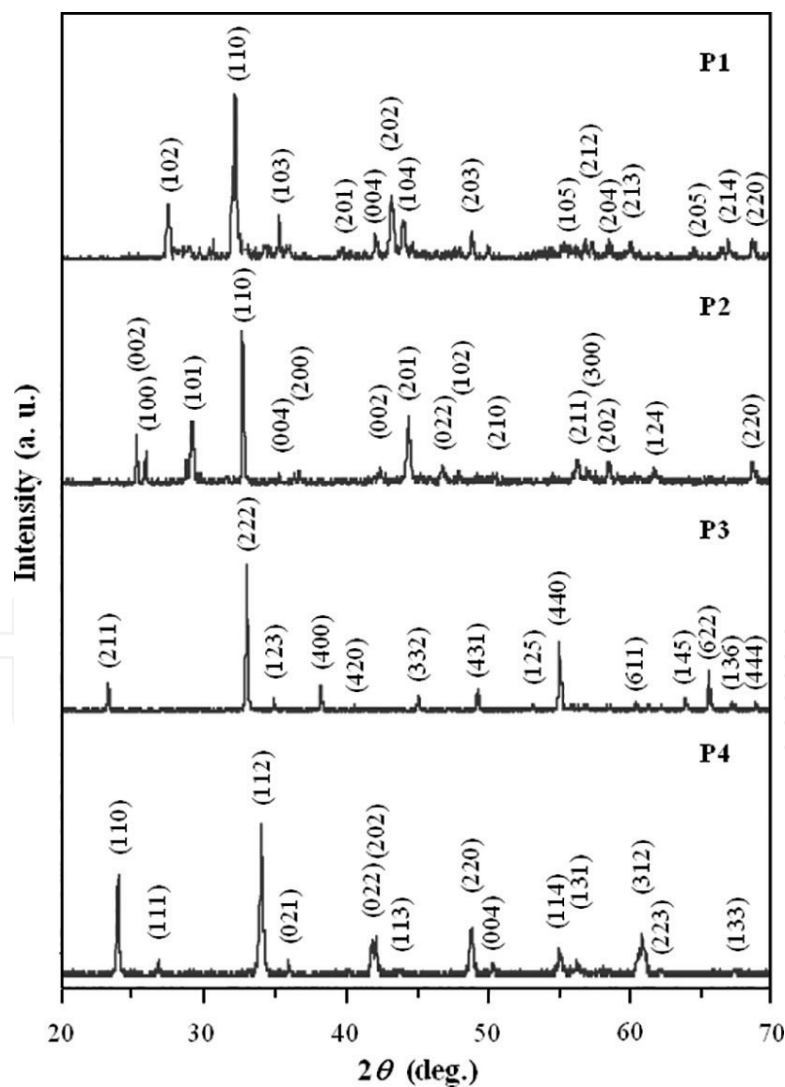
$$C = \frac{c_{in} - c_{out}}{c_{in}} \times 100(\%), \quad (6)$$

where  $c_{in}$  and  $c_{out}$  are the inlet and outlet gas concentration, respectively, measured by a photo-ionization detector (PID-TECH) for gases and VOCs. Data were collected when the flameless catalytic combustion had reached a steady state, after about 20 min at each temperature. These experiments were repeated decreasing the temperature and similar results were obtained, indicating the stability of perovskites over time, and the absence of the deactivation [39–41].

## 4.2. Results and discussion

### 4.2.1. Structural properties

The XRD patterns at room temperature of the analyzed perovskites are shown in **Figure 3**. From the analysis of these diffractograms ensue that samples have a good crystallinity in the specified thermal treatment conditions. All samples were indexed as perovskite structures, without the presence of any foreign phase.



**Figure 3.** X-ray diffraction patterns of the investigated perovskites.

The structure of crystalline phases, average crystallite size  $D_{\text{XRD}}$  derived from XRD data, specific surface area  $S_{\text{BET}}$  and pore volume obtained from nitrogen adsorption/desorption isotherms at 77 K, are given in **Table 1**.

The average crystallite size derived from XRD data was found to be in the range of 40–89 nm. The smallest crystallites were identified in the  $\text{GdAlO}_3$  perovskite.

The surface morphology of the studied perovskites is shown in SEM micrographies given in **Figure 4(a–d)**. Generally, the samples are characterized by a very fine structure being composed of aggregates of nanograins with irregular shapes and sizes, with a pronounced intergranular porosity and channels that are favoring the adsorption or desorption of the gas around particle agglomerates.

The chemical elemental composition of the powders heat treated was confirmed by the energy dispersive X-ray spectra (EDX). The obtained chemical elemental composition is typical for this perovskite (any foreign element is absent). **Figure 4(e–h)** presents the EDX spectrum for this perovskites. Moreover, the composition of the sample is similar to the nominal one,  $\text{ABO}_3$ , that is, the  $A/(A + B)$  or  $B/(A + B)$  ratio is close to 0.5 (where A and B are given in at.%).

#### 4.2.2. Catalytic activity of perovskites

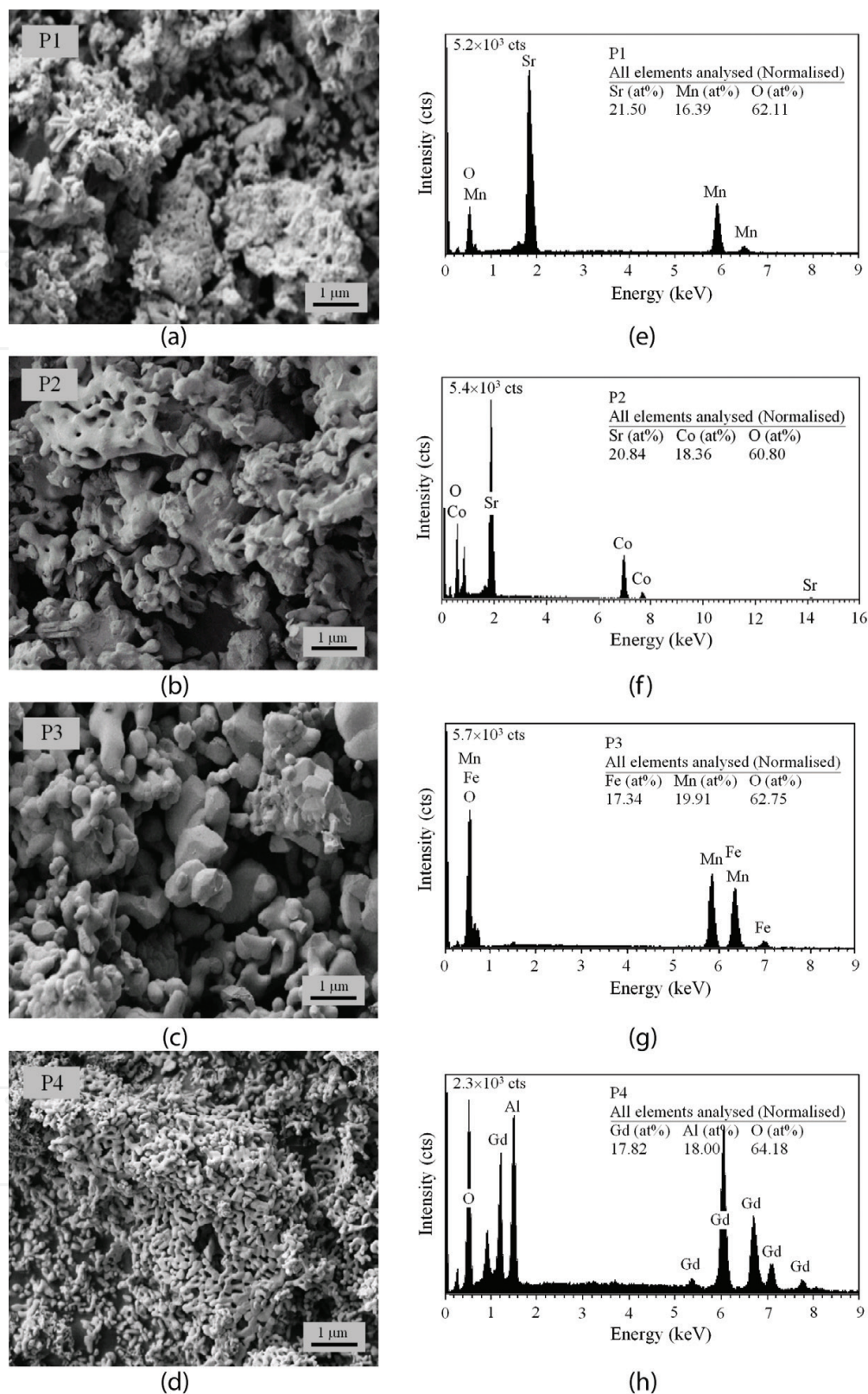
The catalytic performances of the studied perovskites in the flameless combustion of some VOCs (acetone, propane, benzene and Pb free gasoline) were investigated in the temperature range 50–550°C. The results are presented in **Figure 5(a–d)**, where the gas conversion was plotted as a function of the reaction temperature for each perovskite composition.

The catalysts exhibited substantial differences in catalytic activity, in the studied temperature range. Increasing the reaction temperature facilitates gas combustion. The gas combustion over  $\text{SrMnO}_3$  catalyst started at much lower temperatures (at about 100°C) compared to the other perovskites. The greater activity of  $\text{SrMnO}_3$  catalyst toward the conversion of VOCs indicates the availability of reactive oxygen species on the catalyst surface. This suggests oxygen may be less anchored on the perovskite surface and be more available for VOCs oxidation, probably because of the presence of a noteworthy amount of  $\text{Mn}^{4+}$  ions [39, 41].

The  $\text{MnFeO}_3$  and  $\text{SrCoO}_3$  catalysts exhibited high catalytic activity only toward acetone conversion and proved poor catalytic performance in catalytic combustion of propane, benzene and gasoline. This behavior may be related to some rearrangement of their lattice structure and, as a consequence, of the active site structure, on which the catalytic properties of these perovskites depend. It is interesting to point out the strong influence of temperature on the

Sample symbol	Crystalline phases	$D_{\text{XRD}}$ (nm)	$S_{\text{BET}}$ ( $\text{m}^2\cdot\text{g}^{-1}$ )	Pore volume ( $\text{cm}^3\cdot\text{g}^{-1}$ )
P1	Hexagonal	88.9	2.2	0.0010
P2	Hexagonal	59.9	1.9	0.0030
P3	Cubic	59.2	3.2	0.0044
P4	Orthorhombic	39.6	9.8	0.0018

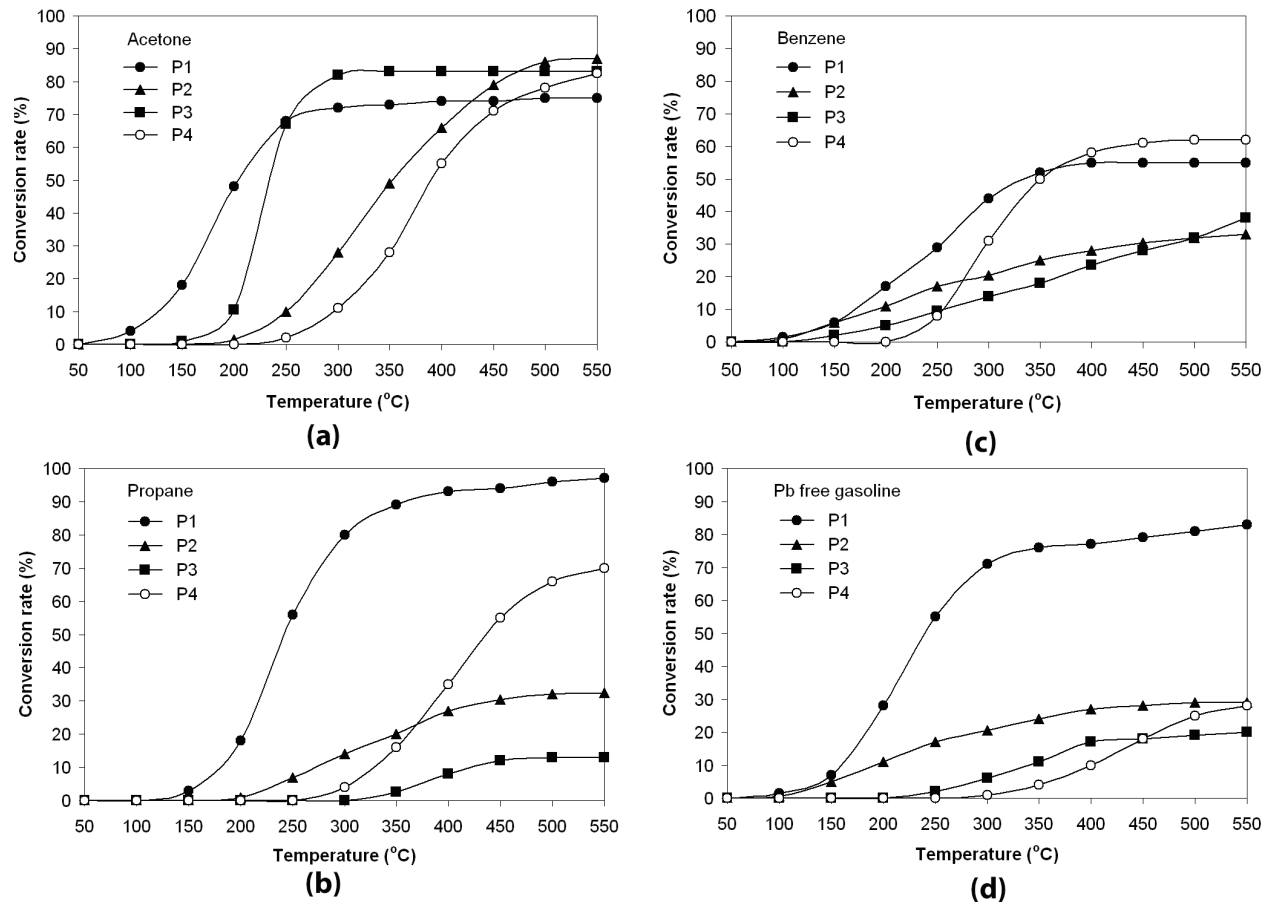
**Table 1.** Structure characteristics of investigated perovskites.



**Figure 4.** SEM micrographs (a–d) and EDX spectra (e–h) for the studied perovskites.

acetone conversion over the  $\text{MnFeO}_3$  catalyst. The acetone conversion started at a low temperature ( $150^\circ\text{C}$ ) and the conversion degree sharply increased from 10 to 80% as the temperature increased from 200 to  $300^\circ\text{C}$  (**Figure 5(a)**). This behavior was not observed with the





**Figure 5.** Conversion vs. temperature for catalytic flameless combustion of acetone (a), propane (b), benzene (c) and Pb free gasoline (d).

other perovskites. In contrast with the  $\text{MnFeO}_3$  catalyst, the  $\text{SrCoO}_3$  catalyst started the acetone conversion near  $200^\circ\text{C}$  and 80% acetone conversion was obtained at a higher temperature, of  $450^\circ\text{C}$  [41].

In **Table 2** are given the values of the gas conversion at  $500^\circ\text{C}$  and the values of the kinetic parameters (reaction rate and apparent activation energy) for gas oxidation over the studied perovskite catalysts. The apparent activation energies for the catalytic reactions were calculated by means of the Arrhenius type plot of the natural logarithm of the rate constant  $k$  at low conversion (below 10–15%) versus inverse temperature ( $1/T$ ). This plot is a straight line, and from its slope, the apparent activation energy was calculated. One can observe that the reaction rate normalized to specific area changes from  $3.8 \times 10^{-2}$  to  $140 \times 10^{-2} \mu\text{mol s}^{-1} \text{m}^{-2}$ . The higher the reaction rate is higher, the more active is the catalyst. Note also the wide variation in activation energies from 40 kJ/mol ( $\text{SrCoO}_3$  toward gasoline combustion) to 98 kJ/mol ( $\text{MnFeO}_3$  toward acetone combustion). The smallest values (31–37 kJ/mol) of the apparent activation energy were obtained for the  $\text{SrMnO}_3$  catalyst with the best catalytic activity.

The differences observed between the activation energies suggest that the nature of the catalytic sites differs from one perovskite to the others. The smaller values of the activation



VOC	Sample	Conv <sub>500</sub> (%)	Reaction rate ( $\mu\text{mol s}^{-1} \text{m}^{-2}$ )	Activation energy ( $\text{KJ mol}^{-1}$ )
Acetone	P1	75	$140 \times 10^{-2}$	37
	P2	85	$16 \times 10^{-2}$	41
	P3	85	$65 \times 10^{-2}$	98
	P4	78	$67 \times 10^{-2}$	89
Propane	P1	95	$9.8 \times 10^{-2}$	31
	P2	32	$3.8 \times 10^{-2}$	48
	P3	32	$6.1 \times 10^{-2}$	80
	P4	65	$7.8 \times 10^{-2}$	71
Benzene	P1	55	$26 \times 10^{-2}$	35
	P2	32	$56 \times 10^{-2}$	44
	P3	32	$17 \times 10^{-2}$	45
	P4	62	$6.5 \times 10^{-2}$	68
Pb free gasoline	P1	83	$55 \times 10^{-2}$	36
	P2	30	$11 \times 10^{-2}$	40
	P3	20	$12 \times 10^{-2}$	47
	P4	25	$4.2 \times 10^{-1}$	62

<sup>a</sup>Reaction rate for VOC concentration at low conversion per unit surface area of catalyst.

<sup>b</sup>Apparent activation energy for low conversions.

**Table 2.** VOCs conversion at 500°C and kinetic parameters (reaction rate<sup>a</sup> and activation energy<sup>b</sup>) for perovskite catalysts.

energy for the samples  $\text{SrCoO}_3$  and  $\text{SrMnO}_3$  can indicate a contribution of the mass transfer effects [41, 42]. The values of the kinetic parameters obtained by us are comparable to those presented by other authors for other perovskite type oxides and VOCs [18, 41, 43].

The  $\text{SrCoO}_3$  and  $\text{MnFeO}_3$  catalysts were able to convert 85% acetone at 500°C, whereas the conversion of the other gases was below 30%. The  $\text{SrMnO}_3$  catalyst was able to convert 95% propane, 83% Pb free gasoline, and 75% acetone at 500°C. The low specific area of the  $\text{SrMnO}_3$  perovskite does not seem to take part in the higher activity of this catalyst. The improved catalytic activity of  $\text{SrMnO}_3$  may be ascribed to the higher oxygen mobility due to the oxygen vacancies generated by the presence of manganese ion with variable valence. The difference in the catalytic activity of the studied perovskites cannot be explained by their different specific surfaces. There are many hypotheses about the mechanism of oxidation of VOCs on the oxide compounds. According to one accepted opinion, at low temperatures (below 400°C), the catalytic activity of the perovskite oxides in the total oxidation reactions of the gases is largely determined by the amount of weakly bound surface oxygen species which in turn depends on the presence of oxygen vacancies [41, 44]. The weaker the oxygen binding at the catalyst surface is, the more active the catalyst for complete oxidation of gases

is [45–47]. The surface oxygen species ( $O$ ,  $O_2^-$ ,  $O^{2-}$ ) involved in the catalytic combustion may come from the gaseous molecular oxygen and from the lattice oxygen [41, 48, 49]. The interaction of surface active oxygen species with reactants has an important role in mechanism of VOCs total oxidation (suprafacial mechanism) over perovskites oxide, and this is widely accepted to explain the gas oxidation over mixed oxide catalysts [39, 41, 44].

## 5. Conclusions

The oxide nanostructured materials, especially the perovskites, can have special catalytic combustion properties, and during the last years, there are several works and accomplishments in this connection. Such materials are especially interesting due to their high thermal stability, reduced cost, wide diversity, selectivity to various reactions, as well as to their availability in large amount for wide consumption products (exhaust muffler, filtering installations, addition in liquid combustibles, cigarettes filters, etc.), as well as for work and environment protection equipment.

A recent method of nanoparticles preparation, including those with perovskite structure is the precursor method of self-combustion, which uses as colloidal precipitation medium the polyvinyl alcohol. This method permits to obtain oxide compounds with homogeneous nanograined porous highly pure structure and reproducible properties. It is superior to other known conventional methods.

By the precursor method of self-combustion followed by heat treatment in air, several nanostructured perovskites with various compositions ( $SrMnO_3$ ,  $SrCoO_3$ ,  $MnFeO_3$  and  $GdAlO_3$ ) were prepared for catalyst applications. The catalytic tests of the perovskites in the flameless catalytic combustion of acetone, propane, benzene, and Pb free gasoline evidenced that the degree of the catalytic activity varied considerably with the composition of perovskite. The  $SrMnO_3$  catalyst is generally more active than the other catalysts. The  $SrMnO_3$  catalyst is able to convert 95% propane, 83% Pb free gasoline and 75% acetone at 500°C. The  $SrCoO_3$  and  $MnFeO_3$  catalysts are able to convert 85% acetone at 500°C whereas the conversion of the other gases was below 30%. It is worth noting the sharp increase of the acetone conversion over  $MnFeO_3$ , from 10 to 80% as the temperature increases from 200 to 300°C. The difference in the catalytic activity of the studied perovskites cannot be explained by their different specific surfaces. A possible explanation for the change in the catalytic properties as result of modification of perovskite composition may be either the different reactivity of the active oxygen species involved in the catalytic oxidation, or the variation in the number of active sites on the perovskite surface determined by the specific structural properties of each perovskite [41, 50].

## Conflict of interest

The author has declared no conflict of interest.

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## References

- [1] Mellado JD, Kindelan M, Sanchez AL. A simplified formulation for heterogeneous catalytic combustion in stagnation-point flows. *Combustion and Flame*. 2003;**132**:596-599. DOI: 10.1016/S0010-2180(02)00493-5
- [2] Masatake H. When gold is not noble: Catalysis by nanoparticles. *The Chemical Record*. 2003;**3**:75-87
- [3] Suzuki Y, Horii Y, Kasagi N. Microcatalytic combustor with tailored Pt/Al<sub>2</sub>O<sub>3</sub> films, In: *Proceedings of the 3rd International Workshop on Micro and Nanotechnology for Power Generation and Energy Conversion Applications (Power MEMS 2003)*; 4-5 December 2003; Makuhari; Japan. pp. 23-26
- [4] Mongkhonsi T, Umpo S, Thongsang P. Oxidation of anhydrides over MgO promoted cobalt and vanadium oxide catalysts. *Chemistry Letters*. 2002;**31**:978-979. DOI: 10.1246/cl.2002.978
- [5] Cimino S, Colonna S, De Rossi S, Faticanti M, Lisi L, Pettiti I, Porta P. Methane combustion and CO oxidation on zirconia-supported La, Mn oxides and LaMnO<sub>3</sub> perovskite. *Journal of Catalysis*. 2002;**205**:309-317. DOI: 10.1006/jcat.2001.3441
- [6] Suhadi DR, Awang M, Hassan MN, Abdullah R, Azizi H. Review of photochemical smog pollution in Jakarta Metropolitan, Indonesia. *American Journal of Environmental Sciences*. 2005;**1**:110-118
- [7] Zhang R, Alamdari H, Bassir M, Kaliaguine S. Optimization of mixed Ag catalysts for catalytic conversions of NO and C<sub>3</sub>H<sub>6</sub>. *International Journal of Chemical Reactor Engineering*. 2007;**5** Article A70
- [8] Andreeva D, Petrova P, Ilieva L, Sobczak JW, Abrashev MV. Design of new gold catalysts supported on mechanochemically activated ceria-alumina, promoted by molybdena for complete benzene oxidation. *Applied Catalysis B: Environmental*. 2008;**77**:364-372. DOI: 10.1016/j.apcatb.2007.08.009
- [9] Pecchi G, Reyes P, Figueroa A, Fierro JLG. Catalytic combustion on toluene on Pd-Cu/SiO<sub>2</sub> catalysts. *Boletín de la Sociedad Chilena de Química*. June 2000;**4**(2):1-7. DOI: 10.4067/S0366-16442000000200007

- [10] Moreira ML, Paris EC, do Nascimento GS, Longo VM, Sambrano JR, Mastelaro VR, Bernardi MIB, Andre's J, Varela JA, Longo E. Structural and optical properties of  $\text{CaTiO}_3$  perovskite-based materials obtained by microwave-assisted hydrothermal synthesis: An experimental and theoretical insight. *Acta Materialia*. 2009;**57**:5174-5185. DOI: 10.1016/j.actamat.2009.07.019
- [11] Costa ACFM, Diniz APA, Gama L, Morelli MR, Kiminami RHGA. Comparison of Ni-Zn ferrite powder preparation by combustion reaction using different synthesize routes. *Journal of Metastable and Nanocrystalline Materials*. 2004;**20-21**:582-587. DOI: 10.4028/www.scientific.net/JNM.20-21.582
- [12] Svensson EE, Nassos S, Boutonnet M, Jaras SG. Microemulsion synthesis of  $\text{MgO}$ -supported  $\text{LaMnO}_3$  for catalytic combustion of methane. *Catalysis Today*. 2006;**117**:484-490. DOI: 10.1016/j.cattod.2006.06.014
- [13] Zhang X, Liu Z, Wei Z, Du X, Gong M, Chen Y. Preparation of high performance methane combustion catalyst and its application to natural gas catalytic combustion fan-boiler. *Chinese Journal of Catalysis*. 2006;**27**:823-826. DOI: 10.1016/S1872-2067(06)60045-4
- [14] Xanthopoulou G. Catalytic properties of the SHS products—Review. *Advances in Science and Technology*. 2010;**63**:287-296. DOI: 10.4028/www.scientific.net/AST.63.287
- [15] Battiston AA, Bitter JH, Heijboer WM, de Groot FMF, Koningsberger DC. Reactivity of Fe-binuclear complexes in over-exchanged Fe/ZSM5 studied by in situ XAFS spectroscopy. *Journal of Catalysis*. 2003;**215**:279-293. DOI: 10.1016/S0021-9517(02)00188-4
- [16] Resini C, Catania F, Berardinelli S, Paladino O, Busca G. Catalytic wet oxidation of phenol over lanthanum strontium manganite. *Applied Catalysis B: Environmental*. 2008;**84**:678-683. DOI: 10.1016/j.apcatb.2008.06.005
- [17] Hirabayashi D, Yoshikawa T, Kawamoto Y, Mochizuki K, Suzuki K. Characterization and application of calcium ferrites based materials containing active oxygen species. *Advances in Science and Technology*. 2006;**45**:2169-2175
- [18] Milt VG, Spretz R, Ulla MA, Lombardo EA, Garcia Fierro JL. The nature of active sites for the oxidation of methane on La-based perovskites. *Catalysis Letters*. 1996;**42**:57-63. DOI: 10.1007/BF00814467
- [19] Hammami R, Aissa SB, Batis H. Effects of thermal treatment on physico-chemical and catalytic properties of lanthanum manganite  $\text{LaMnO}_{3+y}$ . *Applied Catalysis A: General*. 2009;**353**:145-153. DOI: 10.1016/j.apcata.2008.10.048
- [20] Perez-Ramírez J, Vigeland B. Lanthanum ferrite membranes in ammonia oxidation Opportunities for 'pocket-sized' nitric acid plants. *Catalysis Today*. 2005;**105**:436-442. DOI: 10.1016/j.cattod.2005.06.057
- [21] Batis NH, Delichere P, Batis H. Physicochemical and catalytic properties in methane combustion of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+y}$  ( $0 \leq x \leq 1$ ;  $-0.04 \leq y \leq 0.24$ ) perovskite-type oxide. *Applied Catalysis A: General*. 2005;**282**:173-180. DOI: 10.1016/j.apcata.2004.12.009

- [22] Ponce S, Pena MA, Fierro JLG. Surface properties and catalytic performance in methane combustion of Sr-substituted lanthanum manganites. *Applied Catalysis B*. 2000;**24**:193-205. DOI: 10.1016/S0926-3373(99)00111-3
- [23] Tomatis M, Xu HH, He J, Zhang XD. Recent development of catalysts for removal of volatile organic compounds in flue gas by combustion: A Review. *Journal of Chemistry*. 2016;Article ID 8324826::1-15. DOI: 10.1155/2016/8324826
- [24] Alifanti M, Florea M, Pârvulescu VI. Ceria-based oxides as supports for LaCoO<sub>3</sub> perovskite; catalysts for total oxidation of VOC. *Applied Catalysis B*. 2007;**70**:400-405. DOI: 10.1016/j.apcatb.2005.10.037
- [25] Zhang R, Luo N, Yang W, Liu N, Chen B. Low-temperature selective catalytic reduction of NO with NH<sub>3</sub> using perovskite-type oxides as the novel catalysts. *Journal of Molecular Catalysis A: Chemical*. 2013;**731**:86-93. DOI: 10.1016/j.molcata.2013.01.018
- [26] Huang HF, Sun Z, Lu HF, Shen LQ, Chen YF. Study on the poisoning tolerance and stability of perovskite catalysts for catalytic combustion of volatile organic compounds. *Reaction Kinetics Mechanisms and Catalysis*. 2010;**101**:417-427. DOI: 10.1007/s11144-010-0235-6
- [27] Doroftei C, Popa PD, Rezlescu E, Rezlescu N. Structural and catalytic characterization of nanostructured iron manganite. *Composites: Part B*. 2014;**67**:179-182. DOI: 10.1016/j.compositesb.2014.07.005
- [28] Doroftei C, Popa PD, Rezlescu E, Rezlescu N. Nanocrystalline SrMnO<sub>3</sub> powder as catalyst for hydrocarbon combustion. *Journal of Alloys and Compounds*. 2014;**584**:195-198. DOI: 10.1016/j.jallcom.2013.09.054
- [29] Leontie L, Doroftei C. Nanostructured spinel ferrites for catalytic combustion of gasoline vapors. *Catalysis Letters*. 2017;**147**:2542-2548. DOI: 10.1007/s10562-017-2164-8
- [30] Rezlescu N, Rezlescu E, Popa PD, Doroftei C, Ignat M. Nanostructured GdAlO<sub>3</sub> perovskite, a new possible catalyst for combustion of volatile organic compounds. *Journal of Materials Science*. 2013;**48**:4297-4304. DOI: 10.1007/s10853-013-7243-7
- [31] Popa PD, Doroftei C, Rezlescu E, Rezlescu N. Influence of colloidal environment on the properties of nanoferrites MgCuZn prepared by precursor method of self-combustion. *Journal of Optoelectronics and Advanced Materials*. 2010;**12**:876-880
- [32] Rezlescu E, Doroftei C, Popa PD, Rezlescu N. The transport and magnetic properties of La-Pb-Mg-Mn-O manganites at low temperatures. *Journal of Magnetism and Magnetic Materials*. 2008;**320**:796-802. DOI: 10.1016/j.jmmm.2007.08.019
- [33] Doroftei C, Leontie L, Popa A. The study on nanogranular system manganites La-Pb-Ca-Mn-O which exhibits a large magnetoresistance near room temperature. *Journal of Materials Science-Materials in Electronics*. 2017;**28**:12891-12899. DOI: 10.1007/s10854-017-7119-8
- [34] Rezlescu N, Doroftei C, Rezlescu E, Popa PD. The influence of Sn<sup>4+</sup> and/or Mo<sup>6+</sup> ions on the structure, electrical and gas sensing properties of Mg-ferrite. *Physica Status Solidi A*. 2006;**203**:306-316. DOI: 10.1002/pssa.200521043



- [35] Rezlescu N, Iftimie N, Rezlescu E, Doroftei C, Popa PD. Semiconducting gas sensor for acetone based on the fine grained nickel ferrite. *Sensors and Actuators B*. 2006;**114**:427-432. DOI: 10.1016/j.snb.2005.05.030
- [36] Doroftei C, Rezlescu E, Rezlescu N, Popa PD. Gas sensing properties of samarium substituted lithium ferrite. *Journal of Optoelectronics and Advanced Materials*. 2008;**10**:2390-2395
- [37] Doroftei C. Formaldehyde sensitive Zn-doped LPFO thin films obtained by rf sputtering. *Sensors and Actuators B-Chemical*. 2016;**231**:793-799. DOI: 10.1016/j.snb.2016.03.104
- [38] Doroftei C, Popa PD, Iacomi F. Selectivity between methanol and ethanol gas of La-Pb-Fe-O perovskite synthesized by novel method. *Sensors and Actuators A-Physical*. 2013;**190**:176-180. DOI: 10.1016/j.sna.2012.11.018
- [39] Doroftei C, Leontie L. Synthesis and characterization of some Nanostructured composite oxides for low temperature catalytic combustion of dilute propane. *RCS Advances*. 2017;**7**:27863-27871. DOI: 10.1039/c7ra03916f
- [40] Rezlescu N, Rezlescu E, Popa PD, Doroftei C, Ignat M. Some nanograined ferrites and perovskites for catalytic combustion of acetone at low temperature. *Ceramics International*. 2015;**41**:4430-4437. DOI: 10.1016/j.ceramint.2014.11.134
- [41] Rezlescu N, Rezlescu E, Popa PD, Doroftei C, Ignat M. Characterization and catalytic properties of some perovskites. *Composites: Part B*. 2014;**60**:515-522. DOI: 10.1016/j.compositesb.2014.01.006
- [42] Florea M, Alifanti M, Parvulescu VI, Mihaila-Tarabasanu D, Diamandescu L, Feder M, Negri C, Frunza L. Total oxidation of toluene on ferrite-type catalysts. *Catalysis Today*. 2009;**141**:361-366. DOI: 10.1016/j.cattod.2008.05.005
- [43] Song KS, Klvana D, Kirchnerova J. Kinetics of propane combustion over  $\text{La}_{0.66}\text{Sr}_{0.34}\text{Ni}_{0.3}\text{Co}_{0.7}\text{O}_3$  perovskite. *Applied Catalysis A*. 2001;**213**:113-121
- [44] Ivanov DV, Pinaeva LG, Sadovskaya EM, Isupova LA. Influence of the mobility of oxygen on the reactivity of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  perovskites in methane oxidation. *Kinetics and Catalysis*. 2011;**52**:401-408. DOI: 10.1134/S0023158411030086
- [45] Yakovleva IS, Isupova IA, Rogov VA, Sadykov VA. Forms of oxygen in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$  ( $x = 0-1$ ) perovskites and their reactivities in oxidation reactions. *Kinetics and Catalysis*. 2008;**49**:261-270. DOI: 10.1134/S0023158408020146
- [46] Isupova LA, Yakovleva IS, Alikina GM, Rogov VA, Sadykov VA. Reactivity of  $\text{La}_{(1-x)}\text{Sr}_{(x)}\text{FeO}_{(3-y)}$  ( $x=0-1$ ) perovskites in oxidation reactions. *Kinetics and Catalysis*. 2005;**46**:729-735. DOI: 10.1007/s10975-005-0129-1
- [47] Marchetti L, Forni L. Catalytic combustion of methane over perovskites. *Applied Catalysis B*. 1998;**15**:179-187. DOI: 10.1016/S0926-3373(97)00045-3

- [48] Li WB, Wang JX, Gong H. Catalytic combustion of VOCs on non-noble metal catalysts. *Catalysis Today*. 2009;**148**:81-87. DOI: 10.1016/j.cattod.2009.03.007
- [49] Kundakovic L, Flytzani-Stefanopoulos M. Cu- and Ag-modified cerium oxide catalysts for methane oxidation. *Journal of Catalysis*. 1998;**179**:203-221. DOI: 10.1006/jcat.1998.2213
- [50] Sugahara K, Kamata K, Muratsugu S, Hara M. Amino acid-aided synthesis of a hexagonal  $\text{SrMnO}_3$  nanoperovskite catalyst for aerobic oxidation. *ACS Omega*. 2017;**2**:1608-1616. DOI: 10.1021/acsomega.7b00146

