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Shreya Nandi, Jiang Xiang Wu, Pardis Simon, Nicolas Nuns, Martine Trentesaux, et al.. Mn- or Cu-substituted LaFeO₃-based three-way catalysts: Highlighting different catalytically operating modes of La_{0.67}Fe_{0.8}M_{0.2}O₃ (M=Cu, Mn). Applied Catalysis B: Environmental, 2021, 296, pp.120330. 10.1016/j.apcatb.2021.120330 . hal-03322791

HAL Id: hal-03322791

<https://hal.science/hal-03322791>

Submitted on 19 Aug 2021

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Mn- or Cu- substituted LaFeO₃-based Three-Way Catalysts: Highlighting different catalytically operating modes of La_{0.67}Fe_{0.8}M_{0.2}O₃ (M=Cu, Mn).

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Abstract

The present work aims at presenting our investigations on the redox behaviour of Cu- or Mn-doped LaFeO₃-based perovskite powders under three-way catalysis (TWC) relevant conditions. Two distinct La-deficient catalysts of generic formula La_{0.67}Fe_{0.8}Mn_{0.2}O₃ and La_{0.67}Fe_{0.8}Cu_{0.2}O₃ denoted as Mn-dLFO and Cu-dLFO, respectively, were prepared based on the conventional citrate complexation route and systematically investigated using complementary characterisation techniques. This study has made it possible to highlight fundamentally different structures. In Cu-dLFO, most Cu²⁺ cations are expelled from the LaFeO₃ perovskite lattice in the form of a segregated CuO phase. On the other hand, in the case of Mn-dLFO, majority of Mn³⁺ cations are stabilised within the perovskite solid solution, while substantial iron exsolution in the form of an additional α -Fe₂O₃ phase was evidenced. The evolution of both catalysts during CO-TPR using *operando* Raman revealed the formation of polycyclic aromatic hydrocarbons (PAHs) besides the relative structural stability of the LaFeO₃ lattice. The reduction of Mn³⁺ to Mn²⁺, indirectly suggested by Raman analysis, is further supported by a quasi-*in situ* XPS study. The latter also evidenced the reduction of CuO to metal copper to a large extent in Cu-dLFO. In addition, a share of the α -Fe₂O₃ phase present in Mn-dLFO is reduced to metal Fe⁰ during CO oxidation, and is fully re-oxidised upon NO reduction. Our investigation thus evidences that both copper and manganese sites in Cu-dLFO and Mn-dLFO, respectively, are redox-active centres upon CO oxidation / NO reduction with, however, varying operating modes underpinned by their fundamentally different structures.

Introduction

In response to rising concerns on air quality, gasoline-based vehicles are nowadays equipped with efficient catalytic converters, which ensure the concurrent abatement of chief pollutants such as carbon monoxide (CO), nitrogen oxides (NO_x) and unburnt hydrocarbons (HC). Within the catalytic converter, a three-way catalyst (TWC) plays the simultaneous role of oxidizing the CO and HC and reducing the NO_x into molecular nitrogen via a redox process. [1]

The interest towards LaFeO₃ (LFO) perovskite-based materials for TWC application rose immensely with the discovery of their so-called "self-regenerating properties" by Nishihata *et al.* [2]. By means of an *in situ* investigation of a Pd-doped perovskite, LaFe_{0.57}Co_{0.38}Pd_{0.05}O₃, using X-ray diffraction and X-ray absorption spectroscopy, the authors have postulated that the palladium oscillates between lattice position under oxidative conditions and out of the lattice in the form of Pd⁰ nanoparticles under reducing conditions. This particular behaviour was proposed to be responsible for the standing catalytic activity of the perovskite-based catalysts in comparison with their alumina-supported counterparts, by preventing the sintering of noble metal particles and their subsequent deactivation [3]. Since then, this so-called *self-regeneration* phenomenon has been extensively investigated [4] and exploited [5, 6], revealing overall benefits of the use of perovskite-based oxide formulations for TWC applications while drastically lowering the content of platinum-group metals [7, 8].

Previous studies on LaFeO₃-based TWC by Schoen *et al.* have evidenced that purposely prepared La-deficient formulations, La_{1-x}FeO₃ (0.1 < x < 0.33), show better catalytic activity than the stoichiometric LaFeO₃ one, not only in CO oxidation but also in NO reduction [9]. The authors have correlated this catalytic enhancement with the restoration of a Fe/La ratio (XPS) close to unity at the surface of the material while LFO typically features a Fe/La atomic ratio of 0.4 to 0.6 at the surface [9, 10]. This trend is intrinsic to the perovskites prepared using citrate complexation route in combination with mild annealing temperatures (≤ 600 °C), typically preferred over solid-state reaction, for preparing highest possible specific surface area catalysts while keeping the perovskite structure. As a result of this compromise between structural and textural properties, the as-obtained materials show the expected bulk composition and perovskite structure, but feature a clear lanthanum enrichment at the surface. The latter has been assigned to the high reactivity of lanthanum oxides with air to form surface lanthanum hydroxides and carbonates [9–12].

Further, substitution at A- and/or B-site of the perovskite can effectively tune the catalytic properties by

varying the valency of the embedded cations and introducing lattice defects and ionic vacancies [13]. In parallel, the co-existence of two different cations at B-site can bring synergetic effects and hence, can enhance the overall reducibility [14]. It was shown recently by Wu *et al.* that a 20% substitution of Fe by Cu at B-site of a La-deficient $\text{La}_{0.67}\text{FeO}_3$, further denoted as dLFO, significantly lowers the temperature required for reaching 50% of CO conversion, $\theta_{50}(\text{CO})$, under TWC-relevant conditions¹ [15]. Indeed, while the $\theta_{50}(\text{CO})$ measured on dLFO was 385 °C, the $\theta_{50}(\text{CO})$ for Cu-doped dLFO with $\text{La}_{0.67}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ formulation was 260 °C. In general, the same trend is reported for Cu-doped stoichiometric LaFeO_3 , which all show enhanced TWC activity in comparison with the parent LaFeO_3 material [7, 16, 17]. Similarly, although less spectacular, 20% substitution of Fe^{3+} by Mn^{3+} yielding $\text{La}_{0.67}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_3$ stoichiometry also led to a noticeable lowering of the $\theta_{50}(\text{CO})$ by 45 °C under similar conditions. In the case of Cu-doped LaFeO_3 , such beneficial effect has been proposed to originate from a strong interaction between copper and iron-related species [16]. From a structural point of view, it is well established that at ambient pressure, La-Cu mixed oxides rather crystallize in the Ruddlesden-Popper phase (La_2CuO_4) instead of the simple ABO_3 perovskite phase [18–22]. This makes the occurrence of LaCuO_3 phase unlikely in the present case. Moreover, Cu-substitution has been widely carried out for yielding a series of $\text{AB}_{1-x}\text{Cu}_x\text{O}_3$ perovskite-based oxides, which can lead to the formation of the segregated CuO phase with a higher Cu content, typically for $x > 0.4$ [23–29]. On the other hand, Mn-substitution in ferrite perovskites, $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ with x ranging between 0 and 1, mainly results into a solid solution owing to close crystal parameters of LaFeO_3 and LaMnO_3 perovskites [30, 31]. In this paper, we present a systematic comparative study of Cu or Mn substituted $\text{La}_{0.67}\text{FeO}_3$ catalysts using *in situ/operando* spectroscopies to understand the beneficial role of each substituted B-site element under TWC-relevant model reaction. Particularly, we have used *operando* Raman spectroscopy to follow any structure-activity variations in the catalysts in real-time during CO-TPR. Moreover, quasi-*in situ* XPS was drawn upon to detect the chemical changes after a sequential exposure to CO and NO, while the structure and surface composition was refined using Fe K-edge XANES and ToF-SIMS analysis, respectively.

¹This complex feed involves CO and NO together with hydrocarbons and H_2O .

Materials and Methods

Sample preparation. The sample preparation was detailed elsewhere [15]. In brief, powders with $\text{La}_{0.67}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_3$ and $\text{La}_{0.67}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ formulation - further denoted as Mn-dLFO and Cu-dLFO for conciseness - were prepared using the citrate complexation method. Therefore, weighted amounts of nitrate salts of La, Fe, Cu and Mn were dissolved in de-ionised water and allowed to react with citric acid at 60 °C under reflux before being dried at 80 °C, decomposed at 150 °C and further calcined in air at 600 °C overnight.

Operando Raman analyses. The Raman spectra were collected in confocal mode using the 488 nm line of a Ar^+ laser (Melles Griot), focused on the sample placed in an atmospheric chamber (Harrick Scientific) equipped with a dedicated flat silica dome by means of a 50X long working distance objective (NA: 0.6, Olympus). The scattered light was guided through a 150 μm pinhole, dispersed and collected using a Peltier-cooled CCD implemented within a HORIBA HR equipment. The laser power was reduced using neutral density filters in order to avoid sample alteration. The gas feed composition was tuned using mass flow controllers (Brooks), while the gaseous products were analysed by means of a three-columns micro-GC (Agilent). Prior to the CO-TPR, both Mn-dLFO and Cu-dLFO powders were stabilised and dehydrated by means of a thermal treatment under dry air up to 450 °C with a ramp of 5 °C per minute and a dwell time of 1 hour.

Quasi-*in situ* XPS analyses were performed using a Kratos Analytical Axis UltraDLD spectrometer. The excitation was ensured by a monochromatic aluminum $K\alpha$ source at 1486.6 eV, while a pass energy of 20 eV for an analysed surface area of 700 μm x 300 μm was used. Charge compensation was applied to neutralize any charging effects. The measurements were done at a pressure of 10^{-9} mbar in the analysis chamber. All spectra were calibrated against the adventitious C 1s spectrum at 285 eV. Quasi *in situ* measurements were made using the catalysis cell, where the samples were thermally pre-treated under gaseous reactant flow at atmospheric pressure and then transferred to the analysis chamber under ultra-high vacuum (UHV). Both powders were stabilised by a thermal treatment up to 500 °C for 1 hour under O_2 before the CO (5% in He) or NO (2% in He) treatment.

XRD. The X-ray diffraction structural characterization of the powders were carried out using a Bruker AXS D8 Advance diffractometer using $\text{CuK}\alpha$ (1.5418 Å, 40kV, 30mA) radiation operated in the Bragg-

Brentano reflection geometry.

ToF-SIMS. The samples were analysed on a ToF.SIMS 5 spectrometer (ION TOF GmbH, Germany) equipped with a pulsed bismuth liquid metal ion gun with the primary ion cluster of Bi_3^+ (25 keV, 1 pA current) as heavier ions can promote formation of heavier fragments. The analysed area was $500\ \mu\text{m} \times 500\ \mu\text{m}$ for spectral analyses while maintaining static conditions.

XANES. measurements were made at SAMBA beamline in SOLEIL synchrotron facility (France) [32]. The beam size at the sample was $200\ \mu\text{m} \times 300\ \mu\text{m}$ with a focusing monochromator between two bendable cylindrical mirrors with 5-43 keV energy range. Spectra were collected at the Fe K-edge in the transmission mode. Reference powder compounds were recorded accordingly after proper dilution in boron nitride.

Results and Discussion

Ex situ physico-chemical properties

X-Ray diffraction (XRD).

The XRD pattern of Cu-dLFO powder is presented in Fig. 1a). The diffractogram shows the characteristic reflections of the orthorhombic LaFeO_3 perovskite with *pnma* space group (JCPDS PDF 37-1493). The lattice constants are $a=5.545\ \text{\AA}$, $b=7.857\ \text{\AA}$, and $c=5.550\ \text{\AA}$. In addition, patterns of weak intensity are visible at 35.6° and 38.7° , which are assigned to the (-111) and (111) reflections of a segregated CuO phase, respectively.

The diffraction pattern of Mn-dLFO shown in Fig. 1b) displays diffraction peaks at 32.2° , 40° , 46.1° and 57.4° , which can all be indexed according to the (121) , (220) , (202) and (240) reflection planes of single orthorhombic perovskite phase. As compared to Cu-dLFO, the diffraction peaks are broader by 35% on average, and slightly shifted to wider angle values. The lattice constants are $a=5.547\ \text{\AA}$, $b=7.815\ \text{\AA}$, and $c=5.536\ \text{\AA}$ with *pnma* (62) space group (JCPDS PDF 37-1493). No other reflection arising from additional phases such as Fe_2O_3 , La_2O_3 or Mn_2O_3 is observed.

X-Ray Photoelectron spectroscopy (XPS).

Both Fe 2p and Cu 2p photopeaks of Cu-dLFO are shown in Fig. 2. The Fe 2p signal at the binding en-

Figure 1: X-ray diffraction pattern of a) Cu-dLFO and b) Mn-dLFO.

Figure 2: XPS Fe 2p and Cu 2p spectra of Cu-substituted perovskite powder, Cu-dLFO.

ergy of 710.2 eV displays a shake-up satellite feature at 718.8 eV, typical of Fe^{3+} ions [33]. On the other hand, the shape of the Cu 2p photopeak envelope mostly refers to Cu^{2+} with a binding energy of 934.0 eV together with an intense and broad satellite around 943 eV [34]. From a quantitative point of view, a La/(Fe+Cu) atomic ratio of 0.68 is estimated, which is in line with the theoretical bulk composition. The atomic ratio of the B-site cations, Cu/Fe, is of 0.33 instead of 0.25 as per the $\text{La}_{0.67}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_3$

formula, indicating a slight surface over-representation of the copper content. A Fe/La ratio of 1.1 is estimated, which is identical to the one previously reported for $\text{La}_{0.67}\text{FeO}_3$ (dLFO) [9].

The Fe 2p and Mn 2p photopeaks of the as-prepared Mn-dLFO are presented in Fig. 3. The Fe 2p

Figure 3: XPS Fe 2p and Mn 2p spectra of Mn-substituted perovskite powder, Mn-dLFO.

signal is present at a binding energy of 710.4 eV also showing the characteristic Fe^{3+} satellite feature at 719 eV. The Mn 2p photopeak is detected at a binding energy of 641.8 eV, which is characteristic of oxidized manganese. Since the quality of the Mn 3s photopeak was too weak to allow in-depth analysis, the Mn 2p orbital has been used for refining the oxidation state. The Mn 2p spectrum has been fitted by relying on the multiplet splitting parameters given by Biesinger *et al.* as result of their refining of best parameters from various standard references of Mn oxides with fixed peak positions, relative areas and peak widths [33]. This systematic study makes it possible to quantify the average oxidation state(s) of manganese with reasonable reliability when Mn 3s is not available, since it provides robust multiplet splitting parameters to assist the peak fitting of Mn 2p orbital. Hence, the peak decomposition for the Mn 2p photopeak shown in Fig. 3 indicates that 100% of manganese stands as Mn^{3+} . Thereby, the as-received sample of Mn-dLFO perovskite contains both B-site cations in +III oxidation state. A La/(Fe+Mn) atomic ratio of 0.7 has been obtained, which stands in line with the nominal $\text{La}_{0.67}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_3$ formula, as is the case for the as obtained B-site ionic ratio, Mn/Fe, of 0.26.

Raman analysis.

The *ex-situ* Raman spectrum of the Cu-dLFO catalyst is shown in Fig. 4, together with that of the parent LaFeO_3 (LFO) perovskite for structural comparison. All the Raman lines characteristic of the modes

Figure 4: *Ex-situ* Raman spectra of a) Cu-dLFO and b) LFO; $\lambda_{exc.}=488$ nm (*colours online*).

of LaFeO_3 previously discussed in literature are detected at the expected wavenumbers in the Raman spectrum of Cu-dLFO [35, 36]. In brief, the La-centered vibrations, denoted as A modes are observed below 170 cm^{-1} , the FeO_6 octahedra tilt modes (T) are visible between 260 and 290 cm^{-1} while the bending modes (B) are responsible for the Raman lines around 430 cm^{-1} . The Fe-O stretching modes (S) are observed around 500 (anti-symmetric) and 625 cm^{-1} (symmetric). Noticeably, the scattering in the region of T and B modes is not as well resolved as in the parent LFO material, while the S modes region feature a clearly sharper line of larger intensity. In general, the Raman signature of CuO is composed of two sharp lines observed at $290\text{--}300\text{ cm}^{-1}$ (strong, Ag symmetry) and $340\text{--}350\text{ cm}^{-1}$ (weak, Bg) together with a broader component at $\sim 625\text{--}636\text{ cm}^{-1}$ (medium, Bg) [37, 38], while Cu(OH)_2 features Raman lines at ~ 292 and $\sim 488\text{ cm}^{-1}$ [38–40]. In addition, the mixed-valence phase Cu_4O_3 is generally identified from its broad Raman lines at 320 , 540 and 650 cm^{-1} [41]. In the present case, although CuO was detected by XRD, the Raman spectrum of Cu-dLFO showed no clear evidence of any copper oxide species and the poor signal quality has discouraged us to attempt a more detailed analysis. Note, however, that if any, the Raman lines of the copper oxide and related compounds would largely overlap with those of the LFO in the present case, making the technique possibly blind to such a minor

phase.

The Raman spectrum of Mn-dLFO is shown in Fig. 5. On the very first look, this Raman spectrum appears completely different from the parent LFO perovskite structure. Indeed, the overall spectral intensity and the signal-to-noise ratio are significantly higher as compared to the spectra shown in Fig. 4. Moreover, the A, T, B and S modes of LFO discussed earlier are not clearly visible, rather the Raman spectrum of Mn-dLFO is dominated by two intense peaks at ~ 500 and ~ 650 cm^{-1} together with a weak band at around 300 cm^{-1} . Actually, this spectrum is more alike the signature of the orthorhombic LaMnO_3 perovskite [42, 43] showing modes at 493 and 611 cm^{-1} related to oxygen motions. The intensity of those modes was proposed to be enhanced by the Jahn-Teller (JT) distortion [43] induced by Mn^{3+} cations having a d^4 electronic configuration in high spin state (E_g^1) [44]. In comparison with LaMnO_3 , all three modes shown in Fig. 5 feature a noticeable frequency shift towards higher frequencies, as was already reported for $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ solid solutions with perovskite structure [45, 46]. Hence, the Raman signature of Mn-dLFO suggests that a large share of Mn^{3+} cations are inserted at B site of a $\text{La}_{0.67}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_3$ solid solution.

Figure 5: Raman spectrum of Mn-substituted perovskite powder, Mn-dLFO ($\lambda_{exc.} = 488$ nm).

X-Ray absorption spectroscopy.

The Fe K-edge XANES spectra of Cu-dLFO and Mn-dLFO are shown as solid lines in Fig. 6a) and b), respectively. The XANES fingerprints of Cu-dLFO and Mn-dLFO powders show absorption edges of 7128.1 eV and 7127.6 eV, respectively, signifying the presence of Fe^{3+} ions, as expected for the LFO

perovskite [47]. This result is in full agreement with the XPS results, indicating that iron stands as Fe^{3+} cations at both the surface and the bulk of the catalysts. A structural refinement using LaFeO_3 and dLFO as reference materials was made, and the XANES spectrum of the most relevant reference was plotted as dotted lines together with the one of the catalysts in Fig. 6. Hence, the Fe-K edge XANES spectrum of Cu-dLFO is found to be similar to the one of LFO, while the Mn-dLFO is close to that of dLFO. Looking more in detail, the spectrum of Cu-dLFO actually shows a minor decrease of the white line intensity as compared to LaFeO_3 . A linear least-square fitting (LCF) analysis of Cu-dLFO, given in Fig. 6c) performed using reference spectra of iron oxides (Fig.S2 in supporting information) suggested that Cu-dLFO may contain some Fe^{3+} embedded in a minority $\alpha\text{-Fe}_2\text{O}_3$ phase besides the majority LaFeO_3 one.

Figure 6: Compared XANES spectra of (a) Cu-dLFO (blue) and LFO (red dotted), (b) Mn-dLFO (green) and LFO (yellow dotted) recorded at the Fe K-edge in transmission mode. Full XANES regions are shown in the insets. LCF analysis of the XANES spectra of (c) Cu-dLFO and (d) Mn-dLFO using Fe-based references.

On the other hand, the similarity of the XANES spectrum of Mn-dLFO to the one of the La-deficient dLFO material (Fig. 6b)) indicates that a more significant share of Fe^{3+} ions are involved in the $\alpha\text{-Fe}_2\text{O}_3$ phase, as was previously evidenced by our group for the $\text{La}_{0.67}\text{FeO}_3$ (dLFO) catalyst using Raman spectroscopy [48]. This is further confirmed by the LCF results shown in Fig. 6d), where no less

than 33% of the Fe^{3+} ions stands as $\alpha\text{-Fe}_2\text{O}_3$ and rest 67% as LaFeO_3 . The higher content of iron oxide in Mn-dLFO compared to the one of Cu-dLFO suggests that fewer Fe^{3+} are embedded within the perovskite lattice after Mn substitution.

To sum up the results discussed above, Cu-dLFO powder roughly consists of a LaFeO_3 supported CuO catalyst. Our XANES results suggests a possible minority hematite phase segregated on the surface, while we could not completely rule out the insertion of copper at B site of the perovskite as trace amount. On the other hand, Mn-dLFO is more alike the La-deficient material, dLFO, which embeds a mixture of orthorhombic perovskite together with a segregated iron oxide phase. Moreover, our results also suggests that most Mn^{3+} actually substitute Fe^{3+} at B site of the perovskite. This results in a large exsolution of Fe^{3+} as Fe_2O_3 . In order to support this assumption, we have tracked the presence of mixed oxide fragments in the mass spectra of both catalysts using ToF-SIMS analysis.

ToF-SIMS detection of surface mixed oxide fragments.

Figure 7: ToF-SIMS mass spectra of the mixed ionic fragments $\text{La}_2\text{FeMO}_5^+$ and $\text{La}_3\text{FeMO}_6^+$ ($\text{M} = \text{Cu}$ or Mn) from Mn-dLFO (a and c) and Cu-dLFO (b and d), respectively, analyzed in positive mode.

The detection of the mixed oxide ions produced by ToF-SIMS is a direct indication of the presence of a mixed oxide phase and unlikely from ionic recombination [49], which was further confirmed by us in the present case. The most representative mixed oxide fragments, namely $\text{La}_2\text{FeMO}_5^+$ and

$\text{La}_3\text{FeMO}_6^+$, where $M = \text{Mn}$ or Cu , are shown in Fig. 7 for both catalysts. In the case of Mn-dLFO, such ionic fragments are clearly detected, supporting the hypothesis of a single $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_{3\pm\delta}$ phase at the surface. In contrast, the intensity of similar mixed oxide ionic fragments is negligible in the case of Cu-dLFO. Similarly, their isotopes with ^{65}Cu and/or ^{54}Fe are completely absent in the mass spectrum. This highlights the fact that, if any, only a tiny share of Cu^{2+} ions stands at the B-site of the perovskite. Starting from the assumptions made above, a simple reasoning made by linking both the qualitative (from XRD and Raman) and quantitative (LCF of XANES) assessments with the nominal bulk compositions gives the structural picture of both catalysts shown in Table 1. Concerning the surface compo-

Table 1: Experimental bulk composition in Cu-dLFO and Mn-dLFO catalysts.

Sample	Composition		
Cu-dLFO	0.7 LaFeO_3	0.2 CuO	0.05 Fe_2O_3
Mn-dLFO	0.7 $\text{LaFe}_{0.7}\text{Mn}_{0.3}\text{O}_3$		0.15 Fe_2O_3

sition, our XPS results suggest that the surface of Cu-dLFO is largely covered by the segregated CuO phase, whereas there is no hint to support the surface localisation of the exsolved $\alpha\text{-Fe}_2\text{O}_3$ phase in Mn-dLFO.

***Operando* Raman monitoring of CO - temperature programmed reaction (TPR)**

Cu-dLFO

The *operando* Raman spectra recorded under a flow of 5% CO in He during the TPR are shown in Fig. 8.

- Between 25 and 100 °C, minor changes were detected in the Raman spectrum of Cu-dLFO, which include the transient detection of a sharp signal around 2135 cm^{-1} assigned to physisorbed CO together with an increase of the relative intensity of the *S* modes region.
- Between 100 and 250 °C, a broad line assigned to poly-aromatic hydrocarbons (PAHs) gradually emerges at $\sim 1595\text{ cm}^{-1}$. Meanwhile, the *T* and *S* modes of the perovskite decrease in intensity whereas the intensity in the region of *A* and *B* modes remains stable.
- Between 350 and 400 °C, the PAHs were detected yet again -after having vanished at 300 °C- while the intensity of *T* and *S* modes of the perovskite further decreased. Interestingly, the intensity of scattering between 100 and 200 cm^{-1} (*A* modes) was kept quite high. A similar deposition

Figure 8: *In situ* Raman analysis of Cu-dLFO during TPR under 5% CO/He at a) 25 °C, b) 100 °C, c) 200 °C, d) 250 °C, e) 300 °C, f) 350 °C and g) 400 °C. The Raman spectra were collected after 30 min stabilisation at a given temperature.

of PAHs was observed in the copper-free LaFeO_3 and $\text{La}_{0.67}\text{FeO}_3$ counterparts under similar conditions [48].

The corresponding CO consumption measured on-line during this experiment is shown in Fig. 9. During TPR, the CO consumption was accompanied by the formation of CO_2 with an associated carbon balance kept between 96.5 and 100%. As shown in Fig. 9 (left), the consumption of CO to CO_2 , marginal below 100 °C, sharply increased up to $0.105 \text{ mmol} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ at 170 °C. The CO consumption was found to rapidly drop during the plateau at 200 °C. This trend is not surprising in absence of a co-reactant, such as NO, to participate in the re-oxidation and regeneration of the active phase after reduction. Similarly, still less spectacular spurt-drop sequences were further detected between 250 and 350 °C, with another noticeable increase of CO consumption rate up to $0.091 \text{ mmol} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ at 400 °C. Fig. 9 (right) displays the CO consumption under isothermal conditions at 100, 200, 300 and 400 °C plotted against the same time range for allowing a direct visualisation of the deactivation kinetics. At 100, 200 and 300 °C, the CO consumption rate stabilised rapidly to 24.4 , 31.3 and $35.3 \mu\text{mol} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$, respectively. On the other hand, the CO consumption rate was still not stabilised after 1 hour reaction at 400 °C. More precisely, the CO consumption rate follows an exponential decay over time with a constant $\lambda = 0.28 \pm 0.04 \text{ min}^{-1}$ at 200 °C, while it is almost linearly decreasing at 400 °C ($\lambda = 0.028 \pm 0.001 \text{ min}^{-1}$). Keeping in mind that the regeneration of the active sites cannot be mediated by the gas phase and solely relies on

Figure 9: CO consumption rate as a function of temperature during *operando* Raman analysis of $\text{La}_{0.67}\text{Fe}_{0.8}\text{Cu}_{0.2}\text{O}_3$ under 5% CO/He; CO-TPR (left) and time representation (right).

the solid phase, this trend suggests that at mild temperatures (100-200 °C), a limited number of highly active surface oxygen species sustains the decent catalytic activity observed for only a short period of time. On the other hand, a more sizeable pool of less active oxygen moieties are engaged at 400 °C. These observations are in agreement with the commonly agreed description of adsorbed surface oxygen moieties, which drive oxidation reactions at milder temperatures, while bulk oxygens are involved at higher temperatures on migration to the surface [13, 50].

Besides the formation of PAHs and the subsequent increase of the broad lines at 1360 and 1595 cm^{-1} , the return spectrum recorded at 100 °C under He/CO after the CO-TPR is quite similar to the one recorded before under the same conditions with the exception of a slight decrease of the scattered intensity around 500 cm^{-1} (Fig.S1 in supporting information). This indicates that the changes observed in 100-800 cm^{-1} range by the *operando* Raman spectroscopy are mostly related to temperature-driven reversible processes.

Our *operando* Raman investigation has allowed to get only fragmentary data on the structural evolution of the active phase of Cu-dLFO during the model reaction. Hence, while Cu-dLFO was reaching a maximal CO consumption rate between 100 and 200 °C, the Raman signature of the catalyst barely evolved (see b and c spectra in Fig. 8), confirming that the technique was not capable of monitoring the structural evolution of the active phase. However, interestingly the first detection of PAHs at 200 °C coincides with the sharp increment of the CO consumption rate. Two regimes were detected for CO consumption, one fast process involving surface oxygen species present at mild temperatures (150-200 °C), and another one which requires higher temperatures. This higher temperature regime may indicate that

oxygen diffusion from the sub-surface to the surface has become the rate-limiting factor.

Mn-dLFO.

Figure 10: Raman spectra of Mn-dLFO during CO-TPR under 5% CO/He at a) 100 °C, b) 200 °C, c) 300 °C, d) 350 °C, e) 400 °C and f) 450 °C; Intensities of spectra c-f were magnified as indicated.

The evolution of the Raman spectra of Mn-dLFO upon heating under CO/He flux are shown in Fig. 10. While no change is observed up to 200 °C, new low-intensity peaks are visible at 300 °C around the 260-290 cm^{-1} region and 430 cm^{-1} , frequencies corresponding to the *T* and *B* modes of the LaFeO_3 structure. This trend is further confirmed by the comparison of Raman spectra recorded at 100 °C under CO at beginning and end of CO-TPR shown in Fig. 11. Moreover, some PAHs are also detected around 1595 cm^{-1} at 350 °C, while already detected at 200 °C in the case of Cu-dLFO. Although evidenced by XANES, the fingerprints of hematite (212, 280 and $\sim 425 \text{ cm}^{-1}$) were never detected along CO-TPR, as was, in fact, already the case for $\text{La}_{0.67}\text{FeO}_3$ [48]. The apparent recovering of the LaFeO_3 modes suggests that the J-T enhancement typical of the $\text{LaFe}_{1-x}\text{Mn}_x\text{O}_3$ phase is not at play any more. This could point towards a change of Mn^{3+} cations from d^4 electronic configuration featuring strong JT effect towards a JT-inactive one under reducing conditions.

The CO consumption rate recorded on-line during CO-TPR is shown in Fig. 12. In general, the CO consumption rate of Mn-dLFO is lower by at least one half as compared to Cu-dLFO. The maximal CO consumption rate per unit mass of catalyst is observed at 350 °C with a carbon balance maintained above 97% along the experiment. As for Cu-dLFO, the CO consumption rate rapidly decreased over time at

Figure 11: Raman spectra of Mn-dLFO recorded at 100 °C at beginning (black), after CO-TPR (red) under 5% CO/He and their 10X magnified difference spectrum (green).

each temperature plateau, but the pool of both surface and diffusible bulk oxygen species is significantly smaller as compared to Cu-dLFO.

Figure 12: CO consumption rate as a function of temperature during *operando* Raman analysis of Mn-dLFO under 5% CO/He; CO-TPR (left) and time representation (right).

Quasi-*in situ* XPS investigation of CO-NO sequence.

By using the quasi-*in situ* mode, it was possible to detect the chemical changes occurring under CO, especially for the Cu-related species, which was not accessible by *operando* Raman spectroscopy. The perovskites were initially thermally treated under 20% O₂/He for stabilization prior to the CO exposure.

After the CO treatment, the catalysts were also subjected to NO to observe the redox behaviour in each catalyst. Here, the La 3d signal around 834 eV representing the La³⁺ state remains unchanged during the redox treatment, as it is not expected to show any redox activity and therefore is not discussed here.

Cu-dLFO.

Figure 13: Quasi-*in situ* XPS spectra of Cu-dLFO powder recorded under UHV as-received (blue) and after reaction at 500 °C under 20% O₂/He (green), 5% CO/He (black) and 2% NO/He (pink).

The Fe 2p and the Cu 2p photopeaks recorded after activation under O₂ and subsequent reaction under CO and NO are displayed in Fig. 13. Meanwhile, the most relevant extracted quantification data are summarised in Table 2. After the O₂ step, the binding energy of Fe 2p is 710.4 eV, featuring a +III valence state, similar to the as-received state. In case of the Cu 2p, the binding energy is slightly shifted to 934.2 eV still retaining the intense satellite peak typical of Cu²⁺ species. Besides, the La/(Fe+Cu) and Cu/Fe atomic ratios remains unchanged at 0.64 and 0.34, respectively.

Catalyst reduction under 5% CO/He (500 °C). The XPS spectra of the B-site elements after CO exposure are shown in Fig. 13 (black line). The binding energy of Fe 2p, the intensity of the Fe³⁺ satellite as well as the FWHM values remains unchanged after the CO treatment, indicating that iron do not majorly participate in the redox process at play in Cu-dLFO. In contrast, the Cu 2p spectrum

Table 2: Summary of the data extracted from the quasi-*in situ* XPS spectra of Cu-dLFO; *: oxidation state.

	Fresh	After O ₂	After CO	After NO
A/B	0.68	0.64	1.14	0.82
Cu/Fe	0.33	0.34	0.11	0.17
Cu* _{os}	+II, (+I/0)	+II	0	+I, +II
Fe* _{os}	+III	+III	+III	+III
Fe as	LaFeO ₃	LaFeO ₃	LaFeO ₃	LaFeO ₃
Cu as	CuO	CuO	Cu ⁰	CuO, Cu ₂ O

undergoes drastic changes under CO: the Cu²⁺ satellite disappeared completely, the binding energy is shifted from 934.2 eV to 932.1 eV and the peak width is reduced. The latter is indicative of reduced copper species such as Cu⁰ or Cu⁺. Since binding energy for both are experimentally expected at the same value, the modified Auger parameter (α) can be used for accurate assignment of the oxidation state for copper, given by, $\alpha = E_{k(LMM)} + E_{b(Cu)}$, where $E_{k(LMM)}$ is the kinetic energy of the LMM Auger peak of copper (see supporting information) and $E_{b(Cu)}$ is the binding energy of the Cu 2p_{3/2} signal [34]. From our experimental data, α is estimated to be 1851.2 eV corresponding to metallic copper (Cu⁰). From a quantitative point of view, the A/B ratio increased severely after CO exposure from 0.68 to 1.14 (Table 2). This trend is mostly due to the drastic decrease (-78%) of the Cu/La atomic ratio at the surface, while the Fe/La ratio was reduced to a lesser extent by 32%. As a result, the Cu/Fe atomic ratio changed remarkably from 0.34 to 0.11. This evolution accompanies the reduction of Cu(II) to metallic copper, which can denote the reduction of formerly dispersed CuO moieties into larger Cu⁰ nanoparticles.

Catalyst re-oxidation under 2% NO/He (500 °C). Upon reaction with NO, the Cu²⁺ satellite appears in the Cu 2p signal again, along with a clear shoulder of the Cu 2p_{3/2} at 933.9 eV. At this point, the copper is present in two oxidation states, made evident from the presence of the photopeak at 932.1 eV. The calculated value of the α parameter was 1849.4 eV, corresponding to the one expected from Cu⁺ [34]. Thereby, the Cu⁰ formed under the CO step have partly re-oxidized to a mixture of CuO and Cu₂O after the NO exposure. The A/B site and Cu/Fe atomic ratios are only partially shifted back from 1.14 to 0.82 and 0.11 to 0.17, respectively, without recovering their initial levels before the CO or NO treatment. More precisely, while the Fe/La atomic ratio is almost recovered, the Cu/La one is only half restored.

Mn-dLFO.

Figure 14: Quasi-*in situ* XPS spectra of Mn-dLFO powder recorded under UHV as-received (blue) and after reaction at 500 °C under 20% O₂/He (green), 5% CO/He (black) and 2% NO/He (pink).

The quasi-*in situ* Fe 2p and Mn 2p photopeaks under each treatment step are shown in Fig. 14. After activation under oxygen, the surface chemistry did not change for Fe or Mn as compared to the as-received state. Both the Mn and Fe ions are present in the +III valence state.

Table 3: Summary of the data extracted from the quasi-*in situ* XPS and XANES spectra of Mn-dLFO; *: oxidation state.

	Fresh	After O ₂	After CO	After NO
A/B	0.72	0.69	1.37	1.08
Mn/Fe	0.26	0.23	0.31	0.34
Mn o.s.*	+III	+III	+II, +III	+II, +III
Fe o.s.*	+III	+III	0, (+II) +III	+III

Reduction under 5% CO/He (500 °C). After CO exposure, the Fe 2p signal exhibited the presence of metallic iron at 706.8 eV, corresponding to 6% of the total iron probed by XPS. The presence of Fe²⁺ from its satellite structure is not so obvious due to its overlapping with the predominant Fe³⁺ fingerprint. The spectral decomposition reveals less than 5-10% of Fe²⁺ component falling in the same range of uncertainty as the spectral decomposition, while the remaining exists as +III, leading to an average

oxidation state of 2.7 ± 0.1 of iron. The Mn 2p orbital has been decomposed according to the Biesinger parameters [33] as mentioned previously, and the corresponding fitting results (Fig.S3 in supporting information) showed the presence of 67% Mn^{2+} besides 33% Mn^{3+} (average oxidation state=2.3). From a quantitative point of view, Mn^{3+} cations show more extensive reduction at the catalyst's surface than Fe^{3+} , when reduced under CO. On the basis of our XANES results stating that Mn-dLFO embeds substantial amounts of $\alpha\text{-Fe}_2\text{O}_3$, and in comparison with the absence of Fe reduction under same conditions in Cu-dLFO, containing only limited hematite content, we assume that the reduction of Fe observed here mostly occurs at the $\alpha\text{-Fe}_2\text{O}_3$ phase. The reduction of hematite to metal iron involves the mixed II-III valence oxide Fe_3O_4 (magnetite) as intermediate [51].

Re-oxidation with 2% NO in He (500 °C). After the NO treatment, the Fe 2p photopeak returned to the very same shape observed after stabilisation under O_2/He , indicating that iron was fully re-oxidised into 100% of Fe^{3+} . On the other hand, Mn 2p signal, denoted that Mn remained partially reduced with 47% Mn^{2+} and 53% Mn^{3+} (average oxidation state= 2.7 ± 0.1). This means that only 30% of the Mn^{2+} re-oxidised back to Mn^{3+} when heated up to 500 °C under NO.

In brief, our quasi-*in situ* XPS investigation has made it possible to highlight different redox paths in Cu-dLFO and Mn-dLFO catalysts. In Cu-dLFO, the CuO phase participates in the redox process under CO/NO reaction completely, while the iron majorly remains as Fe^{3+} and embedded in the LaFeO_3 phase. The copper is reduced to metal Cu^0 nanoparticles under CO and re-oxidised to Cu^{2+} as CuO and Cu^+ as Cu_2O under NO. The CO/NO cycling is accompanied by a sintering of the copper phase, as revealed by the lowering of both A/B and Cu/Fe ratios. In Mn-dLFO, both Fe and Mn are reduced under CO. Two third of Mn^{3+} involved in the Mn-dLFO phase is reduced to Mn^{2+} on surface while a minor part of Fe^{3+} is reduced to metallic iron and likely some Fe^{2+} . The latter are fully re-oxidised to Fe^{3+} under NO, whereas the re-oxidation of Mn to Mn^{3+} is not complete and thus, led to a balanced mixture of Mn^{2+} and Mn^{3+} . The different reduction paths observed for Mn^{3+} and Fe^{3+} cations can be further made clear using the iron-oxygen thermal diagram. Indeed, it is widely reported that below 570 °C, the nominal Fe(+II) oxide FeO (Wüstite) decomposes into metal iron and magnetite according to the formal equation [52–54]:

Conclusion

Our present investigations have highlighted some major differences in the catalytic operating modes of two formally B-site, 20% substituted perovskites, namely Cu-dLFO and Mn-dLFO. Under dehydrated conditions, Cu-dLFO consists of a LaFeO_3 -supported CuO phase together with a minority iron oxide phase on the catalyst's surface. Under decoupled CO/NO model conditions, CuO is evidenced as being the only redox-active phase. We have also highlighted that all copper moieties are efficiently reduced from Cu^{2+} to metal Cu^0 under CO at 500 °C, while only partly re-oxidised to a mixture of +II and +I cations. Moreover, the Cu-dLFO catalyst retains a noticeable activity in CO oxidation at mild temperatures (around 200 °C), which can indicate the presence of a large pool of highly active surface oxygen moieties.

In contrast, the Mn-dLFO perovskite mostly consists of the perovskite phase together with an XRD- and Raman-blind surface Fe_2O_3 nano-phase, further confirmed by the XANES analysis. The Mn^{3+} ion causes strong JT effect that results in a complete change in the Raman fingerprint as compared to the parent structure of LaFeO_3 , while the reduction of Mn^{3+} to Mn^{2+} under CO allows the partial recovery of LaFeO_3 signature. The reduction to Mn^{2+} in presence of CO was confirmed by the evolution of the Mn 2p photopeak during the quasi-*in situ* XPS experiment. Interestingly, the Fe_2O_3 phase was also found to undergo redox behaviour, which could also play a role in the as-observed activity of the Mn-dLFO catalyst.

Acknowledgements

This work was funded by the European Commission as part of the PARTIAL-PGMs project under Grant Agreement #686086.

Chevreul Institute (FR 2638), Ministère de l'Enseignement Supérieur, de la Recherche et de l'Innovation, Hauts-de-France Region and FEDER are acknowledged for supporting and funding partially this work. The authors are thankful to the SAMBA beamline staff members at Synchrotron SOLEIL for their precious help in running the XAS experiments.

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