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Largely Cu-doped $LaCo_{1-x}Cu_xO_3$ perovskites for TWC: Toward new PGM-free catalysts

A. Glisenti[a,*], M. Pacella[a], M. Guiotto[c], M.M. Natile[a,b], P. Canu[c]

[a] *Dept. of Chemical Sciences - University of Padova, Via F. Marzolo, 1, 35131, Padova, Italy*
[b] *CNR-IENI, INSTM Via F. Marzolo, 1, 35131, Padova, Italy*
[c] *Dept of Industrial Engineering - University of Padova Via F. Marzolo, 9, 35131, Padova, Italy*

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ABSTRACT

Doping of $LaCoO_3$ with copper to add reduction functionality in addition to the known oxidation properties has been investigated, aiming at three-way catalysis (TWC) applications. Nanoscale perovskites with nominal composition $LaCo_{1-x}Cu_xO_3$, ($x = 0$, 0.1, 0.3, and 0.5) have been synthesized by means of the citrate method. A stable perovskitic phase with rhombohedral geometry up to an unprecedented $x = 0.5$ has been obtained and characterized by BET, X-ray diffraction (XRD), Temperature Programmed Reduction (TPR), X-ray Photoelectron Spectroscopy (XPS), and Scanning Electron Microscopy (SEM). The crystallite size decreases with increasing the copper amount and also the morphology differs; moreover the surface reactivity with respect to atmospheric moisture and carbon dioxide is more evident in the sample with $x = 0.5$. Reactivity has been measured in simple NO + CO and CO + O_2 model reactions, as well as with complex mixtures approaching automotive exhaust composition, at both stoichiometric and O_2 limiting conditions. The catalysts have been characterized after reaction as well. The perovskite with the highest Cu amount, $LaCo_{0.5}Cu_{0.5}O_3$, exhibits an interesting compromise of oxidation and NO reduction functionality at interesting, low temperatures with very short contact time (GHSV = 1,000,000 h^{-1}). Still, activity for NO reduction in real mixtures requires substoichiometric O_2.

1. Introduction

Three-way catalysts (TWC) have to achieve the elimination of 3 different types of pollutants simultaneously. They have to facilitate oxidation of CO and unburned hydrocarbons (HC) and reduction of NO. NO should be selectively converted to N_2 instead of NO_2, NH_3 or N_2O, that are toxic or greenhouse-gases. At the present, TWC catalysts still contain expensive noble metals as Pt, Pd and Rh, as well as rare earth metals, most of them included in the list of critical raw materials.

Perovskites, on the other hand, are known as versatile materials which allow the incorporation of different cations in their structure. Thus, the incorporation of inexpensive and largely available, catalytically active transition metal cations can be helpful in developing low-cost active catalysts for TWC.

Most studies on perovskites are focused on the oxidation of CO and HC: among the perovskites reported in the literature, $LaCoO_3$ and $LaMnO_3$ perovskite based oxides, appear to be the more active for the complete oxidation of CO and HC. As early as 1971, $LaCoO_3$ was suggested to be a good catalyst for automobile exhaust treatment [1]. Subsequently, several researchers [2–5] continued to investigate $LaCoO_3$ for exhaust control trying to improve its activity by doping or by means of rhodium; two approaches have been considered: the deposition of Rh onto $LaCoO_3$ surface and the insertion of this element into the perovskite [6,7]. Cimino et al. [6], in particular, studied Rh–La(Mn,Co)O_3 monolithic catalysts for the combustion of methane under fuel-rich conditions. $La_{0.9}Ba_{0.1}CoO_3$ perovskite catalysts have been investigated for the control of CO and Particulate Matter (PM) emissions [8]. Supported lanthanum cobaltate was studied as vehicular exhaust cleaning catalyst in the oxidation of propylene [9].

Several factors influence oxidation capability: the amount of active oxygen species (α-oxygen), as an example and the mobility of lattice oxygen. Oxygen vacancies are directly connected with lattice oxygen mobility: the higher the number of anion defects, the higher the mobility of lattice oxygen [10]. One of the possibilities is increasing the oxygen mobility by means of an aliovalent doping in the perovskite A site. In general, A and B sites doping can induce the formation of structural defects (anionic or cationic vacancies) and of different oxidation states (in the B site) and can thus be funda-

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* Corresponding author. Fax: +39 49 8275161.
E-mail address: antonella.glisenti@unipd.it (A. Glisenti).

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mental for the catalytic activity. Also the presence of cations redox couples is determinant.

Taking into consideration these aspects, several perovskites with rather complex compositions have been investigated, showing promising activity for CO and HC oxidation. In perovskites with B = Co, Cr, V, Mn, Ni, Al, as an example, the influence of B cations on the structure and activity was investigated. In particular it was observed that deformation of the octahedral coordination is evident in the less active perovskites; moreover the more active catalysts are capable of extensive oxygen adsorption [11]. Another important option is doping. The partial substitution of Co with Cu in the B site, as an example, was observed to strongly influence catalyst reducibility and catalytic activity [3]; also the doping in A-site, that can increase the vacancies and affect the oxidation state of the B cations, can be effective to increase the reactivity [12–16]. Beside composition other properties can affect the catalytic activity, such as surface area [17].

On the other hand, the efficiency of perovskites in NO_x reduction is often rather poor and needs further investigations. NO_x can be converted into innocuous gases mainly by three approaches: direct decomposition, selective catalytic reduction or NO_x storage and reduction.

Although, NO_x is thermodynamically unstable and it can decompose to N_2 and O_2, which is the simplest approach to NO_x removal, the decomposition reaction is inhibited by the high activation energy (364 kJ/mol). Therefore, a catalyst is required to facilitate the reaction.

Focussing on the reaction mechanism [18] the perovskite has to be able to promote CO oxidation (and thus the oxygen mobility/exchange) and the dissociative interaction of NO. In addition, the oxygen exchange between these species is likely to happen with the intervention of the surface anion vacancies. Several perovskites have been designed in order to present these properties. Literature data suggest that good activities can be obtained considering Fe, Co, and Mn in the B site [19–21]. For NO reduction significant improvement can be obtained by means of doping in the A-site [22–24]. Another interesting possibility is synthesizing composites in which the catalytic activity can be improved by the addition of several species; as an example, the presence of Co_3O_4 significantly modifies the activity of $LaCoO_3$ [25]. However this is not a general consideration and the influence of the presence of several phases has to be investigated case by case, as confirmed by Belessi et al. [26] that focussed on the influence of Fe_2O_3 addition to the $La_{1-x}FeO_3$ perovskite, in the NO + CO reaction. In spite of the work carried out so far, we believe that perovskites really active in TWC reactions are still lacking.

Copper doped perovskites of the type $LaCo_{1-x}Cu_xO_3$ are reported to be promising oxidation catalysts in spite of the difficulties in their synthesis. Porta et al. [27] concluded that the presence of a single perovskite phase of $LaCo_{1-x}Cu_xO_3$ was solely obtained at relatively high calcination temperature (≥800 °C) with $x < 0.4$. At higher concentration of copper ($x \geq 0.4$), a $LaCu_2O_4$ phase appears in addition to the $LaCo_{1-x}Cu_xO_3$ perovskite. Tien-Thao et al. [28] investigated $LaCo_{1-x}Cu_xO_3$ perovskites ($0 \leq x \leq 0.6$) obtained by reactive grinding from the corresponding oxides. In all cases residual oxide impurities are observed in addition to the rhombohedral phase. Lower copper contents ($x \leq 0.2$, 0.3) are more usual [29–34]; in spite of the rather low amount of copper, however, the presence of minor phases (Co_3O_4, CuO) was almost always observed.

Tien-Thao et al. suggested an interesting use of $LaCo_{1-x}Cu_xO_{3-\delta}$ powders for higher alcohol synthesis [28] whereas Lisi et al. [35] focused on the redox properties and reactivity in methane catalytic combustion and Glisenti et al. [36] on the reactivity in steam reforming and oxidative steam reforming of methanol and ethanol.

Focusing on the TWC application, Zhang et al. [31] studied Cu doped $LaCoO_3$ up to $x = 0.2$, demonstrating that this perovskite was more active in the NO decomposition; the perovskites were obtained by reactive grinding, at ambient temperature. To the best of our knowledge no attempt has been done so far to investigate the reactivity of Cu-rich $LaCo_{1-x}Cu_xO_3$ perovskites.

In this work we prepared and investigated the activity in TWC reactions of $LaCo_{1-x}Cu_xO_3$ perovskites, extending the amount of Cu above earlier synthesis usually reported in the Literature, i.e. $0 \leq x \leq 0.5$. The results are correlated to the XRD (X-ray Diffraction), XPS (X-ray Photoelectron Spectroscopy), TPR (Temperature Programmed Reduction), SEM (Scanning Electron Microscopy), BET characterizations, in order to understand the role played by copper and cobalt. To gain some understanding of the reaction mechanism, we first tested the prepared catalysts in CO + NO and CO + $1/2O_2$ model reactions. In addition, we also tested the TWC activity with complex mixtures simulating an automotive exhaust, that include steam, CO_2 and hydrocarbons. Actual exhaust composition and temperature could be very different with respect to common laboratory conditions (e.g. large NO and CO concentrations, lack of O_2) and extremely challenging to prove the effective activity of the prepared samples, in order to evaluate the effective applicability of such catalytic materials.

2. Experimental

2.1. Synthesis

The samples were prepared by the citrate method starting from La_2O_3 (Aldrich 99.9%), CuO (Strem Chemicals 99.999%) and CoO (Acros 99%). Citric acid monohydrate (Sigma–Aldrich 99%) is added to an aqueous solution of the cations (obtained by mineralization with nitric acid of the corresponding precursors) with a molar ratio of 1.9:1 with respect to the total amount of cations. Then the solution is heated up to 80 °C to promote water evaporation and to obtain a wet-gel. The gel is heated to 400 °C for 2 h in air to decompose the organic framework.

At the end of the heat treatment, the powder is grinded and calcined at 600 °C, for 6 h. The same procedure was adopted for the synthesis of $LaCoO_3$; in this case the powder was calcined at 650 °C (the minimum temperature to obtain the pure perovskitic phase).

2.2. Characterization

The XPS measurements were carried out with a PerkinElmer Φ 5600 ci Multi Technique System. The spectrometer was calibrated by assuming the binding energy (BE) of the Au $4f_{7/2}$ line to be 84.0 eV with respect to the Fermi level. Both extended spectra (survey –187.85 eV pass energy, 0.5 eV·step^{-1}, 0.05 s·step^{-1}) and detailed spectra (for La 3d, Cu 2p, Co 2p, O 1 s and C 1 s –23.50 eV pass energy, 0.1 eV·step^{-1}, 0.1 s·step^{-1}) were collected with a standard Al Kα source working at 300 W. The standard deviation in the BE values of the XPS line is 0.10 eV. The atomic percentage, after a Shirley-type background subtraction [37], was evaluated by using the PHI sensitivity factors [38]. The peak positions were corrected for the charging effects by considering the C 1 s peak at 285.0 eV and evaluating the BE differences [39].

The XRD analyses were performed with a Bruker D8 Advance diffractometer with Bragg–Brentano geometry using a Cu Kα radiation (40 kV, 40 mA, $\lambda = 0.154$ nm). The data were collected at 0.03° at a counting time of 10 s/step in the (2θ) range from 10° to 90°. The crystalline phases were identified by the search-match method using the JCPDS database. The phase compositions, structure, lattice parameters, and crystallite sizes of the powders were determined by Rietveld powder structure refinement analysis of XRD data, by using the MAUD (Material Analysis Using Diffraction) software [40], applying the RITA/RISTA method as developed by