Catalytic activity of LaMnO$_3$ and LaCoO$_3$ perovskites towards VOCs combustion

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Abstract

The catalytic combustion of some volatile organic compounds (VOCs) has been investigated over LaMnO$_3$ and LaCoO$_3$ perovskite-type oxides. Redox titration has shown that cobalt is present in LaCoO$_3$ exclusively in the 3+ oxidation state whereas LaMnO$_3$ contains considerable amount of Mn^{4+} (35%) in addition to Mn^{3+}. VOCs reactivity towards total oxidation follows the trend: acetone > isopropanol > benzene. The oxidation of isopropanol occurs through the formation of acetone in the homogeneous reaction. The increase of the oxygen partial pressure is beneficial for total oxidation of acetone. The adsorptive properties of the catalysts towards the VOCs and H$_2$ have been examined by means of temperature programmed desorption. The LaMnO$_3$ surface is the most reactive to the adsorption of VOCs and H$_2$. The role of the adsorbed oxygen has been studied by examining the variations of the electrical conductivity of the catalysts during the processes of oxygen adsorption–desorption.
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1. Introduction

Volatile organic compounds (VOCs) are considered an important group of air pollutants. They are commonly found in urban and industrial areas because of power generation, vehicle emissions and solvents employment. VOCs, as for example aromatic and aliphatic hydrocarbons, alcohols, ketones, aldehydes [1,2], are easy oxidisable compounds and therefore their catalytic combustion represents an effective tool for air pollution control.

Several researchers have investigated the VOCs reactivity mainly on noble metal supported catalysts [3,4], showing a correlation between their oxidation rate and the bond dissociation energy of the weakest C–H bond [5,6]. Transition metal perovskites as LaMO$_3$ (M = Mn, Co) are known to be very good oxidation catalysts [7,8] and cheaper than noble metal supported catalysts. The redox properties of the M cation, the availability of weakly bonded oxygen at the surface and the presence of lattice defects have been often claimed as responsible of their catalytic activity [9,10].

This works concerns the catalytic combustion of acetone, benzene and isopropanol, which are

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representative of some important classes of VOCs which can derive from aerosols, cleaners, lacquers and adhesives, paints and gasolines. The investigation of the catalytic activity was complemented with the study of the catalyst adsorptive properties and of the electrical conductivity measurements during oxygen adsorption–desorption processes.

2. Experimental

Perovskite-type oxides of general formula $LaMO_3$ (M = Mn, Co) have been prepared from citrate precursors [11]. La, Mn (or Co) nitrates have been mixed together in suitable proportions to give a concentrated solution. Citric acid has been then added to the metal solution to have the same amounts of equivalents. The solution has been evaporated at 90 °C to produce a viscous syrup, and the final product, after grinding, was calcined at 800 °C for 5 h.

The oxidation state of the transition metals in the $LaMO_3$ catalysts has been determined dissolving the samples in a known excess of Mohr salt,

$Fe(NH_4)_2(SO_4)_2·6H_2O$, standard solution acidified with sulfuric acid and by back titrating the excess of Fe^{2+} with $KMnO_4$. Phase analysis and lattice parameters determination have been performed by X-ray powder diffraction using a Philips PW 1029 diffractometer with Ni-filtered Cu Kα radiation. BET surface areas of the materials have been measured by nitrogen adsorption at −196 °C in a vacuum glass apparatus.

Catalytic experiments have been carried out in a tubular continuous flow reactor 1 cm o.d., employing catalysts samples of 0.08–0.12 g, which were pre-treated at 450 °C in 4/1 He/O_2 mixture. After a pre-treatment in helium and oxygen (ratio 4/1) at 450 °C and a cooling down to the reaction temperature in the same stream, a flow of VOC in air has been allowed through the catalyst with a VOC/O_2 ratio equal to 1/100. Ratios equal to 1/50 or 1/200 were also employed in some cases. The flow of the gases has been controlled by means of MKS electronic mass flow controllers. The oxidation reaction has been investigated in the range of 150–260 °C for acetone and isopropanol and in the range of 240–350 °C for benzene. The products and reagents were analyzed
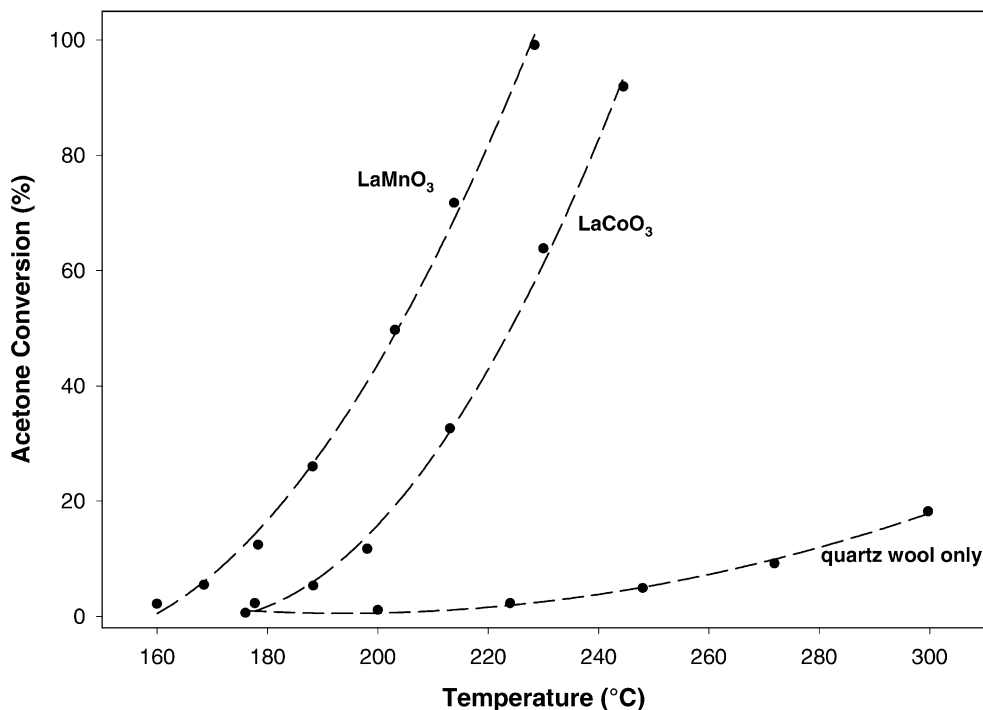

Fig. 1. Conversion of acetone to CO_2 vs. temperature (samples amount 0.1 g, ratio VOC/O_2 1/100, space velocity $14,100 h^{-1}$).
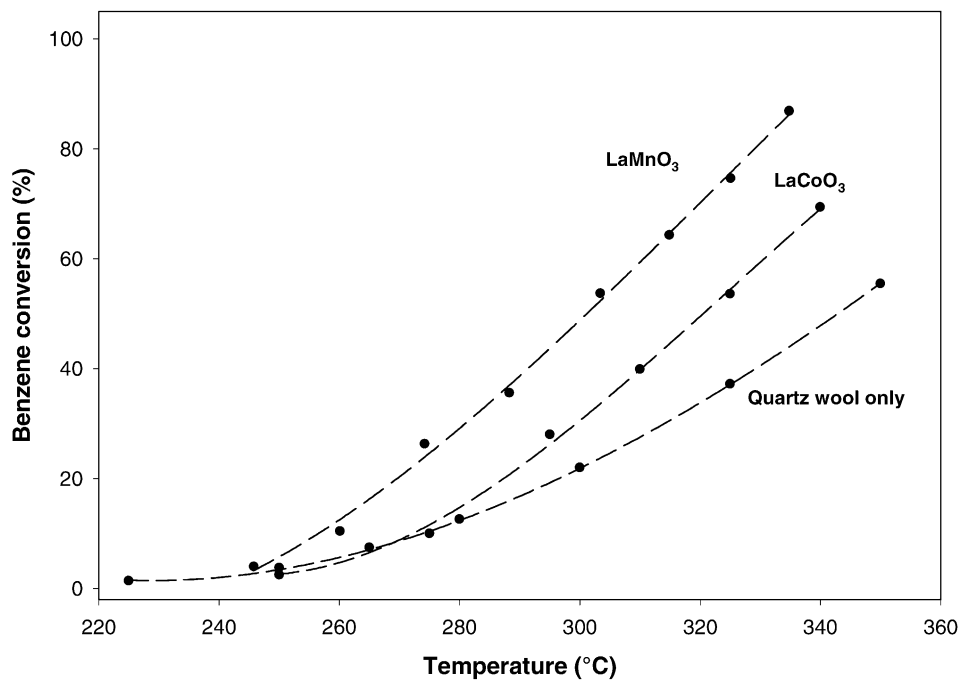
Fig. 2. Conversion of benzene to CO_2 vs. temperature (samples amount 0.1 g, ratio VOC/O_2 1/100, space velocity 14,100 h^{-1}).
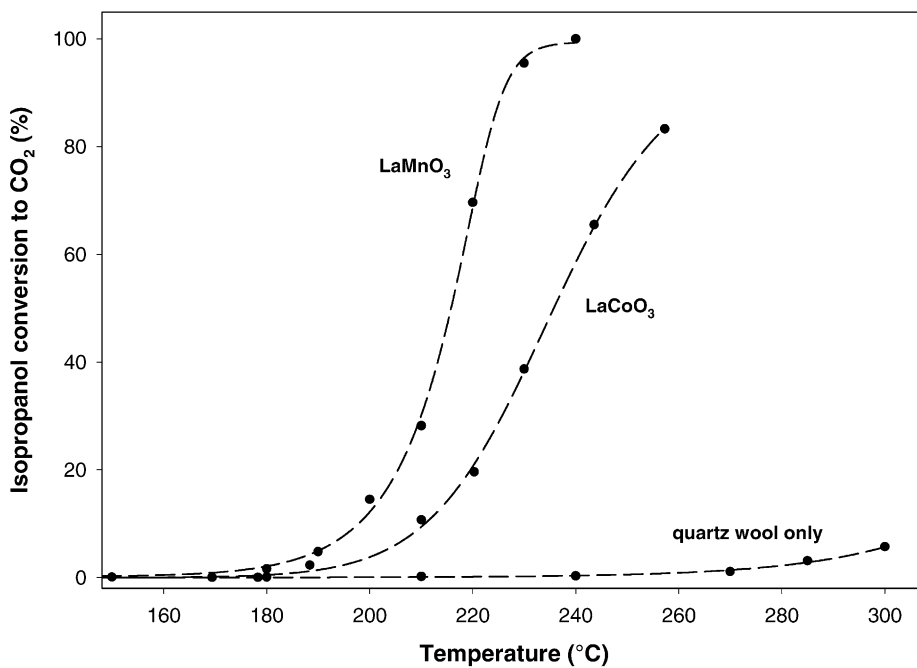

Fig. 3. Conversion of isopropanol to CO_2 vs. temperature (samples amount 0.1 g, ratio VOC/O_2 1/100, space velocity 14,100 h^{-1}).

by means of Perkin-Elmer Autosystem gas chromatograph. The reaction has been carried out by increasing stepwise the temperature and analyzing the reaction mixture in steady state conditions at every predetermined temperature. Negligible deactivation phenomena occurred only at the highest temperatures.

TPD runs after VOCs or H_2 adsorption were carried out in a tubular reactor loaded with 0.04–0.08 g of sample, after the same oxidative pre-treatment used in the catalytic activity measurements, by cooling down the samples in a flow of pure helium to room temperature to remove the excess of oxygen. Adsorption properties were measured at room temperature for 1 h and then desorption was performed in a flow of helium as carrier gas at a heating rate of 4–16 °C min^{-1}. In all experiments, the flows of the gases, dried and purified with suitable filters and with a liquid nitrogen trap, were controlled with Brooks electronic mass flow controllers, and the peaks were detected by means of a TCD detector.

Electrical conductivity measurements have been performed, according to [12], in the same plant using a tubular continuous flow reactor, with 0.14–0.25 g of catalyst placed between two platinum plates provided

with many holes and connected by platinum wires to a source of electrical potential. In every experiment, after the already described pre-treatment, oxygen flow was switched off and the catalyst electrical resistance was measured during desorption in a flow of pure helium. Subsequently, the oxygen flow was switched on and the electrical resistance was measured during adsorption in a He–O_2 flow.

3. Results and discussion

Phase analysis, performed by X-ray powder diffraction, has shown that the LaCoO$_3$ and LaMnO$_3$ catalysts are single phase perovskite oxides, with primitive rhombohedral cell, $R\bar{3}m$ space group. The observed unit cell parameters agreed with those reported in the literature [13].

BET specific surface areas are similar for LaMnO$_3$ (22 m^2 g^{-1}) and LaCoO$_3$ (15 m^2 g^{-1}). Redox titration showed that LaMnO$_3$ contains a substantial fraction (35%) of Mn^{4+} in addition to Mn^{3+}, whereas no Co^{4+} was detected in LaCoO$_3$. Since the perovskite structure can not host interstitial oxygen to compensate the
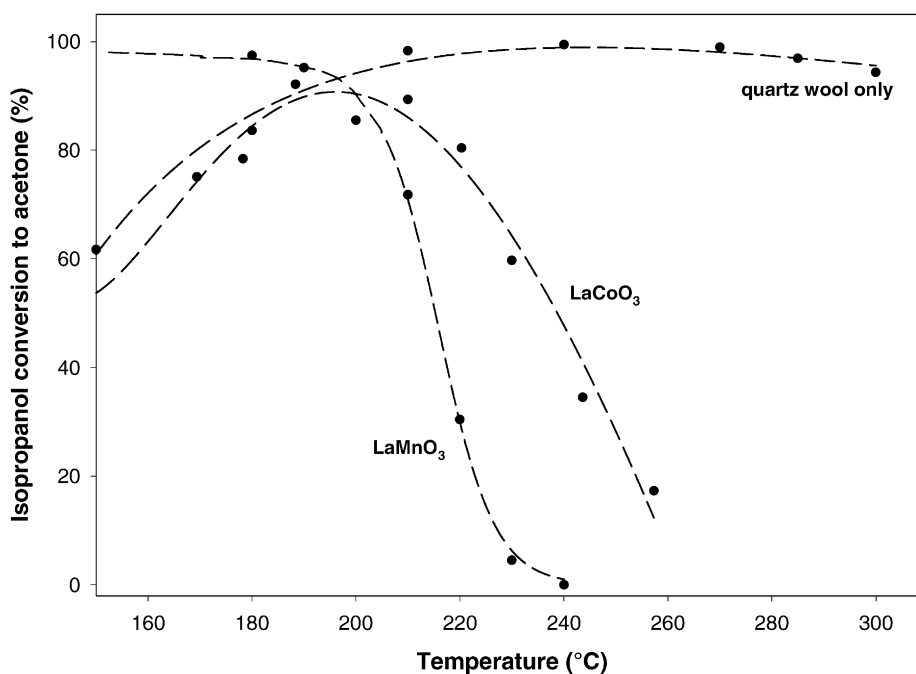

Fig. 4. Conversion of isopropanol to acetone vs. temperature (samples amount 0.1 g, ratio VOC/O$_2$ 1/100, space velocity 14,100 h^{-1}).

Table 1
Values of temperature, T_{50}, at which 50% conversion to CO_2 is reached for VOC/O_2 = 1/100

	LaMnO$_3$			LaCoO$_3$		
	Benzene	Isopropanol	Acetone	Benzene	Isopropanol	Acetone
T_{50}	301	216	203	323	237	222
On O_2 adsorption $(\Omega\,m\,s)^{-1}$	1.5×10^{-6}	3.1×10^{-8}	2×10^{-8}	2.4×10^{-5}	4.8×10^{-5}	4.8×10^{-5}
On O_2 desorption $(\Omega\,m\,s)^{-1}$	4.3×10^{-6}	3.6×10^{-7}	2.6×10^{-7}	1.5×10^{-5}	$2.9 \cdot 10^{-5}$	2.5×10^{-5}

Absolute values of the maxima of the rate of variation of the electrical conductivity at T_{50} for VOC/O_2 = 1/100.

higher charge of Mn^{4+}, cation vacancies in both the 12-coordinated and octahedral metal sites of the perovskite structure are present in LaMnO$_3$ [14,15].

The catalytic activity for the VOCs combustion (VOC/O_2 ratio = 1/100) is presented, as a function of temperature, in Figs. 1–3. In every experiment LaMnO$_3$ resulted to be more active than LaCoO$_3$. Different ranges of temperature must be employed for VOCs combustion, as proved by the plots in Figs. 1–4 and by the T_{50} values reported in Table 1, where T_{50} represents the temperature at which 50% conversion to CO_2 is reached for each catalyst and

each VOC. In particular, benzene combustion requires much higher temperature than the other VOCs. As a matter of fact, the energy necessary to break the weakest C–H bond in benzene (426 kJ mol^{-1}) is higher with respect to isopropanol and acetone (381 and 411 kJ mol^{-1}, respectively) [15]. The values of T_{50} are dependent on the VOC/O_2 ratios. In particular, T_{50} for the total oxidation of acetone decreases with the increase of oxygen partial pressure: 220 °C for VOC/O_2 = 1/50, 203 °C for VOC/O_2 = 1/100, and 195 °C for VOC/O_2 = 1/200. An increase of oxygen partial pressure is thus beneficial for this reaction.
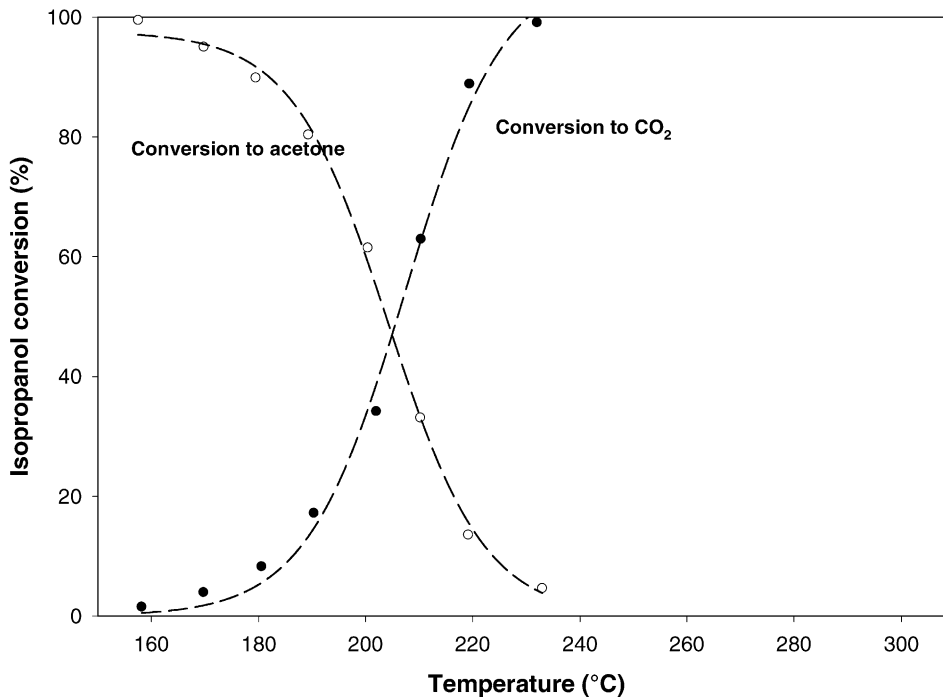

Fig. 5. Conversion of isopropanol to CO_2 and acetone vs. temperature on LaMnO$_3$ (samples amount 0.1 g, ratio VOC/O_2 1/200, space velocity 60,000 h^{-1}).
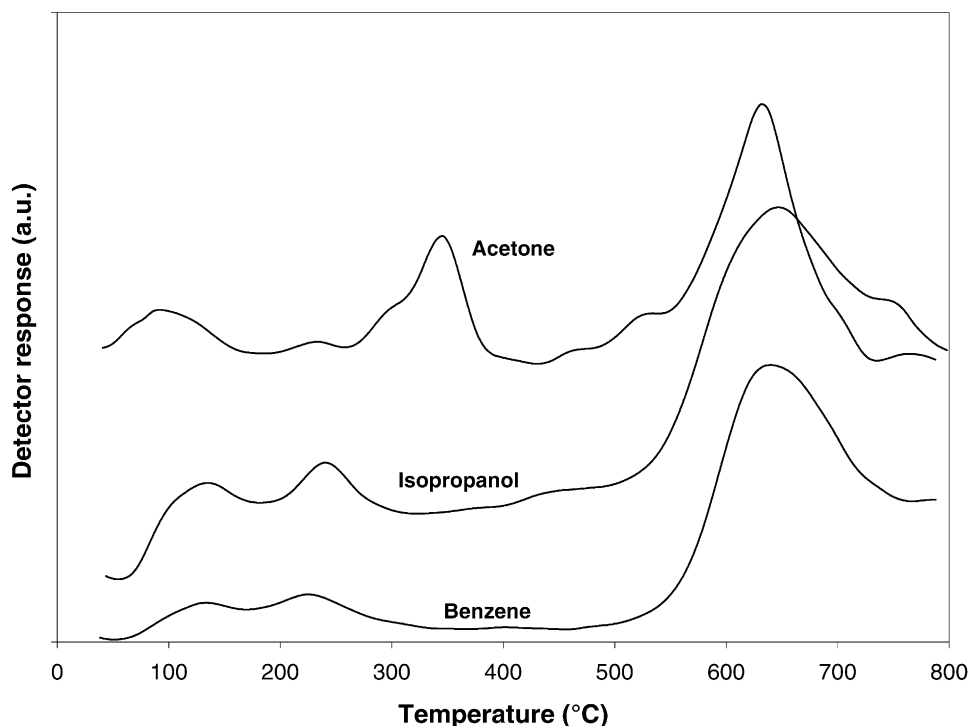
Fig. 6. TPD profiles obtained on $LaMnO_3$ with acetone, benzene and isopropanol adsorbed in continuous flow at room temperature (sample amount 0.06 g, heating rate 8 °C min^{-1}, carrier flow rate 30 ml min^{-1}). The three curves are shifted on *y* axis for clarity.

The contribution of the homogeneous reaction, ascertained in blank experiments without catalyst, is very small in the acetone and isopropanol combustion, but it is sensibly higher in benzene total oxidation. Note that in the isopropanol oxidation blank experiments were found to produce mainly acetone and small amounts of acetic acid. Fig. 4 shows the partial conversion of isopropanol to acetone in blank and catalytic conditions. The isopropanol conversion to acetone curves on $LaCoO_3$ and on quartz wool are almost superimposed until 200 °C. At 200 °C acetone starts to be converted to CO_2 on $LaCoO_3$ (Fig. 2), therefore the isopropanol conversion to acetone becomes lower with respect to quartz wool. On $LaMnO_3$ as well, the contribution of the homogeneous reaction is very high up to 200 °C. This suggests that the isopropanol combustion on the examined perovskite catalysts occurs through the formation and combustion of acetone formed during the homogeneous reaction.

Fig. 5 clearly shows that for isopropanol oxidation on $LaMnO_3$ the increase of the conversion to CO_2 cor-

responds to a decrease of the conversion to acetone, supporting the view that the isopropanol total oxidation takes place via acetone formation.

Temperature programmed desorption experiments were useful to gain a deeper insight in the reaction mechanism. Since the results of oxygen TPD for these catalysts have already been reported [16], the attention has been mainly focused on desorption experiments of pre-adsorbed VOCs. Figs. 6 and 7 show the desorption features after pre-adsorption of acetone, benzene and isopropanol on $LaMnO_3$ and $LaCoO_3$, respectively. A first peak, centered slightly above 100 °C, is due to the desorption of O_2 and the VOC, whereas only acetone has been found in the case of isopropanol pre-adsorbed on $LaCoO_3$. A second peak, in the range 200–350 °C (starting temperatures of the combustion reactions), is due to the desorption of the pre-adsorbed VOC and CO_2. The peak of pre-adsorbed acetone on $LaMnO_3$ is shifted to higher temperature and the amount of desorbed CO_2 is higher with respect to $LaCoO_3$. A third peak with maximum above 600 °C, much larger for
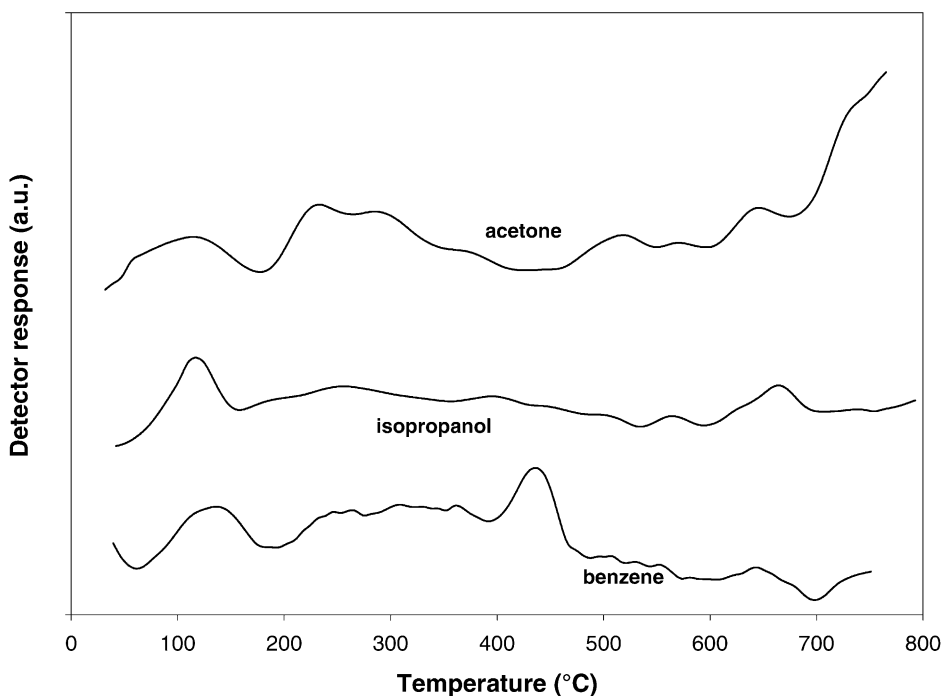
Fig. 7. TPD profiles obtained on LaCoO$_3$ with acetone, benzene and isopropanol adsorbed in continuous flow at room temperature (sample amount 0.06 g, heating rate 8 °C min^{-1}, carrier flow rate 30 ml min^{-1}). The three curves are shifted on y axis for clarity.

the LaMnO$_3$ catalyst, corresponds to the desorption of O$_2$ and CO$_2$.

In summary, TPD experiments show that:

(i) TPD profile of isopropanol pre-adsorbed on LaCoO$_3$ is mainly constituted by oxygen and acetone, whereas no CO$_2$ is detected, thus confirming that isopropanol is converted first to acetone and subsequently to CO$_2$;

(ii) benzene desorption is larger on LaCoO$_3$ with respect to LaMnO$_3$. Probably the stronger surface interactions between LaMnO$_3$ and benzene can promote the catalytic combustion;

(iii) acetone is extensively adsorbed on both catalysts;

(iv) the strong peaks at about 600 °C detected on LaMnO$_3$ could be also due to a loss of oxygen, related to the reduction of Mn^{4+} to Mn^{3+}. In LaCoO$_3$ the peaks are less pronounced.

H$_2$ chemisorption also was investigated, by means of TPD, since it is related to the possibility of formation of O–H bonds and the consequent evolution of water during desorption. In Fig. 8 the TPD spectra of hydrogen desorption on the LaMnO$_3$ and LaCoO$_3$ catalysts are reported. For LaMnO$_3$ a large peak at high temperature (550–800 °C) and a smaller band at much lower temperature are visible. They are due to the interaction of hydrogen with strongly and weakly bound oxygen species, respectively. On the contrary LaCoO$_3$ presents only much minor amounts of desorption products at high temperature. These features indicate the availability of reactive oxygen on the LaMnO$_3$ surface, in agreement with its higher catalytic activity.

The variation of the electrical conductivity of the catalysts during the processes of adsorption–desorption of oxygen has been considered as an effective tool to define the different mobility of surface oxygen species of the perovskites. In fact, the electrical conductivity during the oxygen adsorption–desorption cycles is related to the movement of the electrons, whose number depends on the following reversible processes:
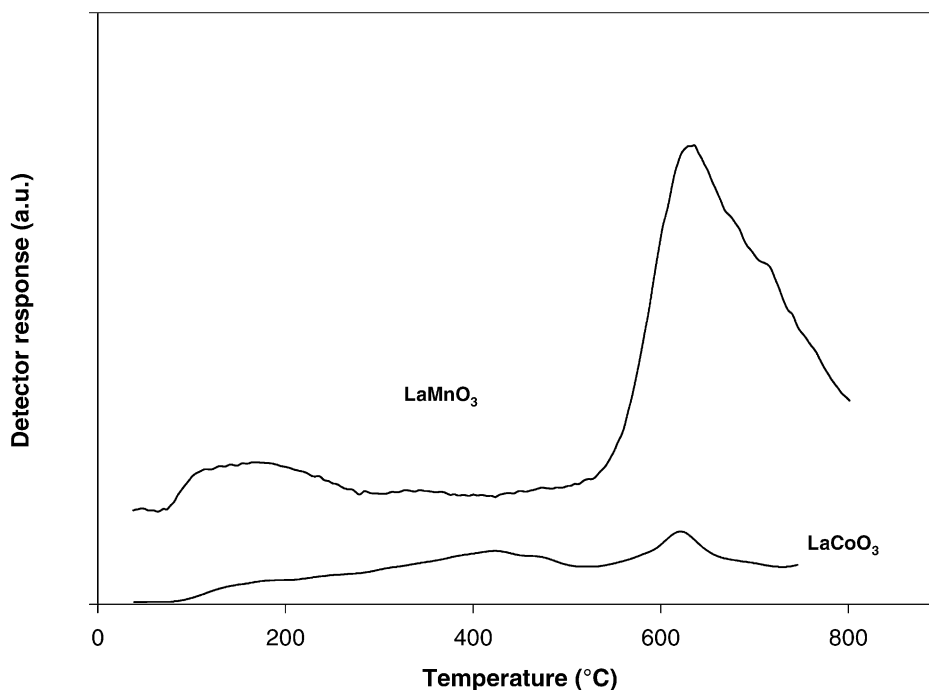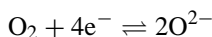
$$O_2 + 2e^- \rightleftharpoons 2O^-$$
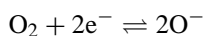
Fig. 8. TPD profiles obtained with hydrogen adsorbed in continuous flow at room temperature (sample amount 0.06 g, heating rate 8 °C min^{-1}, carrier flow rate 30 ml min^{-1}). The two curves are shifted on y axis for clarity.

or

$$O_2 + 4e^- \rightleftharpoons 2O^{2-}$$

The electrical conductivity measured during these experiments can thus be related to the mobility of the surface oxygen species and to the ease of the oxygen uptake–depletion processes.

The experiments have been carried out at T_{50} temperatures with a VOC/O$_2$ ratio = 1/100, that is at temperatures at which the catalytic activity for the total oxidation of benzene, isopropanol and acetone is sufficiently high and the interactions between catalyst surface and reactants are intense. The derivative of the curves conducibility versus time thus indicates the rate of the depletion or the uptake of oxygen. The results are summarized in Table 1, where the maximum values of derivatives, used as indicators of the ease of the process, are shown. It is inferred that for LaCoO$_3$ the rate of oxygen adsorption is slightly higher than that of oxygen desorption. In fact, the O$_2$ desorption depends on the redox properties of the octahedrally coordinated B cation in the perovskite lattice. Since

cobalt is present only in the 3+ oxidation state, oxygen is strongly anchored on the surface and difficult to be removed. On the contrary, for LaMnO$_3$ the rate of oxygen desorption is greater than that of oxygen adsorption. This may suggest that oxygen could be less easily anchored on the surface and more available for VOCs oxidation, probably because of the presence of a noteworthy amount of Mn^{4+} ions (about 35%). The availability of O$_2$ during the desorption process could explain the greater activity of LaMnO$_3$ towards the total oxidation of VOCs.

4. Conclusions

Electrical conductivity measurements support the hypothesis that the presence of oxygen surface species, easily available and sufficiently mobile, is a fundamental requisite for a high catalytic activity, as found in LaMnO$_3$.

VOCs, especially oxygenates, can be adsorbed on the catalyst surface to a large extent and interact

strongly with adsorbed oxygen, as testified by their contemporary desorption with or without reaction.

As suggested by H_2 TPD, the interactions between VOCs hydrogen atoms and catalysts surface oxygen species play an important role in determining catalytic activation of VOCs themselves. By decreasing the VOC/O_2 ratio in the reactant mixture, the temperature of complete conversion of VOC to CO_2 can be lowered.

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