

# Ceria-based oxides as supports for LaCoO<sub>3</sub> perovskite; catalysts for total oxidation of VOC

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Available online 21 June 2006

## Abstract

Supported LaCoO<sub>3</sub> perovskites with 10 and 20 wt.% loading were obtained by wet impregnation of different Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> ( $x = 0-0.3$ ) supports with a solution prepared from La and Co nitrates, and citric acid. Supports were also prepared using the “citrate method”. All materials were calcined at 700 °C for 6 h and investigated by N<sub>2</sub> adsorption at -196 °C, XRD and XPS. XRD patterns and XPS measurements evidenced the formation of a pure perovskite phase, preferentially accumulated at the outer surface. These materials were comparatively tested in benzene and toluene total oxidation in the temperature range 100–500 °C. All catalysts showed a lower  $T_{50}$  than the corresponding Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> supports. Twenty weight percent LaCoO<sub>3</sub> catalysts presented lower  $T_{50}$  than bulk LaCoO<sub>3</sub>. In terms of reaction rates per mass unit of perovskite calculated at 300 °C, two facts should be noted (i) the activity order is more than 10 times higher for toluene and (ii) the reverse variation with the loading as a function of the reactant, a better activity being observed for low loadings in the case of benzene. For the same loading, the support composition influences drastically the oxidative abilities of LaCoO<sub>3</sub> by the surface area and the oxygen mobility.

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**Keywords:** Supported perovskite; Ceria support; VOC catalytic combustion

## 1. Introduction

Increasing pollution problem needs a fast and effective answer [1]. The progress made in the last 30 years for atmosphere quality preservation since the large-scale application of TWC were accompanied by a parallel development of non-environmental-friendly industries. Among various types of pollutants, volatile organic compounds (VOC) are of particular concern due to their high toxic potential and their easiness of spreading over large areas through the atmosphere. With this respect, drastic international regulations were applied for different sources of such compounds [2]. Usually, VOC streams are lean. This requires very active catalysts and if possible with a high heat capacity, especially when reverse-flow reactors are used [3,4]. Noble metals are the most used catalysts for environmental protection against VOCs but in view of economical and practical features the trend is their replacement with cheaper oxides [5–7]. Improved properties of mixed oxides against simple ones are well

known, especially in the environmental protection field [7,8]. Tunable properties or synergetic effects due to composition places these materials on top of preferences for large scale applications. Among mixed oxides, perovskites occupy an important place both for fundamental studies (usually physics, solid physics) and applicability [9]. Perovskites were largely studied as substitutes for the actual total oxidation catalysts. However, the major limitation of these results were their lower surface area and their increased tendency to sinter. In this view, the only solution of increasing the contact surface between the VOC and the perovskite is to disperse it on a large surface area and thermally stable support. Two problems arise when supporting an active phase: the preservation of the structure or accepting/generating a controlled alteration and a good and uniform dispersion. With respect to the first requirement different attempts have been made, using mainly alumina-based supports [10–13]. However, in spite of the advantages offered by alumina, the drawback of catalytically inactive spinel-phase formation with the transitional metals usually used for catalytic purposes focused the research to other directions. Other papers claim that magnesia [14,15] offers a good matrix for perovskite dispersion. Ceria is a basic component of various catalytic converters due to

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its properties of oxygen buffer [16,17]. The use of ceria and zirconia as suitable supports for La–Co-perovskites is previously reported and interesting in the presented works are the enhanced catalytic activities with respect to the corresponding bulk perovskites. High catalytic activities for propane combustion, exceeding even the one of bulk  $\text{LaCoO}_3$  or  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$  were obtained by using inert  $\text{ZrO}_2$  and  $\text{CeO}_2$  as supports [18].  $\text{LaCoO}_3$  and  $\text{LaFeO}_3$  supported on  $\text{ZrO}_2$  were more active than the corresponding bulk perovskites for CO oxidation [19,20]. Apart from increased activity, such materials possess a good heat capacity pointing to their possible employment in adiabatic reverse-flow reactors and were successfully tested for methane combustion [3,21].

With respect to the second requirement for a supported catalyst, namely a uniform coating of the carrier, some authors pointed to the use of the citrate method for obtaining mixed oxides supported phases with a good control of stoichiometry and small particle size and suggested that this approach is promising for both the preparation of supported perovskites and ceria–zirconia supports [22–24]. Previous results reported by our team for toluene complete oxidation were obtained on catalysts prepared by incipient wetness impregnation [25]. The catalytic results were promising but, however, the physico-chemical characterizations pointed to certain heterogeneity of the coating with the dispersed perovskite phase. Aiming at obtaining a uniform coating of the support, in the present study another approach for perovskite dispersion, namely wet impregnation by allowing a longer contact time between the precursor and the carriers, is used [25].

Present work deals with preparation of supported  $\text{LaCoO}_3$  by wet impregnation on different  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  supports and comparative investigation of the catalytic behaviour for benzene and toluene complete oxidation.

## 2. Experimental

### 2.1. Catalyst preparation

$\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  solid solutions were prepared as previously reported, using a method based on complexation with citric acid and calcined at 700 °C for 6 h and further used in powder state as supports [26].  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aldrich) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Aldrich), and citric acid monohydrate (Merck) were used as starting materials. Aqueous solutions with cation ratio La:Co of 1:1 were prepared. Typically, the weight of the solution was 10 times higher than that of the support powder and the amount of salts was calculated to obtain loadings of 10 and 20 wt.%  $\text{LaCoO}_3$ . The slurry was stirred for 5 h and water was slowly evaporated at 40 °C in a rotary evaporator. The drying process was completed by heating the powder in a vacuum oven set at 60 °C under a pressure of 200 kPa for 16 h. Obtained powder was calcined at 700 °C for 6 h in static air.

### 2.2. Catalyst characterization

Specific surface areas (SSA-BET) were determined by nitrogen adsorption at –196 °C on a Micromeritics ASAP 2000

instrument. Before measurement the catalyst powder was outgassed for 2 h at 150 °C under a pressure of 0.1 Pa. XRD patterns were collected on powder samples by means of a Kristalloflex Siemens D5000 diffractometer using the  $\text{Cu K}\alpha$  radiation at  $\lambda = 1.5418 \text{ \AA}$ . Data acquisition was realized in the  $2\theta$  range 2–65° with a scan step size of 0.03°. XPS spectra were recorded at room temperature and under a vacuum of  $10^{-7}$  Pa on a SSX-100 model 206 Surface Science Instrument spectrometer using monochromatized  $\text{Al K}\alpha$  radiation ( $h\nu = 1486.6 \text{ eV}$ ). Charge neutralization was achieved using an electron flood-gun operating at 10 eV and placing a Ni grid 3 mm above the sample. The charge correction was made considering the C 1s signal of contaminating carbon (C–C or C–H bonds) positioned at 284.8 eV.

### 2.3. Catalytic activity evaluation

Toluene and benzene complete oxidation was performed in a down-flow tubular reactor (i.d. 10 mm) made of quartz, operating at atmospheric pressure, loaded typically with 0.1 g of powder catalyst deposited between two quartz wool plugs.

For catalytic activity evaluation, a mixture of 1700 ppm vol of benzene or toluene and air flowing at  $100 \text{ ml min}^{-1}$  (total  $\text{GHSV} = 60,000 \text{ ml g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) was admitted and the temperature was raised up to 600 °C in steps of 25 °C. The  $\text{CO}_2$  level in the outlet was continuously monitored by means of an on-line coupled IR–Fisher–Rosemount multichannel analyzer while the CO production was on-line checked by a IAQ CALC-METER model 8762 from COLE-PARMER. Hydrocarbons and by-products were analyzed using a Poropak Q column mounted on a HP 5890 Series II GC equipped with a TCD detector. During catalytic runs, temperature was increased to a superior value only after reaching a steady level of  $\text{CO}_2$  in the outlet (typically after 25–30 min). Conversion levels at decreasing temperature superposed on the levels at increasing temperature. Each catalytic run was performed twice, considering only the results for which the differences between two sets of results were below 10%. Carbon balance closed for all investigated materials and the analysis of spent catalysts did not show any carbonaceous deposits at the surface.

## 3. Results and discussions

From nitrogen adsorption-desorption isotherms BET surface area of investigated solids were obtained (Table 1). As mentioned before [3,25] perovskite deposition caused a decrease of surface area of the initial support induced by pore blocking due to the deposited phase. This drop in surface area increased with loading (Table 1). However, by comparing these materials with the similar ones but obtained by incipient wetness [25], a slight increase of the surface area is observed, very likely indicating a more uniform coating of the carriers and a better penetration into the pores.

Separate experiments were performed to check if the excess of water used for impregnation affects the texture of the carriers. All four pure supports were stirred with excess of water followed by slow evaporation and further calcined at

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