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Ceria-based oxides as supports for LaCoO₃ perovskite; catalysts for total oxidation of VOC

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Abstract

Supported LaCoO₃ perovskites with 10 and 20 wt.% loading were obtained by wet impregnation of different Ce_{1-x}Zr_xO₂ (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 N2 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_{1-x}Zr_xO₂ supports. Twenty weight percent LaCoO₃ catalysts presented lower T_{50} than bulk LaCoO₃. 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 LaCoO₃ by the surface area and the oxygen mobility. © 2006 Elsevier B.V. All rights reserved.

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-environmentalfriendly 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

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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 LaCoO₃ or La_{0.8}Sr_{0.2}CoO₃ were obtained by using inert ZrO₂ and CeO₂ as supports [18]. LaCoO₃ and LaFeO₃ supported on ZrO₂ 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 physicochemical 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 LaCoO₃ by wet impregnation on different $Ce_{1-x}Zr_xO_2$ supports and comparative investigation of the catalytic behaviour for benzene and toluene complete oxidation.

2. Experimental

2.1. Catalyst preparation

 $Ce_{1-x}Zr_xO_2$ 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]. La(NO₃)₃·6H₂O (Aldrich) and Co(N-O₃)₂·6H₂O (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.% LaCoO₃. 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 Cu K α radiation at $\lambda = 1.5418$ Å. Data acquisition was realized in the 2θ 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 Al K α radiation ($h\nu = 1486.6$ 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 an 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 ml min⁻¹ (total GHSV = 60,000 ml $g_{cat}^{-1} h^{-1}$) was admitted and the temperature was raised up to 600 °C in steps of 25 °C. The CO₂ 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 byproducts were analyzed using a Porapaq 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 CO₂ 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

Table 1 Specific surface area of the supports and of the bulk and supported LaCoO₃

Support	LaCoO ₃ loading (wt.%)	Surface area $(m^2 g^{-1})$		
CeO ₂	-	23.0/23.6 ^a		
$Ce_{0.9}Zr_{0.1}O_2$	_	37.9/37.3 ^a		
$Ce_{0.8}Zr_{0.2}O_2$	_	36.0/36.4 ^a		
$Ce_{0.7}Zr_{0.3}O_2$	_	28.5/28.7 ^a		
_	100	11.3		
CeO ₂	10	18.8		
CeO ₂	20	15.7		
$Ce_{0.9}Zr_{0.1}O_2$	10	23.6		
$Ce_{0.9}Zr_{0.1}O_2$	20	22.7		
$Ce_{0.8}Zr_{0.2}O_2$	10	25.3		
$Ce_{0.8}Zr_{0.2}O_{2}$	20	20.3		
$Ce_{0.7}Zr_{0.3}O_2$	10	18.4		
$Ce_{0.7}Zr_{0.3}O_{2}$	20	15.1		

^a After impregnation with water and recalcination at 700 °C.

700 °C as in the case of wet impregnation with LaCoO₃. The results presented in Table 1 show practically no effect of the water and recalcining on the surface area of supports, pointing to no textural modification. With this respect the surface area of supported perovskites is generated only by the interaction between the deposited phase and carrier.

XRD patterns for 20 wt.% samples are shown in Fig. 1. The most intense reflections correspond to cubic ceria with a shift toward larger 2θ angles as Zr content increase. This corresponds to a replacement of Ce by Zr in cubic ceria lattice, accounting for a solid solution formation [26]. However, the important features of these solids are the reflections centred at $2\theta = 23.3^{\circ}$ and 40.67° and the shoulders at 33.1° and 59.1° that correspond to rhombohedral LaCoO₃ (JCPD-ICDD 48-0123) [27]. A semiquantitative and comparative image of LaCoO₃ penetration into pores by the two deposition methods used, i.e. incipient wetness [25] and wet impregnation in this work, can be obtained by comparing the intensity ratio of the reflection line of LaCoO₃ centered at 40.67° and the most intense reflection line of the support (centered around 29°, depending on the composition). It is worth noting that, according to this interpretation of the results, even if it is not absolute, however, can give a good hint on the suitability of the preparation method, the ratios were in all cases lower in the present work,



Fig. 1. XRD patterns for 20 wt.% LaCoO₃/Ce_{1-x}Zr_xO₂ samples.

Table 2 XPS atomic ratios for supports, bulk and supported LaCoO₃ perovskite

Support	Co/La: loading (wt.%)		Ce/Zr: loa (wt.%)	ding
	0	20	0	20
CeO ₂	_	0.35	_	_
$Ce_{0.9}Zr_{0.1}O_2$	-	0.41	8.83	8.57
$Ce_{0.8}Zr_{0.2}O_2$	_	0.36	3.90	3.56
$Ce_{0.7}Zr_{0.3}O_2$	_	0.37	1.96	1.75
LaCoO ₃	0.38	-	-	_

pointing to a deeper penetration into the pores and, consequently, to a better dispersion. Perovskite phase formation was observed even for loadings as low as 10 wt.% (not shown). No other signals could be detected accounting for no strong interactions between La and/or Co and support that may lead to apparition of new phases.

Table 2 compiles the XPS superficial atomic ratios for selected catalysts, namely the supports and the ones loaded with 20 wt.% LaCoO₃. The catalysts with 10 wt.% were also investigated but the signal quality was poor and large deviations for superficial cation ratios were observed comparing to bulk LaCoO₃ and corresponding 20 wt.% catalysts. With this respect, only data for 20 wt.% LaCoO₃ are shown. Co/La atomic ratios are less than unity for all catalysts (Table 2) and the values for supported LaCoO₃ are close to that of bulk LaCoO₃. It is useful to understand here that similar catalysts prepared via incipient wetness showed larger deviations of Co/La ratio with respect to bulk LaCoO₃ [25]. Present results seems to indicate that a better homogeneity of the dispersed species, i.e. a supported phase with a stoichiometry very close to bulk LaCoO₃, can be achieved by wet impregnation. The longer contact time between the precursor and the carrier and the stirring of the suspension appeared to be the factors influencing in a beneficial way the deposition of LaCoO₃ on Ce_{1-x}Zr_xO₂ supports.

Ce/Zr atomic ratio was not significantly influenced by the perovskite deposition route and is very closed to the chemical ratio indicating a homogeneous distribution of cations in the



Fig. 2. La/Ce atomic ratios for 20 wt.% LaCoO₃/Ce_{1-x}Zr_xO₂ samples.

Table 3	
Binding energies (eV) for selected catalysts	

Support	La 3d ₅ : loading (wt.%)		Co 2p ₃ : loading (wt.%)		Ce 3d ₅ : loading (wt.%)		Zr 3d ₅ : loading (wt.%)	
	0	20	0	20	0	20	0	20
CeO ₂	_	834.2	_	780.0	882.3	882.0	_	_
$Ce_{0.9}Zr_{0.1}O_2$	_	834.0	_	780.1	882.1	882.1	181.8	181.6
$Ce_{0.8}Zr_{0.2}O_2$	_	834.2	_	780.2	882.2	882.0	181.9	181.8
$Ce_{0.7}Zr_{0.3}O_2$	_	833.8	_	779.9	882.0	882.2	181.8	181.7
LaCoO ₃	834.0	_	779.9	_	_	_	_	-

bulk and at the surface. The preservation of Ce/Zr ratio for supported perovskites also indicates no interaction of the support with La or Co that might lead to a superficial enrichment to one of the cations of the carrier oxide (Table 2).

The values of the superficial [La/Ce] atomic ratio and of the corresponding "stoichiometric" ratio (calculated by considering the amount of each compound in the solid) are represented in Fig. 2. A larger accumulation of the deposited material at the surface of the carriers is observed on the supports with the lowest surface area, i.e. CeO₂ and Ce_{0.7}Zr_{0.3}O₂ as it is indicated by the differences between the two values. This observation sustain the decrease of the surface area observed after impregnation (Table 1). But, with respect to the samples prepared by incipient wetness [25] the depletion of superficial La with a factor of about 30% is observed. This also points to a better penetration of the perovskite into the pores by wet impregnation.

From XPS measurements no shift of the binding energies of the elements occurs with respect to bulk $LaCoO_3$ (Table 3). This points out to no interaction of La and Co with the Ce or Zr from the carrier. Both the oxidation states of La and Co were typically in the range reported for perovskites [28,29].

The supports and the catalysts were tested in toluene and benzene complete oxidation. All supported perovskites exhibited a good activity toward total oxidation of the two aromatic hydrocarbons. In all the outlet streams only unreacted hydrocarbons, CO_2 and water were detected. In the temperature range of our experiments no thermal destruction of the oxidized molecules has been detected.

The supports were the less active materials presenting T_{50} temperatures well below the ones for bulk and supported LaCoO₃ (Table 4). The effect of LaCoO₃ loading is similar for both substrates. The oxidative abilities are enhanced by a higher amount of active phase. Table 4 shows a parallel decrease of T_{50} with the loading regardless of the composition of the support. However, correlating T_{50} with the nature of the hydrocarbon

clearly appears that benzene is more difficult to be oxidized, the shift of T_{50} towards larger values being on a range of 80-170 °C. Bulk LaCoO₃ appeared to be the most active catalyst for benzene, total oxidation with T_{50} was lower with 3 and 7 °C than the most active catalysts, namely 20 wt.% LaCoO₃ supported on Ce_{0.9}Zr_{0.1}O₂ and CeO₂, respectively (Table 4). As the Zr amount in the support increases, T_{50} increases with 20– 25 °C. In the case of toluene, the situation is different: all 10 wt.% LaCoO₃ catalysts are less active than bulk LaCoO₃ but the increase of the deposited amount to 20 wt.% led to catalysts presenting T_{50} lower with 50 °C (Ce_{0.9}Zr_{0.1}O₂), 37 °C $(Ce_{0.8}Zr_{0.2}O_2)$ and 26 °C (CeO₂). All T_{50} for toluene are lower than the corresponding values obtained for the catalyst prepared by incipient wetness. Correlating these results with specific surface and XPS data recorded for the samples prepared by incipient wetness [25] it might be concluded that a better dispersion is a prerequisite condition for a good oxidative activity. At the first look it appears that the surface area is the primary factor influencing the light-off temperature. However, a careful look at the catalysts using CeO₂ and Ce_{0.7}Zr_{0.3}O₂ as carriers, that developed similar surface areas, contradicts the above assumption. A tentative explanation will be offered below.

A clear distinction of the importance of the hydrocabon structure in the total oxidation reactions and a better image on the activity of the supported perovskite phase is obtained expressing the catalytic activity in terms of reaction rates. The results expressed per mass unit of perovskite were obtained assuming a first order kinetics with respect to benzene and toluene and zero order for oxygen, in a plug-flow reactor [3]. For all supported perovskites and for bulk LaCoO₃ the corresponding Arrhenius plots were linear for conversion levels between 10 and 90% where diffusional effects are considered not occurring, suggesting a single kinetic domain. Fig. 3 shown the light-off curves and the Arrhenius plots for selected catalysts. The apparent activation energies were in the

Table 4

Comparison of catalytic activity for benzene (BZ) and toluene (TOL) combustion expressed by T_{50} as a function of LaCoO₃ loading and nature of the support

Loading (wt.%)	CeO ₂		Ce _{0.9} Zr _{0.1} O ₂		Ce _{0.8} Zr _{0.2} O ₂		Ce _{0.7} Zr _{0.3} O ₂		LaCoO ₃	
	BZ	TOL	BZ	TOL	BZ	TOL	BZ	TOL	BZ	TOL
0	526	380	445	295	466	357	479	310	330	244
10	355	275	345	268	370	292	382	296	_	_
20	337	218	333	192	349	207	355	240	-	-



Fig. 3. Light-off curves for benzene and toluene complete oxidation and the corresponding Arrhenius plots on bulk $LaCoO_3$ and 10 and 20 wt.% $LaCoO_3/Ce_{0.9}Zr_{0.1}O_2$.

50–70 kJ mol⁻¹ for benzene and 35–60 kJ mol⁻¹ for toluene that are the ranges reported in literature for perovskites, that is 40–80 kJ mol⁻¹.

Fig. 4 presents the reaction rates calculated from the corresponding Arrhenius plots at 300 °C for both benzene and toluene transformation. Looking comparatively, two features are striking: (i) the activity order that is more than 10 times higher for toluene and (ii) the reverse variation of specific activity (per gram of perovskite) with the loading as a function of the reactant. It is accepted that the reactions of complete oxidation (combustion) proceed via activation of the weakest C–H bond of the reactant [30]. The homolitically initiated radical will complete the oxidation of the VOC by interaction with an oxygen from the surface that might be either lattice or

adsorbed. If one considers the strength of the C–H bond expressed by means of bond dissociation enthalpy, we may compare and explain the differences observed between the reactivity of benzene ($\Delta H_{C-H} = 465 \text{ kJ mol}^{-1}$) and toluene ($\Delta H_{C-H} = 370 \text{ kJ mol}^{-1}$) [31] on identical catalysts (Fig. 3). Based on previous results obtained on methane combustion [3], where the specific reaction rate decreased with the loading similar to the case of benzene, it appears that the most active sites are located in the first layer of perovskite, that is in intimate contact with the support. Under these conditions, a phase cooperation between ceria from the support and LaCoO₃ might be supposed [32]. On the other hand, the energetic requirements for the activation of C–H bond of toluene are lower. As stated before and previously shown [3] the stronger



Fig. 4. Reaction rates at 300 °C for benzene (a) and toluene (b) complete oxidation; 1700 ppmv hydrocarbon in air, 0.1 g catalyst, total flow 100 ml min⁻¹.

active sites are located at the contact between the ceria-based support and $LaCoO_3$, further increase of loading leading to less active layers of perovskite. The increase of the reaction rate for toluene with the perovskite loading suggest a very likely dependence to the number of the active sites. That is more important than their strength.

Fig. 4 also shows that bulk LaCoO₃ is much less active, i. e. one order of magnitude, than supported LaCoO₃, irrespective to the support composition. The first explanation of this behavior is associated with the increased exposed surface area of perovskite, assumption sustained by the parallel variation of the activity order for both benzene and toluene complete oxidation. This variation follows the evolution of the surface area (Table 1). Notable is the increased activity of LaCoO₃/CeO₂ with respect to LaCoO₃/Ce_{0.7}Zr_{0.3}O₂ even if they developed similar surface areas. As previously shown [25], the composition of the oxygen mobility that is influenced by Zr presence in the cubic lattice of ceria.

4. Conclusions

In this study supported LaCoO₃ catalysts were prepared by wet impregnation of different Ce_{1-x}Zr_xO₂ supports with a mixture of La and Co citrates. Perovskite phase formation at 700 °C was evidenced by XRD and XPS investigations. XPS measurements indicated no interaction between the support and the elements of the perovskite as well as a reduced tendency of accumulation of the deposited phase at the external surface of the support with respect to similar samples prepared by incipient wetness impregnation.

LaCoO₃ is an active catalyst for benzene and toluene removal from diluted streams of VOC. Its dispersion at the surface of ceria–zirconia solid solutions decreases the light-off temperatures and increases with an order of magnitude the reaction rates with respect to bulk perovskite. Two factors concurred at increasing activity of ceria–zirconia supported LaCoO₃: (i) the larger exposed surface and (ii) the composition of the support that provide increased oxygen mobility.

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