



# Enhancing catalytic activity of perovskite-based catalysts in three-way catalysis by surface composition optimisation



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## ABSTRACT

Fe-based perovskites prepared with purposely lowered La-content, La<sub>1-y</sub>FeO<sub>3±δ</sub> (y=0, 0.1, 0.2, 0.33), by sol-gel synthesis were investigated for application in 3-way catalysis. It was proven by XPS that surface composition control can be achieved by controlling the bulk composition. The decrease of La-content leads to a lower La excess at the surface whereas the orthorhombic perovskite structure with smaller crystallite sizes remains unaffected. Catalytic activity of La<sub>1-y</sub>FeO<sub>3±δ</sub> was investigated under 3-way catalytic conditions. Surface composition optimisation strongly enhanced the catalytic performance of the perovskite by increasing the accessibility of the active Fe<sup>3+</sup> sites on perovskite and segregated Fe<sub>2</sub>O<sub>3</sub>. The estimation of Arrhenius parameters showed that CO and propylene oxidation seemingly proceed on different sites.

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## 1. Introduction

Nowadays, the catalytic after-treatment of exhaust gas from gasoline engines is very efficient for the simultaneous conversion of NO, CO and hydrocarbons (3-way catalysis – TWC). Such catalysts usually contain high loadings of precious metals (palladium or platinum and rhodium) as well as rare earth metal oxides such as ceria–zirconia [1]. However, the European commission recently listed these components as critical raw materials [2] and alternative solutions for TWC application have to be developed to avoid any risk associated with their supply or higher cost for catalytic converters in the future.

Perovskite catalysts were proposed a long time ago as potential candidates for TWC application [3,4]. More recently, Nishihata et al. [5] underlined the stabilization of noble metals on perovskite structure for TWC application. As found earlier by our group, the presence of oxygen and water in the feed at mild temperature (500 °C) induced a strong sintering of Pt nanoparticles on alumina whereas the use of LaFeO<sub>3</sub> perovskite as support prevented the growth of Pt nanoparticles. Direct visualization by high resolution TEM of Pt nanoparticles even with high loadings highlights stronger metal/support interactions on LaFeO<sub>3</sub> [6,7].

However, LaFeO<sub>3</sub> usually presents surface lanthanum enrichment evidenced by X-ray photoelectron spectroscopy by several groups [7–9] which was also reported for other La-based perovskites [10].

More recently we proposed the possibility to improve the catalytic performances as well as thermal resistance to deactivation through the use of lanthanum-deficient synthesis for perovskite [11]. Higher intrinsic reaction rates were obtained on La-deficient perovskites after ageing at 900 °C overnight. In the present study, we will present the impact of La/Fe ratio on La<sub>1-y</sub>FeO<sub>3</sub> solids using lanthanum-deficient synthesis for three-way catalysis application. The surface composition as well as physico-chemical properties were tentatively related to catalytic activity enhancement.

## 2. Materials and methods

### 2.1. Synthesis and characterisation

A series of perovskite catalysts was prepared by purposely reducing the lanthanum content, La<sub>1-y</sub>FeO<sub>3±δ</sub> (y=0, 0.1, 0.2, 0.33). The solids were synthesized by conventional citrate method [12] from the corresponding metal nitrates (La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) respecting a molar ratio of (n<sub>La</sub> + n<sub>Fe</sub>)/n<sub>citric acid</sub> = 1. Nitrate decomposition was done separately in a muffle oven before the ground solid was calcined at 600 °C for 8 h under air flow. The employed nomenclature is based on the nominal composition, i.e. the La/Fe atomic ratio of the precursors used during synthesis. To

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**Table 1**  
Composition of reaction mixtures in lean, stoichiometric (stoic) and rich conditions. Helium was used as balance.

[Gas] (vol.%)	NO	CO	CH <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O
Lean	0.1	0.5	0.0150	0.030	0.0150	0.167	0.935	15	10
Stoic	0.1	0.7	0.0225	0.045	0.0225	0.233	0.777	15	10
Rich	0.1	0.9	0.0300	0.060	0.0300	0.300	0.609	15	10

allow for easier reading, hereafter, we will use the simplified notation of La<sub>1-y</sub>FeO<sub>3</sub> instead of La<sub>1-y</sub>FeO<sub>3±δ</sub>.

A commercial hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) sample (Merck (p.A.)) was used for comparison. Furthermore, a mechanic mixture of hematite (12.4 wt.%) with the calcined LaFeO<sub>3</sub> (87.6 wt.%) was tested for comparison of catalytic performance with La<sub>0.7</sub>FeO<sub>3</sub>.

XRD analyses were performed on a Bruker AXS D8 Advance diffractometer as described earlier [11]. Likewise, unit cell parameters and crystallite sizes were determined by Rietveld refinement as before [11]. Specific surface areas (SSA) were determined by N<sub>2</sub> physisorption at -196 °C on 0.5 g of sample previously outgassed at 200 °C under vacuum during 2 h using the Micromeritics TriStarII. H<sub>2</sub>-TPR experiments were undertaken with a Micromeritics Autochem II 2920 using a flow of 5% H<sub>2</sub>/Ar. The H<sub>2</sub> consumption was monitored during a heating ramp of 5 K min<sup>-1</sup> from room temperature to 1100 °C.

Elementary analyses were performed by SCA (ISA-CNRS) using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

XPS analyses were carried out either on an AXIS Ultra DLD Kratos spectrometer equipped with a monochromatised aluminium source (150 W) and charge compensation gun or on a VG Scientific Escalab 220i-XL equipped with a non-monochromatised aluminium source (300 W), the energy of the Al source being 1486.6 eV. All binding energies were calibrated with C 1s core level at 285 eV.

SEM were recorded on a Hitachi SU70 SEM FEG. Samples were prepared by depositing the calcined powder on a conductive double-faced adhesive tape.

## 2.2. Catalytic performance measurements

NO<sub>x</sub> and reductants concentrations were measured in a fixed bed continuous-flow reactor during temperature-programmed reactions at a gas hourly space velocity of 60,000 mL h<sup>-1</sup> g<sup>-1</sup> (using 0.2 g (100–200 μm) of catalyst and a total flow rate of 12 L h<sup>-1</sup>) from 110 °C to 500 °C. The catalysts were successively exposed to stoichiometric, lean, and rich conditions and again to stoichiometric conditions at the end of this sequence to verify the occurrence of deactivation phenomena.

Complex realistic reaction mixtures containing major pollutants as well as inhibitors as CO<sub>2</sub> and H<sub>2</sub>O naturally present in gasoline engine exhaust gas were employed. Their compositions under stoichiometric, lean or rich conditions are listed in Table 1. Conversions were calculated according to Eq. (1) and molar flow rates.

$$X_i = \frac{F_{i,\text{inlet}} - F_{i,\text{outlet}}}{F_{i,\text{inlet}}} \quad (1)$$

## 3. Results and discussion

### 3.1. Chemical composition

Elementary analysis results (Table 2) are in line with the expected theoretical compositions. Surface atomic concentrations were investigated by XPS on the La<sub>1-y</sub>FeO<sub>3</sub> series. Compared to the nominal composition, all samples exhibit an excess of La at the surface. This non-stoichiometric behaviour at the surface of LaFeO<sub>3</sub>

**Table 2**  
Surface and bulk properties of La<sub>1-y</sub>FeO<sub>3</sub> (y = 0, 0.1, 0.2, 0.33) calcined at 600 °C.

	La/Fe atomic ratio		SSA (m <sup>2</sup> g <sup>-1</sup> )	d <sub>crystallites</sub> (Rietveld) (nm)
	XPS	ICP-AES		
LaFeO <sub>3</sub>	2.13	1.01	13.9	20.1
La <sub>0.9</sub> FeO <sub>3</sub>	1.64	n.a.	22.0	16.4
La <sub>0.8</sub> FeO <sub>3</sub>	1.31	n.a.	17.6	18.2
La <sub>0.67</sub> FeO <sub>3</sub>	0.88	0.66	21.5	12.6

was reported before [7–9]. In the investigated series, the extent of La excess at the surface decreases with the purposely decreased La-content.

As shown in Fig. 1, the atomic surface La to Fe ratio changes linearly with the nominal composition. In fact, the decreasing La-content in the bulk correlatively leads to a similarly decreasing surface La concentration. The intended impact of La-deficient synthesis to control surface composition was confirmed.

For all perovskites prepared with decreased La-content, the Fe 2p photopeaks (Figure S1) confirm the presence of trivalent Fe cations, this is in agreement with the supposed co-existence of LaFeO<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. It is very difficult to differentiate between Fe in LaFeO<sub>3</sub> and hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, because the chemical environment is very similar. A slight decrease in surface carbonates and other adsorbed oxygen species can be deduced from lower relative intensities of the corresponding bands in C 1s ( $\approx$ 289.9 eV) and O 1s ( $\approx$ 531.5 eV) photospectra (Figure S1).

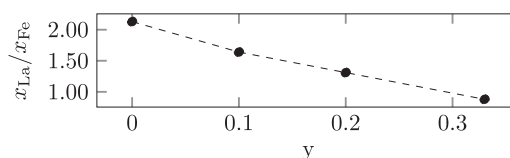
### 3.2. Textural properties

The textural properties of the solids with decreased La-content are differing from LaFeO<sub>3</sub>. In both cases, isotherms are a composite of type II, indicating a low affinity toward the adsorbate such as in macroporous solids, and type IV, indicating the additional presence of mesoporosity. This latter trend is favoured for lower La-content as highlighted by the broad opening of the hysteresis compared to the stoichiometric LaFeO<sub>3</sub> (Fig. 2). Hence, the broadest hysteresis showing mesoporosity has been observed for the sample prepared with the lowest La-content.

Pore volumes are slightly increased for the samples with lower La-content. The pore size distributions show an increased share of very low diameter mesopores ( $d_{\text{pore}} < 5$  nm) for decreasing La-content, confirming the growing contribution of type IV in the isotherms. This happens at the expense of the macropores ( $d_{\text{pore}} > 50$  nm). However, the microstructure morphology does not seem to evolve among all investigated samples as can be observed by SEM (Figure S2). The data in Table 2 reveals that the specific surface areas are higher for solids with decreased La-content. This increase was already observed before for Fe- and Mn-based perovskites [13,14].

### 3.3. Structural properties

The orthorhombic perovskite structure of LaFeO<sub>3</sub> is obtained for all solids of the La<sub>1-y</sub>FeO<sub>3</sub> series (Fig. 3). Only minor phase segregation of hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, is observed in the diffractogram for



**Fig. 1.** Evolution of surface atomic ratio La/Fe (XPS) on La<sub>1-y</sub>FeO<sub>3</sub> (y = 0, 0.1, 0.2, 0.33) series calcined at 600 °C.

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