A simple non-aqueous route to nano-perovskite mixed oxides with improved catalytic properties

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ABSTRACT

Highly crystalline LaB_xO_3 (B = Co, Mn) perovskites are produced through a simple non-aqueous benzyl alcohol (BA) route. Textural properties of BA-derived materials were compared to those obtained for solids of comparable composition, prepared by classical citric acid complexation method. Oxygen mobility in synthesized materials was evaluated by oxygen isotopic (^{18}O) exchange (OIE). Perovskites obtained with the BA route shows much larger specific surface area, smaller crystallite size and superior oxygen mobility. Such improvement in properties is in favor of low temperature catalytic oxidation, as evaluated by CO oxidation.

1. Introduction

Oxidic perovskites, of general formulae ABO_3 (where A and B are two cations), are important materials for heterogeneous catalysis [1–5]. Most of applications proposed for perovskites concentrate in the environmental catalysis (NO_x reduction [6], soot [7], CO [8], oxidation [9–11]). The B-cation, a transition metal, present redox characteristics that allow significant mobility of oxygen either on the surface or in the bulk of the solids conferring activities in redox-type reactions [3]. In addition to the fact that oxygen from the structure properties can be adjusted through network composition, these materials are recurrently proposed as noble metal substitutes since the 1970s [12,13], with always up to date interest of the academic community for the synthesis and application of these structures in heterogeneous catalysis processes [3,14]. The great composition versatility ($A_{1-x}A'_xB_{1-y}B'_yO_{3\pm\delta}$ – with possibility of A- and/or B- cation partial substitution, with obviously geometric and charge constraints), the excellent high-temperature thermal and

hydrothermal stabilities, and sufficient activity added to low cost of the constituting elements are at the origin of the infatuation of academicians for these materials [3,15–18]. The $LaBO_{3\pm\delta}$ compositions, with B = Co, Mn, are among the most studied compositions. While these solids both adopt perovskite structure, fundamental differences exist between these two materials: for $LaCoO_3$, cobalt oxidation number is initially +III and redox couple involved for catalysis is +III/ +II; for $LaMnO_{3+\delta}$, manganese presents initially both +IV and +III oxidation number, and +IV/+III is the redox couple involved in catalysis. Redox properties and catalytic performances of perovskites are however directly dependent on their textural and structural properties. Generally, conventional methods for perovskite preparation, such as calcination-milling, coprecipitation, complexation, etc. lead to large grain size, low specific surface area, and consequently limited activities are reported [2,3,19,20]. Large grain size in these solids comes from the high temperature needed for perovskite structure crystallization. This temperature is conditioned by the precursor homogeneity from the micro- to the atomic scale, which explains temperature of crystallization from 1000 °C and more (for calcination-milling synthesis, starting from poorly homogeneous precursor) to 600 °C (for complexation approaches, starting from atomically homogeneous precursor). In order to approach perovskite performances to that of noble metal catalysts, attempts to develop nanocrystalline porous materials,

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presenting smaller crystal domain size and higher surface area, was proposed using advanced synthesis approaches. Examples include reactive grinding [21], nanocasting [22] and flame-spray pyrolysis [23]. Reactive grinding is a top-down approach allowing the production of high surface area porous perovskite, starting from micron-sized oxide precursors [21,24]. Nanocasting objective is to synthesize perovskite in a confined environment that will ensure a limitation of the crystal growth during crystallization. Finally, concept proposed for the flame-spay pyrolysis consists in the short-time high temperature treatment of nano- to microsized drop of precursors, to generate isolated nanoparticles. Also, it is interesting to mention that nanocrystals of perovskites could be obtained through stabilization over porous supports [25].

Recently, another approach emerged for the production of oxide and mixed oxides. This route, the benzyl alcohol route, a water free organic-inorganic assembly process, offers excellent control over particle size and shape, crystallinity, order, purity, while it avoids the use of any surfactants or templates [26,27]. In this study, this original approach was adapted to the production of transition metal containing perovskites, LaB_xO_3 (B = Co, Mn). Oxygen mobility and redox capability, important parameters conditioning catalytic oxidation performances [3,28], are evaluated over these materials, and properties paralleled with properties for low temperature oxidation. CO oxidation is selected as reaction since it informs on the low temperature catalyst surface reactivity, which is a parameter to improve in order to make base metal catalysts competitive with classical Pt- and Pd-containing active oxidation catalysts.

2. Experimental section

$LaCoO_3$ and $LaMnO_{3+\delta}$ are synthesized according to the adapted procedure proposed for the synthesis of $LaFeO_3$ [28], based on water free benzyl alcohol assembly route. The complete description of the procedure to achieve perovskite crystallization is given in ESI file, Section 1.

Characterisation of materials is performed using X-ray diffraction (XRD), N_2 physisorption, Transmission Electron Microscopy coupled with energy dispersive X-ray spectroscopy (TEM-EDXS), scanning electron microscopy (SEM-EDX). Reducibility of cations is evaluated using H_2-temperature-programmed reduction (H_2-TPR). All procedures used for characterization are available in the ESI file, Section 2.

Temperature-programmed oxygen isotopic exchange $^{18}O/^{16}O$ (TPOIE) is performed in a recycling U-shaped microreactor. The recirculation volume (V = 60 cm^3; recirculation rate = 170 cm^3 s^{-1}) is coupled to a quadrupolar mass spectrometer (PFEIFFER VAC-UUM), with continuous gas sampling (regulated by a thermo-valve adjusted to maintain a constant pressure of 1×10^{-6} mbar in the ionization chamber of the mass spectrometer). 20.0 mg of calcined perovskite is inserted in the microreactor, heat treated up to 300 °C under O_2 (rate = 5 °C min^{-1}, total flow rate = 20 mL min^{-1}), and cooled down to 100 °C. Thereafter, the sample is evacuated under dynamic vacuum for 30 min 65 mbar of pure $^{18}O_2$ is introduced into the recirculation volume. The temperature-programmed exchange experiments are performed from 100 °C to 600 °C (temperature increase rate = 2 °C min^{-1}), and partial pressure evolution in $^{18}O_2$ (mass 36), $^{16}O_2$ (mass 32), and $^{16}O^{18}O$ (mass 34) are recorded by mass spectrometry during the heating process. N_2 (mass 28) is also recorded to detect any possible leak. Quantification of the ^{18}O fraction in the gas phase (α), the number of oxygen atom exchanged (N_{ex}), and the fraction of the solid exchanged at the end of the experiment (O_{ex}).

Activity of perovskite is evaluated for the CO oxidation reaction. The complete descriptions of activity tests are located in ESI file, Section 3.

3. Results and discussion

3.1. Perovskite structural and textural properties

X-ray diffraction patterns recorded for LaCo and LaMn samples by the non-aqueous benzyl alcohol route (BA), heat-treated at different temperatures from 600 °C to 1000 °C, and citrate reference samples issued from classical complexation route (CA), are presented in Fig. S1. Pure $LaCoO_3$ and $LaMnO_{3+\delta}$ phases are obtained, fitting with orthorhombic structures of $LaCoO_3$ (JCPDS card 48-0123) and $LaMnO_{3+\delta}$ (JCPDS card 50-0298), as classically reported [29–32]. After calcination at 600 °C, all materials, either from CA route or from BA route, are presenting reflexion attributable exclusively to the perovskite phase. For the BA-derived materials, reflections are of significantly lower intensities than for CA-perovskite (Fig. S1). Despite of the presence of only reflections located at 2θ positions corresponding to perovskite references, it is not possible to conclude on the obtaining of a fully crystalline material, free of amorphous matter and of single oxide phases. These reflections present intensities far above the noise background signal, and are exclusively located at awaited position for perovskite phase. Such result lets us to suppose that the perovskite phase is the main phase in these BA-derived materials, even after low temperature of calcination (600 °C). Increasing the calcination temperature induces, whatever the composition, an increase in intensity of the reflection added to a decrease in FWHM of peaks. This, coherent with literature data [33,34], shows an increase in crystal domain size with the increase in calcination temperature. When compared at 600 °C, the BA-derived solids present reflections that are less intense and broaden than that of CA-derived solids. Such result indicate that the BA-route is producing materials having crystals of lower size that using CA-route, when similar calcination temperature is used. Indeed, LaCo-BA presents crystal size of 14.8 nm after heating at 600 °C, a value to be compared to 31.1 nm for LaCo-CA activated at the same temperature. Comparable trend is obtained for the LaMn-derived materials (18.4 nm *vs.* 28.0 nm). This result is reflected in values of B.E.T. surface area (S_{BET}) and crystal domain size (S_{th}) in Table S1. However, as classically observed, a significant growth in crystal size is observed with the calcination temperature (Fig. S1), with for example, a size increasing from 14.8 nm (600 °C) to ~90 nm (after calcination at 1000 °C).

Indeed, larger surface area (21.7 m^2 g^{-1}, case of LaCo-BA) are obtained using the BA route after calcination at moderate temperatures (600 °C-Table S1), much higher than the value obtained by the CA route (8.9 m^2 g^{-1}, case of LaCo-CA). Similar trend is obtained for the LaMn-type material (26.3 m^2 g^{-1} vs. 17.5 m^2 g^{-1}) for LaMn-BA and LaMn-CA respectively. Then, materials having lower crystal domain sizes results in solids exhibiting larger surface areas.

Important differences between the S_{BET} value (measured by N_2 physisorption) and the theoretical surface area, S_{th} (calculated from crystal size determined by XRD, assuming a cubic-shaped crystal and supposing no contact between the elementary particles), are observed whatever the sample composition (Table S1). The S_{th}/S_{BET} ratio gives an indication of the fraction of surface lost by contact between nanoparticles in aggregates [25,35]. Then a ratio of 1 indicates no contact between the particles, assumed to be cubic, while high values of S_{th}/S_{BET} ratio indicate formation of dense aggregates with significant loss of exposed surface by contact between elementary crystals. It was found that the S_{th}/S_{BET} ratio is of great importance for the properties of the perovskites in oxygen mobility and kinetics of reaction [17]. Then, lower S_{th}/S_{BET} ratio is obtained for BA-derived materials, suggesting that this approach induce the formation of more porous aggregates than using CA route. In addition, the S_{BET} and S_{th}/S_{BET} ratio are plotted as a function of the calcination temperature for the LaCo-BA and LaMn-BA solids (Fig. 1). First of all, a decrease in S_{BET} is observed with the increase in