Design of nanocrystalline mixed oxides with improved oxygen mobility: a simple non-aqueous route to nano-LaFeO$_3$ and the consequences on the catalytic oxidation performances†

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LaFeO$_3$ nanoparticles, with improved oxygen mobility, leading to enhanced catalytic oxidation activities, are obtained through a simple nonaqueous route.

Perovskite oxides have demonstrated high potential in environmental heterogeneous catalysis. Some compositions have been proposed to be potential alternatives to the commercially supported noble metals as three-way catalysts (TWCs) since 1971. More recently, noble metal containing perovskites were industrially developed for automotive application, and in 2010, Li et al. confirmed the real potential of some of these materials for automotive pollution control, including as lean NO$_x$ trap catalysts. Among perovskites, LaFe-based perovskite structures attract much attention, due to their great versatility, excellent stability as well as interesting activities, in addition to low cost of the constituting elements. Besides, it is known that the redox properties and catalytic performance of perovskites depend critically on their physical properties. However, the conventional methods for perovskite preparation suffer from large grain size ($D$) and low specific surface area (SSA) over the final samples. Subsequently, some improved synthesis approaches, such as reactive grinding, nanocasting and flamespray pyrolysis, have been developed, preserving smaller crystal sizes ($<20$ nm) and larger SSA ($30$–$50$ m$^2$ g$^{-1}$) even after thermal treatment at temperature as high as $500^\circ$C. Achievement of better catalytic performances was then confirmed over these as-synthesized materials. Over particle size, shape, crystallinity, purity, and assembly behavior, avoiding the use of any eco-unfriendly additional surfactants or templates. Furthermore, nanocrystalline Ba(Sr)TiO$_3$ perovskites with diameters of 4–10 nm were successfully obtained, providing a novel and effective route to prepare other perovskite compositions.

In this study, LaFeO$_3$ nanoparticles were prepared. Besides, since oxygen mobility capacity, rather than redox ability, has been well correlated with the oxidation performance over Fe-based perovskites, oxygen isotopic exchange reaction was herein utilized to investigate the oxygen mobility capacities of the obtained samples, aiming at interpreting the different CO or CH$_4$ oxidation activities between the benzyl-alcohol-route (BA) and conventional citric-acid-route (CA) LaFeO$_3$.

The successful synthesis of nanocrystalline BaTiO$_3$ according to the BA route [ESI, materials section and XRD results section] was verified. Afterwards, a series of La and Fe sources as well as different solvolothermal reaction conditions were attempted, until the pure LaFeO$_3$ crystal phase was achieved. LaFeO$_3$ according to the CA method (details are provided in ESI, materials section and XRD results section) was also prepared.

The evolutions of SSA and $D$ versus calcination temperature for BA and CA samples are presented in Fig. 1. A SSA beyond $50$ m$^2$ g$^{-1}$ was achieved in the BA route after calcination at $450^\circ$C, which is among the highest values reported for the Ln-containing compositions. Moreover, the BA material shows a surface area of $43.6$ m$^2$ g$^{-1}$ after calcination at $500^\circ$C, which is nearly twice the value of the CA-500°C sample ($23.1$ m$^2$ g$^{-1}$), and is also superior to that of LaFeO$_3$ synthesized by reactive grinding ($30.5$ m$^2$ g$^{-1}$) after calcination at the same temperature. With thermal treatment at temperatures ranging from $500^\circ$C to $800^\circ$C, the SSA of the BA material is always twice higher and more than that for the CA material, while the $D$ value remains smaller. On closer inspection, it is observed that the differences between the theoretical ($S_{\text{th}}$) and BET ($S_{\text{BET}}$) surface area ratios (BA:CA) were found to be remarkable and became larger at higher temperatures (Table 1), sufficiently illustrating that the BA route mainly prevented the potential agglomeration of LaFeO$_3$ crystal grains.
in order to achieve excellent SSA, especially at high-temperature. Despite important modifications in surface areas between CA- and BA-materials, the isotherm shape always remains of type II according to the IUPAC classification. This result shows that the surface areas generated in both CA- and BA-derived materials in all cases originate from porosity developed in aggregates of elementary crystals.

Representative TEM and SEM images of the BA- and CA-LaFeO$_3$ samples calcined at 500 °C are shown in Fig. 2 and 3. BA material entirely consisted of relatively individual and quasi-spherical 10–20 nm particles, without large clusters or agglomerates (Fig. 2A and 3A). In contrast, a more compact aggregation of many interconnected particles was obtained through the CA route (Fig. 2B and 3B), leading to the large bulk and atactic arborescent structures. Such structures of CA-LaFeO$_3$ fully confirm the reason for its much lower SSA (43.6 m$^2$ g$^{-1}$ for BA vs. 23.1 m$^2$ g$^{-1}$ for CA) mentioned above. Besides, LaFeO$_3$ structure with its atomic ratio of La:Fe close to 1 was confirmed using EDX analysis for both samples, revealing the successful synthesis of homogeneous, bi-cationic assembly of nanoparticles (Fig. 3, inset). In addition, XPS analysis evidenced an Fe-surface enrichment over the BA-derived materials compared to CA-samples (ESI† file, XPS results section).

An apparently improved redox capacity over BA-LaFeO$_3$ was observed by H$_2$-TPR results shown in Fig. S5 and Table S2 (ESI†), attributed to its excellent physicochemical properties (see details in ESI,† H$_2$-TPR results section).

Temperature-programmed oxygen isotopic exchange (TPOIE) was undertaken given a general comparison of the oxygen mobility capacity over the two LaFeO$_3$ samples mentioned above. As presented in Fig. 4, it is noticed from the evolutions of $N_e$ that the first 25% (below 330 °C) oxygen atoms in both LaFeO$_3$ samples exhibited similar mobility, while more oxygen atoms were available in the medium temperature zone in the BA sample. From the evolutions of $R_e$ the exchange process over CA-LaFeO$_3$ could be apparently assigned to two steps: 260–380 °C and 380–600 °C. These two successive steps can be ascribed to the surface/subsurface (low temperature) and bulk (high temperature) exchanges, with different activation energies. This agrees with the observation over the CA-LaFeO$_3$-550 °C sample. 10 In the surface activation step, about 41% of the total oxygen atoms [$N_e$ (380 °C)/$N_e$ (600 °C)] were exchanged, with a $R_{max}$ of 7.13 $\times$ $10^{17}$ atoms g$^{-1}$ s$^{-1}$ at 330 °C. However, in the case of BA-LaFeO$_3$, the existence of the two corresponding steps was not so obvious, with a much higher $R_{max}$ of 1.37 $\times$ $10^{18}$ atoms g$^{-1}$ s$^{-1}$ at 345 °C for the first exchange step, during which 75% of the oxygen atoms from the solid participated in the exchange reaction. It is noted

![Fig. 1](image1.jpg)

**Fig. 1** Evolutions of SSA (obtained from BET measurement) and $D$ (calculated from X-ray line broadening) of LaFeO$_3$ samples versus calcination temperature.

**Table 1** The theoretical ($S_{th}$) and BET ($S_{BET}$) surface area ratios between BA and CA samples (BA : CA) obtained at each temperature

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800</th>
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<tbody>
<tr>
<td>Ratio of $S_{th}$</td>
<td>1.22</td>
<td>1.38</td>
<td>1.15</td>
<td>1.06</td>
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<tr>
<td>Ratio of $S_{BET}$</td>
<td>2.07</td>
<td>2.27</td>
<td>2.83</td>
<td>4.23</td>
</tr>
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* The theoretical surface areas were calculated from the surface area developed by a cubic unit volume of single crystal grain, assuming no agglomeration. $S_{BET}$ was obtained from BET measurement.

![Fig. 2](image2.jpg)

**Fig. 2** TEM images for BA-500 °C (A) and CA-500 °C (B).

![Fig. 3](image3.jpg)

**Fig. 3** SEM micrographs (main) and EDX spectra (inset) obtained for BA-500 °C (A) and CA-500 °C (B). Quantifications are given in atom%.

![Fig. 4](image4.jpg)

**Fig. 4** Evolution of the number of exchanged oxygen atoms ($N_e$) and exchange rate ($R_e$) versus temperature of reaction for CA- and BA-500 °C samples in TPOIE.
that the ratio of $k_{\text{max}}$ is so close to that of $S_{\text{Bulk}}$ (1.92 vs. 2.07) that it demonstrates the crucial effect of the SSA on oxygen mobility: higher SSA leads to availability of more surface/subsurface oxygen atoms for exchange. Besides, the contribution of the lower crystal domain size, $D$, cannot be excluded, as already identified in the case of LaCoO$_3$ type materials.\textsuperscript{21} Additionally, being the oxygen diffusion channel, the redox sites – Fe$^{3+}$/Fe$^{2+}$ – increased on the surface/subsurface (Table S1, ESI$^+$), which also promoted the oxygen mobility. Meanwhile, the nearness of the two exchange steps implies that the surface/subsurface and bulk oxygen activation temperatures were close, and numerous bulk oxygen atoms were exchangeable in the first step, according to the measured value of 75%. Consequently, about 34% [75% (for BA) – 41% (for CA)] = 34% of oxygen atoms were much easier to be activated in BA-LaFeO$_3$, which could be assigned to the enhancement of bulk oxygen mobility, compared to the CA one (see detailed description in ESI$^+$ TPOE part).

Finally, the $N_e$ values reached a plateau at 600 °C, which matches an equilibrium between the concentrations of $^{18}$O in the gas phase and in the solid. Taking into account the conditions of the TPOE experiment, the experimental values indicate that all the oxygen atoms, either from CA or BA, are exchangeable. Then, the slower exchange observed over CA is consequently related to a slower migration of the oxygen atoms from the bulk to the surface for exchange.

The CO or CH$_4$ oxidation activity results obtained for both LaFeO$_3$ samples calcined at 500 °C are presented in Fig. 5 and Fig. S6 (ESI$^+$). The temperature of 500 °C was selected to ensure the absence of the external Fe$_2$O$_3$ phase that can influence catalytic activity (see ESI$^+$ Fig. S7 and the associated discussion).

Much higher oxidation activity is obtained over the BA sample (see ESI$^+$ activity tests section). It has been proved in our previous study that CO oxidation reaction over LaFeO$_3$ perovskites proceeded through a redox surface oxidation mechanism in which surface oxygen from the solid is consumed, rather than through a pure suprafacial mechanism.\textsuperscript{22} Thus, a higher mobility of oxygen on the surface or even the subsurface as well as a better surface Fe$^{3+}$ redox capacity are absolutely favorable to this reaction, which can be correlated with the activity improvement achieved over BA LaFeO$_3$. For CH$_4$ oxidation, in view of the conversion occurring at higher temperatures than for CO oxidation, a contribution of the bulk oxygen mobility to the activity was noticed,\textsuperscript{21} and an intrafacial mechanism can be followed. Bulk oxygen atoms, which account for most of the total oxygen atoms in the solid, were activated at high temperature, in addition to the surface/subsurface ones. Therefore, the improved CH$_4$ activity over BA LaFeO$_3$ is explained by its enhanced oxygen mobility in the first exchange step which involves the bulk oxygen mobility, as compared to the CA one.

In conclusion, the successful extension of the benzyl alcohol route to the preparation of pure LaFeO$_3$ nanoparticles was described. BA-LaFeO$_3$ exhibited enhanced redox capacity and oxygen mobility, leading to strongly increased catalytic performances for CO and CH$_4$ oxidation reactions. Additionally, the synthesis of BA-LaCoO$_3$ and BA-LaMnO$_3$ will be reported soon, with further challenge to the substitution of BA-perovskite.

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Notes and references