Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 112 (2006) 169–173

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Effect of $LaCoO_3$ perovskite deposition on ceria-based supports on total oxidation of VOC

M. Alifanti [a], M. Florea [a], V. Cortes-Corberan [b], U. Endruschat [c], B. Delmon [d], V.I. Pârvulescu [a,*]

[a] *Department of Chemical Technology and Catalysis, University of Bucharest, B-dul Regina Elisabeta 4-12, Bucharest 030016, Romania*
[b] *CSIC-ICP, Cantoblanco 28049, Madrid, Spain*
[c] *W.C. Heraeus GmbH and Co. KG, Chemicals Division, Heraeusstr. 12-14, 63450 Hanau, Germany*
[d] *Unité de Catalyse et de Chimie des Matériaux divises, Université catholique de Louvain, Croix du Sud 2/17, B-1348 Louvain la Neuve, Belgium*

Abstract

Supported $LaCoO_3$ perovskites with 10 wt.% loading were prepared by impregnation of different supports containing ceria with a solution of La and Co nitrates and citric acid. All precursors were calcined at 700 °C for 5 h. XRD investigations indicated the perovskite formation via "citrate" precursor only on ceria support. All catalysts were tested for toluene total oxidation in the temperature range 100–600 °C. In spite of a large surface area, alumina-supported perovskites showed a lower global activity. It appears then the necessity of the presence of a perovskite phase for good oxidative activity. In terms of reaction rates higher reaction rates per perovskite weight were observed for all supported catalysts when compared to bulk $LaCoO_3$.

Keywords: Supported perovskite; Ceria-based supports; Catalytic toluene combustion

1. Introduction

The catalysts used for environmental purposes are either noble metals or metal oxides. Although noble metals are the most active and effective catalysts for VOC decomposition, they lack of high sintering rate, volatility and high price [1]. Under these circumstances, oxides appear to be a tempting solution, especially in the view of price and rather easier ways for preparation. Perovskites are mixed oxides with specific cubic structure, described by the general formula ABO_3. They have been studied for three decades as substitutes for the noble metal total oxidation catalysts [2,3]. Some formulations present similar or higher activity than Pt-supported on alumina catalysts [4,5]. In spite of such a history and performances, the main limitation of using perovskites on a large scale emerged from their reduced ability to develop large surface areas. Moreover, above 600 °C they drastically sinter. It appears therefore necessary to increase the contact surface between the perovskite and the reactant by deposition on adequate supports. This mission is challenging because "classical" supports (Al_2O_3 and SiO_2) form non-active spinels with the majority of the transition metals [6,7]. New supports or amelioration of the known ones by coating with inert materials toward perovskite components seem to be the only solutions [8–11]. Zirconia and ceria containing materials are promising as supports due to their inability to enter into the perovskite lattice with any of the most used cations for environmental purposes, e.g. La, Co, Mn or Fe [12–16]. Another aspect to be considered is the choice of the preparation method for impregnated perovskites. Several synthesis methods for perovskite preparation were proposed but they lack of practical applicability due to either complicated procedures, low surface areas or the final material is an impure perovskite phase. We have shown previously that the thermal decomposition of citrate precursors offers the possibility to obtain perovskite-type oxides at relatively low temperatures, such as 600–700 °C [17,18]. Zhang et al. [19] also reported that

---

* Corresponding author. Tel.: +40 214103178; fax: +40 213159249.
E-mail address: v_parvulescu@chem.unibuc.ro (V.I. Pârvulescu).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.11.017

the citrate process leads to perovskites with small particle size and suggested that this process was promising for the preparation of supported perovskites [20,21].

The present work aims to discriminate different factors that may influence the activity of $LaCoO_3$ on different supports. For such a purpose, the perovskite behavior in total oxidation of toluene is compared with its performances after deposition on CeO_2 or on composite CeO_2–Al_2O_3 supports.

2. Experimental

2.1. Catalyst preparation

2.1.1. Support preparation

The experiments used the following supports: commercial Al_2O_3 balls (2 mm in diameter, 250 m^2/g) denoted A in the text and home-made CeO_2 (23 m^2/g) denoted C in the following text. CeO_2 was prepared by the ‘‘citrate method’’ [22] and calcined at 700 °C for 3 h. $LaCoO_3$ (denoted as P) was considered as perovskite. In order to prevent the formation of $CoAl_2O_4$ spinel and $LaAlO_3$ perovskite with Al from the support, previous $LaCoO_3$ perovskite deposition, Al_2O_3 balls were impregnated with a solution of $Ce(NO_3)_3·6H_2O$ and citric acid monohydrate in such a manner to result a monolayer of CeO_2. After contacting Al_2O_3 balls with cerium citrate, the water excess was eliminated in a rotary evaporator at 40 °C followed by drying in a vacuum oven set at 60 °C for 16 h under a pressure of 200 kPa. The resulting material was calcined at 700 °C for 3 h yielding ceria-stabilized alumina further denoted as CA.

2.1.2. Supported perovskites

$La(NO_3)_3·6H_2O$ and $Co(NO_3)_2·6H_2O$, and citric acid monohydrate were used as starting materials. Aqueous solutions with cation ratio La:Co of 1:1 were prepared. The citric acid was added in 10 wt.% excess to the stoichiometric amount necessary to form the corresponding citrates. A 10 wt.% $LaCoO_3$ was dispersed by incipient wetness on both supports.

After a slow evaporation, the drying process was completed by heating the powder in a vacuum oven set at 60 °C under a pressure of 200 kPa. Part of supported perovskite loaded on ceria-stabilized alumina was further impregnated with $Pt(NO_3)_2$ and $Rh(NO_3)_3$ in order to have a metal loading of 0.15 and 0.03 wt.%, respectively.

For comparison purposes, bulk $LaCoO_3$ was prepared by ‘‘citrate’’ method according to the procedure described in Ref. [18].

All the samples were calcined for 5 h at 700 °C in air.

2.2. Catalyst characterization

BET specific surface areas (SSA) were determined by nitrogen adsorption at the temperature of liquid nitrogen on a fully computerized Micromeritics ASAP 2000 instrument. The catalyst powder was degassed 2 h at 150 °C under a pressure of 0.1 Pa before each analysis.

XRD patterns were recorded on powder samples using a Kristalloflex Siemens D5000 diffractometer. Cu Kα radiation at $\lambda = 1.5418$ Å was employed. Data acquisition was realized in the 2θ range 2–65° at a 0.03° scan step.

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 with monochromatized Al Kα radiation ($h\nu = 1486.6$ eV). Charge neutralization was achieved using an electron flood-gun adjusted at 10 eV and placing a Ni grid 3 mm above the sample. Atomic composition of the surface was calculated using the sensitivity factors (Scofield) provided by the instrument software. Charge correction was made centering the C 1s signal of contaminating carbon (C–C or C–H bonds) at 284.8 eV.

2.3. Catalytic activity evaluation

Toluene complete oxidation was performed at atmospheric pressure in a quartz tubular reactor (i.d. 10 mm). Catalyst powders were obtained by crushing and sieving to 40–80 μm particle size the P/CA catalyst or by pelleting, crushing and sieving to the same particle size the powders of bulk P, C and P/C. Catalyst loading was typically 0.1 g and it was deposited between two quartz wool plugs. Before each catalytic run, the catalyst powder was activated in air (100 ml/min) for 1 h at 600 °C, in order to remove adsorbed species and to decompose residual carbonaceous deposits at the surface, and then cooled down to 150 °C.

For catalytic activity evaluation, 1700 ppm volume of toluene in air flowing at 100 ml/min was admitted and the temperature was raised up to 600 °C using steps of 25 °C. The CO_2 evolution in the outlet was continuously monitored by means of an on-line coupled Fisher–Rosemount multichannel analyzer. CO and hydrocarbons were checked as well using a Porapaq Q column mounted on a HP 5890 Series II GC equipped with a TCD detector. During catalytic runs, temperature was increased only after reaching a steady level of CO_2 in the outlet (typically after 25–30 min). Conversion levels at decreasing temperature superposed on the levels at increasing temperature.

3. Results and discussions

Surface area developed by P/C is 17.5 m^2/g with respect to that of bulk P (10.2 m^2/g). A similar decrease of the support surface area after impregnation with perovskite was observed for alumina, the surface area of P/CA being 125 m^2/g. It appears that $LaCoO_3$ tends to accumulate at the entrance of the support pores, blocking part of them. For the CA support the drop in surface area had a larger extent, very likely due to the smaller pore diameter of alumina with respect to ceria and $LaCoO_3$. Further impregnation of P/CA with Pt^{2+} and Rh^{3+} led to no textural modifications.

XRD pointed to a ‘‘clean’’ perovskite phase formation by citrate decomposition (Fig. 1(a)). It appeared then suitable to impregnate the supports via citrate precursors. Indeed, at the surface of CeO_2, the formation of $LaCoO_3$ can be followed by

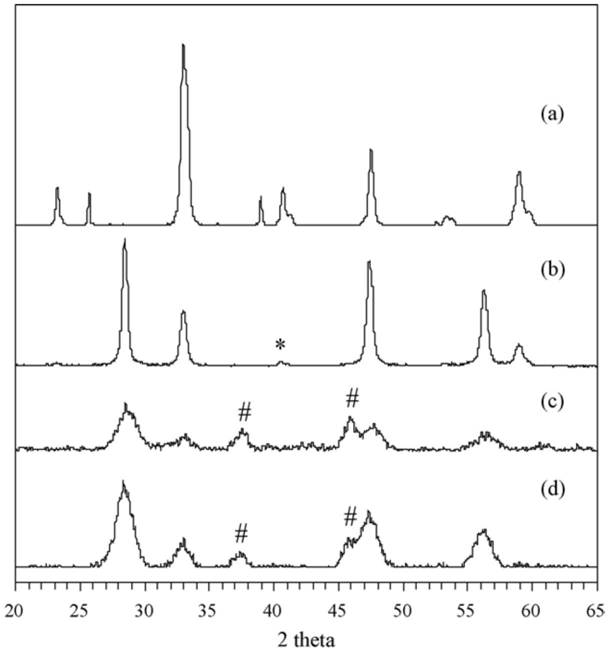

Fig. 1. XRD patterns for unsupported (a) and supported P ($LaCoO_3$): (b) C (CeO_2); (c) one layer of CeO_2 on Al_2O_3 (CA); (d) two successive monolayers of CeO_2 on Al_2O_3 (CA); (*) perovskite phase and (#) spinel phase.

less intense reflections of the perovskite phase (Fig. 1(b)). No other reflections that could be assigned to Co_3O_4 pointing to an incomplete reaction between La and Co are detected. On alumina support, in addition to the reflections of ceria, two lines centered at $2\theta = 37.9^\circ$ and 46.3° that might be ascribed to $CoAl_2O_4$ spinel were also detected (Fig. 1(c)). It resulted that one ceria monolayer was not enough for a complete coverage and, consequently, an effective stabilization of alumina surface prior perovskite deposition was achieved by deposition of two successive layers. XRD pattern of this support is presented in Fig. 1(d). The intensity of spinel lines decreased after the deposition of a second monolayer of CeO_2 (Fig. 1(d)). However, the spinel formation was not completely hindered. At the same time the remaining La_2O_3 possibly reacted with aluminium yielding $LaAlO_3$. However, on alumina-based supports no reflections of any perovskite phase were detected, very likely due to a dilution effect due to the fact that diffractograms were recorded on powders obtained by crushing the balls. Other previous works [16] showed that for lower surface area supports such as zirconia (82 m^2/g), for loadings below 12 wt.% the evidence of perovskite formation was proven by other alternative techniques such as XAS. In our case it is obvious that the real loading is below 10 wt.%, part of Co interacting with the support. At the same time a high dispersion degree of $LaCoO_3$ perovskite cannot be ignored and consequently, for such low loadings, the XRD signal cannot be followed.

Table 1
XPS results and specific reaction rates (at 300 °C) for all investigated catalysts

Support	La $3d_5$	Co $2p_3$	Ce $3d_5$	Chemical/ XPS [La/Ce]	Specific reaction rate (μmol s^{-1} g$^{-1}_{\text{perovskite}}$)
P/C	834.3	780.2	882.1	0.18/0.46	11.5
P/CA	834.5	779.8	881.8	0.15/1.4	2.7
Pt, Rh/ P/CA	834.6	780.2	881.9	0.15/1.4	4.2
C[a]	–	–	882.3	–	0.6
P[a]	834.0	779.9	–	–	1.6

[a] Values for bulk materials.

XPS measurements showed that the values of binding energies for supported La^{3+} and Co^{3+} are in the ranges corresponding to their oxides (Table 1). Moreover, there is practically no difference between the binding energies in bulk P and P/C and no shift and apparition of new peaks was observed (Fig. 2). This points out to no specific chemical interaction of La^{3+} and Co^{3+} of the active phase and CeO_2 support. On the other hand, on CA support the Co $2p_3$ level presented the

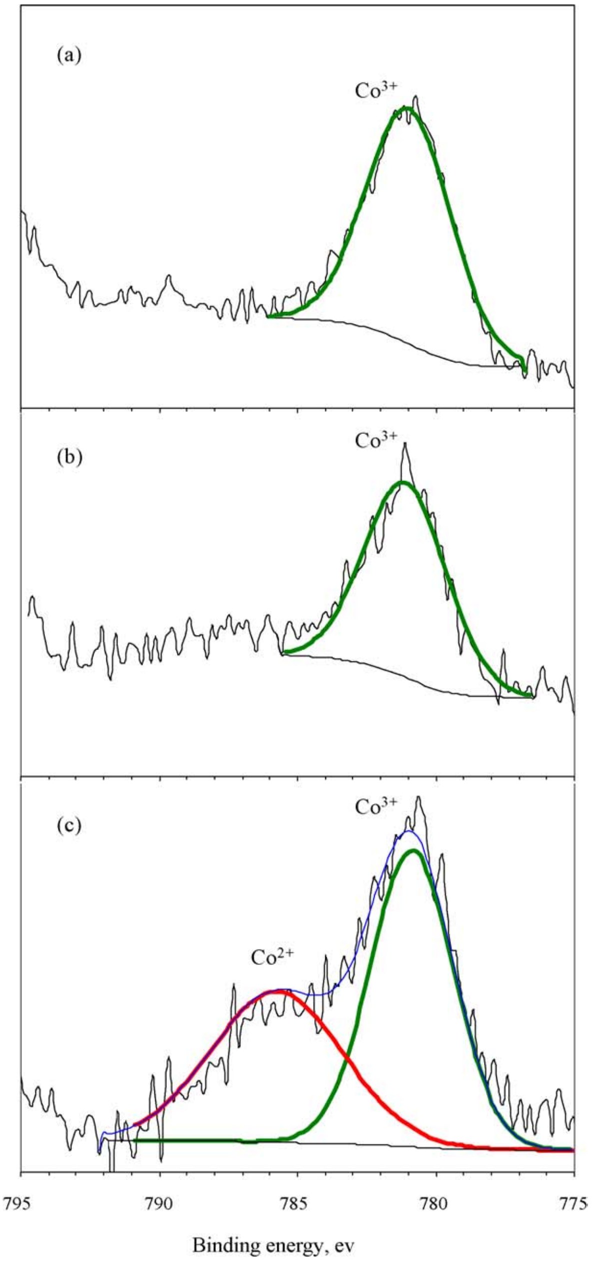

Fig. 2. XPS spectra in the region of Co $2p_3$: (a) P; (b) P/C; (c) P/CA.

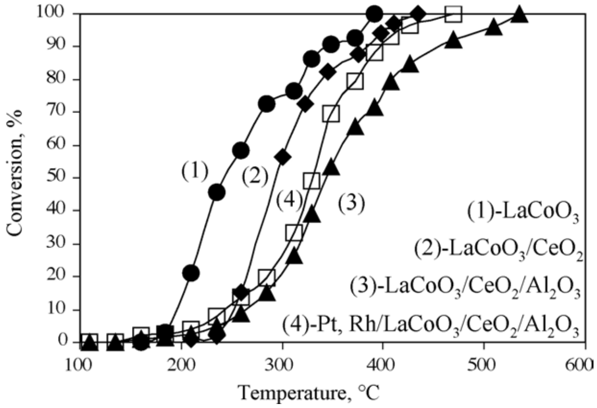

Fig. 3. Light-off curves for 1800 ppmV toluene in air on different catalysts.

characteristic satellite of Co^{2+} at 786 eV suggesting a partial interaction with aluminium from the support, yielding $CoAl_2O_4$. This sustains very well the data obtained by XRD (Fig. 1c and d). Due to the overlapping with the Al 2p signal, Pt was evaluated by means of the $4d_{5/2}$ core level. Pt and Rh are both dispersed in an oxidized form, having a binding energy of 318.3 and 308.6 eV, respectively.

The comparison between XPS and chemical [La/Ce] ratios point to a preferential accumulation of deposited phase at the external surface of the support. This observation can very well explain the drop in surface area after $LaCoO_3$ deposition by pore access blocking. The increased amount of La on CA supports with respect to C support is normal in view of Co reaction with aluminium yielding $CoAl_2O_4$.

Fig. 3 presents the catalytic behavior of supported samples containing 10 wt.% $LaCoO_3$ compared with pure perovskite. $LaCoO_3$, both in bulk and supported form, is a very active catalyst for complete oxidation reactions, completely converting toluene at temperatures below 500 °C. The global activity expressed by the light-off curves presented in Fig. 3 points out that the most active is the non-supported $LaCoO_3$ (P) that is characterized by a T_{50} of 240 °C, which is with 40 °C lower than in the case of P/C catalyst. P/CA catalyst presents a light-off curve shifted with about 100 °C to higher temperatures with respect to P sample and 80 °C with respect to P/C. Impregnation with noble metals brings about a 30 °C shift of the light-off curve towards lower temperatures. However, considering a first order kinetics with respect to toluene and zero order with respect to oxygen which is in large excess, applied for a plug-flow reactor [18] and expressing these results as reaction rates per mass unit of perovskite, a more complete image of the real effects of perovskite deposition may be obtained. The experimental conversions in the 10–90% range were considered. For all investigated catalysts, Arrhenius plots were linear, regardless the nature of the support.

The specific reaction rates, derived for a temperature of 300 °C, are listed in Table 1. By supporting $LaCoO_3$ its specific activity increased by a factor varying between 1.7 and 7.2 for 10 wt.% loading. Deposition of Pt and Rh on previously supported $LaCoO_3$ improves the reaction rate with a factor of 2.6. Only pure ceria used as support was less active than non-supported $LaCoO_3$.

The improve of combustive activity of $LaCoO_3$ can be related in a first approximation to a higher dispersion degree, all supported catalysts having a larger surface area than non-supported $LaCoO_3$. On CeO_2 the perovskite phase formation is sustained by the XRD patterns. When ceria impregnated alumina (CA) is used as support, the experimental evidences are not so obvious. The formation of perovskite at the surface of CeO_2/Al_2O_3 was not evidenced, although small size particles may exist. These are XRD silent. The two alumina-supported catalysts, namely P/CA and Pt, Rh/P/CA, were at least twice more active in terms of reaction rate than non-supported $LaCoO_3$, account taken mainly to the fact that the real loading of perovskite phase is below 10 wt.% since a part of La and Co reacted with alumina support. This fact can be an indirect evidence of the formation of such phases.

4. Conclusions

The results obtained in this work showed that $LaCoO_3$ is an active catalyst for toluene complete oxidation. Toluene total oxidation on perovskite-based systems is conducted to only non-noxious CO_2 without any CO or by-products formation. Deposition of $LaCoO_3$ on ceria-based supports brings an improvement in the specific activity with respect to bulk perovskite. Although a partial interaction of $LaCoO_3$ and ceria-stabilized alumina support cannot be avoided, leading to non-active $CoAl_2O_4$, the resulting catalyst presented a higher specific activity than non-supported $LaCoO_3$ very likely to a higher dispersion degree of the perovskite phase.

References

[1] R.M. Heck, R.J. Farrauto, Catalytic Air Pollution Control. Commercial Technology, Van Nostrand Reinhold, New York, 1995.

[2] R.J.H. Voorhoeve, in: J.J. Burton, R.L. Garten (Eds.), Perovskite Oxidation–Reduction Catalysts, Academic Press, New York, Adv. Mater. Catal. (1977).

[3] L.G. Tejuca, J.L.G. Fierro, J.M.D. Tascon, in: D.D. Eley, H. Pines, P.B. Weisz (Eds.), Structure and Reactivity of Perovskite-Type Oxides, Academic Press, New York, Adv. Catal. 36 (1989) 237.

[4] H. Arai, T. Yamada, K. Eguchi, T. Seiyama, Appl. Catal. 26 (1986) 265.

[5] D. Klvana, J. Kirchnerova, J. Chaouki, J. Delval, W. Yaïci, Catal. Today 47 (1999) 115.

[6] P. Arnoldy, J.A. Moulijn, J. Catal. 93 (1985) 38.

[7] F.E. Massoth in, D.E. Eley, H. Pines, P.B. Weisz (Eds.), Advances in Catalysis, vol. 27, Academic Press, NewYork, 1978, p. 265.

[8] S.D. Peter, E. Garbowski, V. Perrichon, M. Primet, Catal. Lett. 70 (2000) 27.

[9] P.E. Marti, M. Maciejevski, A. Baiker, Appl. Catal. B: Environ. 4 (1994) 225.

[10] R. Burch, P.J.F. Harris, C. Pipe, Appl. Catal. A: Gen. 210 (2001) 63.

[11] B. de Collongue, E. Garbowski, M. Primet, J. Chem. Soc. Faraday Trans. 87 (1991) 2493.

[12] H. Fujii, N. Mizuno, M. Misono, Chem. Lett. (1987) 2147.

[13] A.K. Ladavos, P.J. Pomonis, Appl. Catal. B: Environ. 2 (1993) 27.

[14] S. Chand, A.K. Sharma, A. Garg, I.M. Mishra, J. Sci. Ind. Res. 59 (2000) 944.

[15] S. Colonna, D. de Rossi, M. Faticanti, I. Pettiti, P. Porta, J. Mol. Cat. A: Chem. 187 (2002) 269.

[16] S. Cimino, S. Colonna, S. de Rossi, M. Faticanti, L. Lisi, I. Pettiti, P. Porta, J. Catal. 205 (2002) 309.

[17] D. Ferri, L. Forni, Appl. Catal. B: Environ. 16 (1998) 119.

[18] J. Kirchnerova, M. Alifanti, B. Delmon, Appl. Catal. A: Gen. 231 (2002) 65.

[19] H.M. Zhang, Y. Teraoka, N. Yamazoe, Chem. Lett. (1987) 665.

[20] H.M. Zhang, Y. Teraoka, N. Yamazoe, Appl. Catal. 41 (1988) 137.

[21] J.W. Geus, J.C. van Giezen, Catal. Today 47 (1999) 169.

[22] M. Alifanti, B. Baps, N. Blangenois, J. Naud, P. Grange, B. Delmon, Chem. Mater. 15 (2003) 395–403.