

# Catalytic Oxidation of Volatile Organic Compounds

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## ABSTRACT

The *volatile organic compounds* (VOC) include a set of hydrocarbons with high vapor pressure. VOCs are highly harmful to health and the environment [1]. Catalytic oxidizers are one of the rising alternatives for remove them at low temperatures [2]. Several researches propose the substitution of noble metals for less expensive and more robust materials like transition metal oxides. This work evaluates the use of perovskite-type catalysts for the oxidation of VOC and the development of a functional catalytic filter prototype.

Perovskites were synthesized using the autocombustion method. These materials were evaluated in both powder and supported on a ceramic monolith for the oxidation of several model VOC (hexane, 2-propanol and toluene); which represent several groups of common VOC. The conversion of VOC was monitored by mass spectrometry and the catalysts were characterized by spectroscopic techniques as XRD, SEM, Raman and XPS.

This is a project developed between Hath-Indisa and the University of antioquia, which promotes cooperation industry-university to impulse science and technology in the field of nanomaterials and environmental remediation.

**Keywords:** VOC, catalytic oxidation, perovskite, monolith

## 1 INTRODUCTION

VOC are highly harmful to the human health and the environment [1]. Between the developed technologies for their control, catalytic oxidizers are a rising alternative for the oxidation of VOC at low temperatures compared with pure thermal oxidizers [2][3]. Actually, catalytic systems based on noble metals such as platinum and paladium are the most common for the catalytic oxidation of VOC. However, several researches propose the substitution of noble metals by cheaper materials, as for example transition metal oxides; being very studied some oxides from cobalt, copper, cerium, among others [4]. The synthesis method of these materials is a fundamental factor for their catalytic activity and physicochemical properties [5]. The most required properties of a precursor for catalytic oxidation of VOC are stability at high temperatures and nanometric sizes, high redox potential and capacity to form highly

oxygenated structures. However, costs, time and energetic factors are also important in the synthesis method. Autocombustion is a simple way to obtain nanometric materials at industrial level [6]. However, the setup of the catalyst is a key facto to control pressure drops, transfer speed of mass and heat, residence times and operating temperatures. Honeycomb ceramic monoliths are ideal supports for the control of contaminated gases because allow a good contact between gas and catalyst with a minimum pressure drop. Further, these materials are highly refractory and inert. In general, they are named monolithic catalysts when an active phase is deposited on his surface, although sometimes the active phase is incorporated in the monolith since its production [7].

## 2 EXPERIMENTAL

### 2.1 Synthesis of the catalysts

Three different perovskite-like catalysts based on La-Co (LC), La-Co-Mn (LCM) and La-Mn (LM) were synthesized by autocombustion method. Metallic nitrates were used as precursor of the perovskites. Glycine (Gly) was used as combustion agent, keeping a ratio (Gly/NO<sub>3</sub> = 1). The reactants were mixed in a baker adding a minimal quantity of water to homogenize the mixture. The system was kept with magnetic stirring along the heating. Initially, the temperature was set at 80°C for 30 min to evaporate water excess. Next, the temperature was set at 400°C to carry out the combustion of the mixture. The obtained material was calcined at 700°C with a rate of 10°C/min.

The catalysts were supported on cordierite ceramic monoliths using a optimized washcoating method, similar to that reported by Dwyer et al [8]. The obtained catalytic systems were labeled as LC-S, LCM-S and LM-S in the case of supported catalyst; and LC, LCM and LM for the powder catalysts.

### 2.2 Characterization of the catalysts

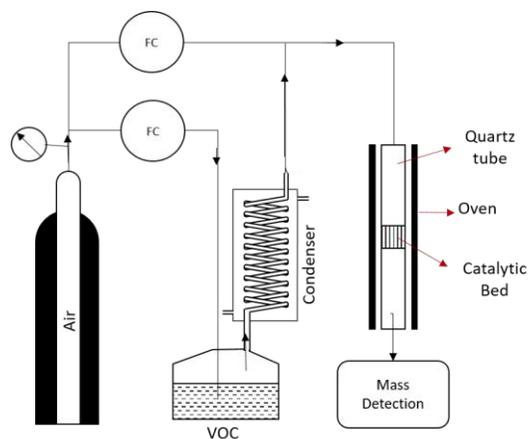
Powder and supported catalysts were characterized by X-ray diffraction, using a diffractometer Panalytical Epyream Serie 2 with radiation of Co  $k\alpha = 1.78901 \text{ \AA}$ , operated at 40 kV and 40 mA. The X-ray patterns were recorded in the  $2\theta$  range of 10-90° with a pass of 0.026°.

Scanning electron microscopy (SEM) was carried out using a system JEOL JSM-7100, equipped with a Field Emission Gun, FEG, and a Auxiliary detector of retro-scattered electrons; operating with an acceleration voltage of 15 kV.

Surface analysis of the catalysts was made using a X-ray photoelectronic spectrometer Specs, with an analyzer PHOIBOS 150 1D-DLD, and using a monochromatic source of Al-  $\text{K}\alpha$  (1486.7 eV, 13 kV, 100 W) with a pass energy of 100 eV for the general spectra and 30 eV for high resolution spectra. For the monolithic catalysts, the Flood Gun at 7 eV and 60 mA was used.

### 2.3 Evaluation of catalytic activity

The activity of the catalysts was evaluated for the oxidation of hexane, toluene and 2-propanol in both individual and for a mixture of all of them. The experimental setup is showed in **Figure 1**. The catalytic oxidation was evaluated at atmospheric pressure, using as reactor a quartz tube inside a electrically heated ceramic oven. The reaction temperature was measured inside the catalytic bed with a type K thermocouple.



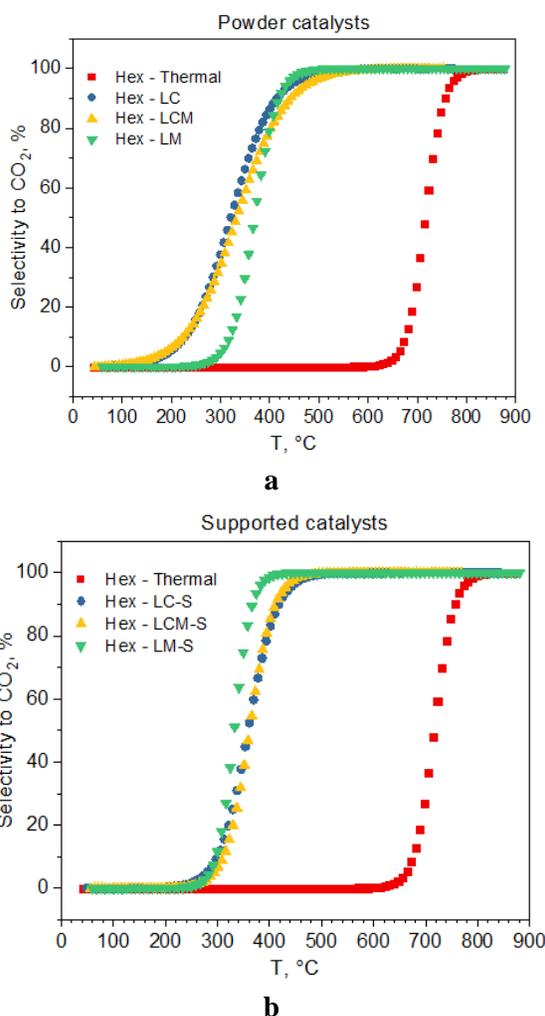
**Figure 1.** Setup for catalytic oxidation of VOC.

For the evaluation of powders, 100 mg of catalyst were used supporting them on quartz wool and putting them inside of a quartz tube of 9.65 mm of diameter. On the other hand, the monoliths were cutted in pieces of 20.65 mm of diameter and 50 mm of length. The gas mixture had 1000 ppm of VOC in air for all the experiments. To adjust the VOC concentration, a controlled air flow was bubbled inside the liquid VOC, while a saturation system was used to condense the excess of VOC. The space velocity was set to  $5000 \text{ h}^{-1}$  and the selectivity to  $\text{CO}_2$  was monitored by mass spectrometry.

## 3 RESULTS AND DISCUSSION

### 3.1 Catalytic activity of powder and supported materials

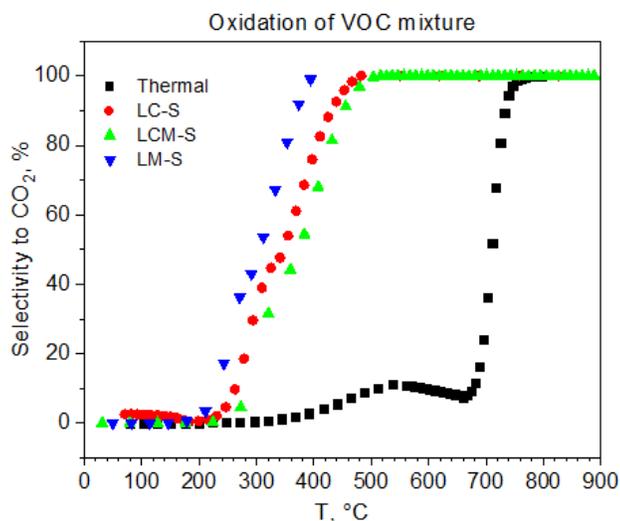
The thermal oxidation of the VOC occurred in a temperature range of  $650^\circ\text{C}$  to  $800^\circ\text{C}$ . Both powder and supported catalysts showed activity for the oxidation of hexane, toluene and 2-propanol; enabling the decreasing of the oxidation temperature in more than  $300^\circ\text{C}$ . For all the cases, toluene showed the higher oxidation temperature respect to the other VOC. An example of the obtained oxidation profiles is showed in **Figure 2** a and b, for the powder catalysts (LC, LCM and LM) and the supported catalysts (LC-S, LCM-S and LM-S); where we can observe a clear decreasing in the range of oxidation temperature, that means, a greater slope when the monolithic catalysts were used. That indicates a more homogeneous oxidation for the supported catalyst, maybe because of a better diffusion of gas in the monoliths compared with the powder catalysts.



**Figure 2.** Catalytic oxidation of hexane: a. powder catalysts; b. monolithic catalysts.

On the other hand, in the **Figure 2** we can observe that LM catalyst allows total oxidation temperatures lower than the other catalysts LC and LCM. This tendency was

observed in both powder and monolithic catalysts for all the evaluated VOC. The experiments with the mixture of VOC (**Figure 3**) confirmed the LM-S catalyst as the most promissory. Further, there was no significant changes in the range of temperature for the oxidation of the VOC mixture, respect to the values obtained for the individual VOC.

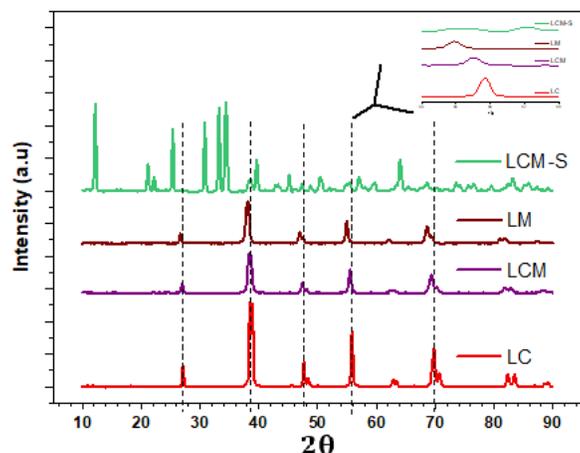


**Figure 3.** Catalytic oxidation of mixture of VOC.

### 3.2 Characterization of catalysts

A gravimetric analysis allowed to determine that the percentage of loaded catalyst on the monoliths was 8% ( $\pm 1\%$ ).

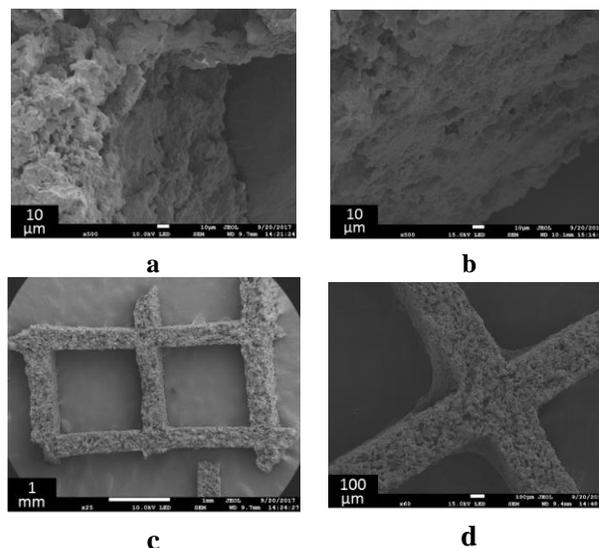
The XRD analysis (**Figure 4**) confirmed the obtaining of perovskite-like phases for all the powder catalysts LC, LCM and LM. The inset shows a displacement of the diffraction peaks due to the modification in the elements of the catalysts. However, XRD does not allowed to analyze the supported catalysts due to the interference of high intensity peaks of cordierite in the monolithic systems.



**Figure 4.** Diffractograms of the catalysts.

In the SEM analysis we observed a good deposition of the

catalysts on the monolithic Surface. This can be noticed in the change of the rugosity of the clean monolith Surface, **Figure 5a** after the impregnation with the perovskite-like catalyst, **Figure 5b**. Additionally, there was also a clear change in the square geometry of the clean monolith (**Figure 5c**) towards a more oval geometry (**Figure 5d**), caused by the accumulation of catalyst on the corners of the monolithic channels.



**Figure 5.** SEM micrographs of monolithic catalysts.

The Surface of the catalysts was also characterized by XPS. The general spectra showed a significant increasing in the quantity of surface oxygen for the supported catalysts. The results for the LM and LM-S systems are illustrated as example (**Table 1** a y b).

**Table 1.** XPS Surface analysis of LM and LM-S catalysts.

LM				
Name	Pos.	FWHM	Area	At%
C 1s	283.99	2.90	4924.93	47.65
O 1s	527.99	4.06	11950.75	39.46
La 3d	832.99	7.11	34233.47	6.96
Mn 2p	640.99	4.35	8521.77	5.93

**a**

LM-S				
Name	Pos.	FWHM	Area	At%
O 1s	531.79	3.49	23090.58	52.78
C 1s	283.79	3.24	1530.11	10.25
La 3d	832.79	6.97	6848.98	0.96
Mn 2p	640.79	4.32	1314.00	0.63
Si 2s	153.79	3.90	5044.28	35.38

**b**

Complementary, the high resolution spectra for O1s (**Figure 6** a y b) showed that for the supported catalysts exist a greater amount of adsorbed oxygen species O<sub>2</sub><sup>2-</sup> (OII) and O<sub>2</sub><sup>-</sup>, (OIII); while for the powder catalysts, the lattice oxygen species are in greater proportion [9]. This promotes the hypothesis of a clear interaction between the

perovskite-like catalyst and the cordierite monolith, which could be associated to a high number of oxygen vacancies on the Surface of the supported catalysts that improvement the oxygen diffusion through the lattice.

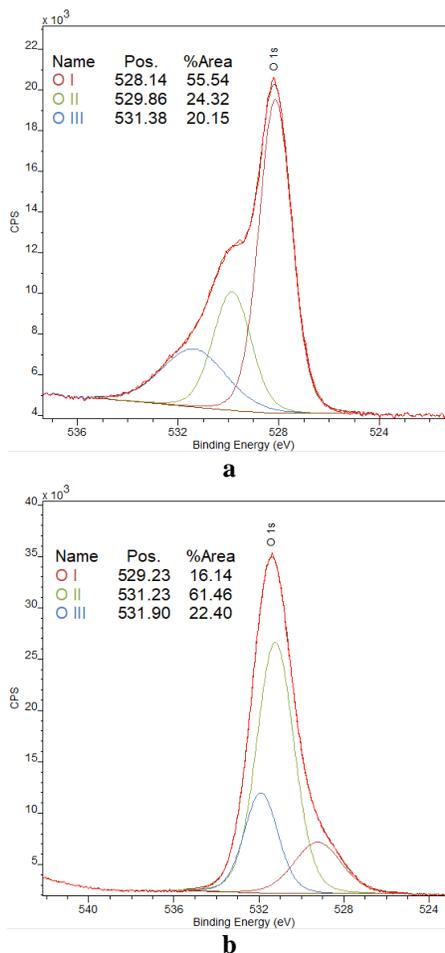


Figure 6. XPS spectra for O1s from a.LM and b.LM-S.

## 4 CONCLUSIONS

The autocombustión method, together with the subsequent thermal treatment, allows to synthesize the perovskite-like phases satisfactorily for the different catalysts, as it was shown by XRD. Further, this method allows to obtain sufficient quantities of catalyst in relatively short times.

The used washcoating method allowed to reach a good deposition of catalyst on the monoliths. After 2 depositions, a percentage around 8% was deposited successfully. The SEM analysis confirmed changes in the surface and the geometry of the channels due to the deposition of catalyst.

Both powder and supported catalysts showed catalytic activity for the oxidation of hexane, toluene and 2-propanol. The oxidation temperature for those VOC was diminished in more than 300°C with the using of the perovskites. Differences in the oxidation profiles for powder and supported catalysts were associated to changes

in the surface composition of the catalysts, probably due to an interaction between the perovskite and the monolith.

LM-S catalyst showed the higher catalytic activity for the oxidation of individual and mixture of VOC, and its using is required to analyze additional parameters of efficiency, such as space velocity, VOC concentration and moisture effect.

## 5 ACKNOWLEDGEMENTS

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