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# The influence of Ba addition on thermal stability and catalytic activity of Cubased mixed oxide

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ARTICLE INFO	A B S T R A C T				
Keywords: La <sub>2</sub> CuO <sub>4</sub> Barium NO reduction N <sub>2</sub> O Thermal stability	Catalytic reduction of NO by CO was studied over $La_{2.x}Ba_xCuO_4$ (x = 0.0 or 0.4) mixed oxides prepared by coprecipitation method. The catalysts were characterized by X ray diffraction (XRD), O <sub>2</sub> temperature-programmed desorption (O <sub>2</sub> -TPD), H <sub>2</sub> temperature-programmed reduction (H <sub>2</sub> -TPR) and X-ray absorption near edge structure (XANES). NO + CO reaction was carried out in a fixed-bed flow reactor, from room temperature to 500 °C, at atmospheric pressure. Both fresh catalysts were active for the NO + CO reaction but when were submitted to thermal aging, the barium free catalyst significantly lost its activity. The partial substitution of La by Ba enhanced the thermal stability and although the activity of the catalyst has decreased, it remains high, approaching 100 % at 500 °C. These results can be associated with reducible copper species observed by XANES in the thermal aged catalyst containing Ba.				

### 1. Introduction

Three-way catalyst (TWC) system consists of a complex mixture of noble metals such as Pd, Pt and Rh, promoter oxides and stabilizer agents [1,2]. The NO reduction by CO is one of the reactions that occur in this system. However, a high selectivity to  $N_2$  is only achieved at high temperatures (400 °C or higher) and depends on the catalyst formulation and the extent of deactivation. At low temperatures, nitrous oxide is preferably formed and emitted in the environment, since the catalyst is not effective in converting  $N_2O$  to  $N_2$  under these conditions.

One of the factors contributing to the  $N_2O$  emission from these catalysts is the presence of noble metals [3–5]. Studies using commercial TWC catalyst (bench test) confirmed the  $N_2O$  emission from the catalyst under real conditions [6,7].

In order to minimize the nitrous oxide emissions and for economic reasons, the replacement of noble metals by transition metals in TWC is highly advisable [8–17]. The use of copper has been investigated since its electronic structure is similar to that of noble metals, such as silver and gold, with completely filled d-subshells, in addition to being more environmentally friendly and lower cost. It was noticed that copper metal species act as effective active sites for NO chemical adsorption and reduction [18]. Despite the numerous studies carried out, few of these catalysts had their selectivity and thermal stability (due to high operating temperatures [19]) evaluated.

Perovskites related materials have been studied for vehicular

emission control for more than 45 years [19]. High activity and thermal stable structure make these materials appropriate catalysts for largescale applications [20]. In perovskite (ABO<sub>3</sub>) and perovskite-like oxides with  $A_2BO_4$  structure, the valence of cations of B-site, as well as the number of non-stoichiometric oxygen can be controllable by substitution of cations A or B, without destroying the structure of the matrix [21]. The perovskite type mixed oxides containing lanthanum have shown good catalytic properties, furthermore, it is possible to synthesize multi-component perovskites through partial cation substitutions [22,23].

La<sub>2</sub>CuO<sub>4</sub> catalyst, have already been tested in NOx reduction reaction and its structure is an orthorhombic (a = 5.363 Å, b = 5.409 Å, c = 13.17 Å) distortion of the tetragonal structure of K<sub>2</sub>NiF<sub>4</sub> [24,25]. It consists of Cu octahedron and La polyhedron coordinated to nine oxygen atoms [26] and is related to that of the LaCuO<sub>3</sub> perovskite [27], in which Cu environment is the same, but different for La. Fig. 1 shows a structural model of La<sub>2</sub>CuO<sub>4</sub> (ICSD 56528) and LaCuO<sub>3</sub> (ICSD 9428), build with Diamond [28]. As can be seen, the Cu octahedron in the K<sub>2</sub>NiF<sub>4</sub> type structure has more neighboring La atoms than in the perovskite one. Consequently, a displacement of the layer of the perovskite (LaCuO<sub>3</sub>) whose structure is rhombohedral, results in a structure with tetragonal symmetry (La<sub>2</sub>CuO<sub>4</sub>) [30].

A property of great interest of perovskites or perovskite-type mixed oxides is just the oxygen ions mobility  $(O^-, O^2)$ , which depends mainly on the existence of defects in the catalyst crystalline lattice. As the

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Fig. 1. Structural model in the view toward plane 110 of (a) La<sub>2</sub>CuO<sub>4</sub> and (b) LaCuO<sub>3</sub>. Octahedra correspond to Cu, gray balls to La and black balls to O.

oxygen ions are large, they are transported mostly by mechanisms involving vacancies and in a few rare cases by mechanisms involving interstitial oxygen [29-31]. The increase in the ionic radius can lead to an increment of the oxygen ion transport due to a decrease in the oxygen bond length and an increase of vacancy concentration [23,32]. Partial replacement of lanthanum by barium in the A-sites of these materials is considered a promising alternative not only due to its low oxidation state (+2), but also for its potential capacity to NO<sub>x</sub> storage [33–35]. Partial replacement by barium in LaMnO<sub>3</sub> perovskites has been shown to directly affect the redox properties and the lattice oxygen mobility, promoting oxygen vacancies formation and the rapid migration of lattice oxygen from the bulk to the surface [36]. It is also accepted that barium addition can also suppress the catalysts sintering [37]. According to Johnson [38] and Cao et al. [39], the alumina sintering was significantly reduced using barium as additive. Alumina textural properties were improved with Ba addition in low contents.

Thus, the present study aims to evaluate the influence of La partial substitution by Ba on La<sub>2</sub>CuO<sub>4</sub> oxide performance in the catalytic reduction of NO by CO focusing on activity, selectivity (N<sub>2</sub>O formation) and thermal stability.

### 2. Experimental

The mixed oxides with nominal formulas La2CuO4 and La<sub>1,6</sub>Ba<sub>0,4</sub>CuO<sub>3,8</sub> (20 % molar replacement of La by Ba) were synthesized by coprecipitation method adapted from the method described by Liu et al. [40]. Two distinct solutions, Na<sub>2</sub>CO<sub>3</sub>/NaOH with Na concentration equal to 3.0 mol  $L^{-1}$  and the metal nitrates of La/Ba and Cu with a concentration of 1.0 mol  $L^{-1}$ . The solutions were added dropwise and simultaneously to a beaker containing 100 mL of distilled water. The addition was carried out by dosing pumps and the pH was controlled to maintain it constant around 10. It was obtained a gelatinous precipitate, which was washed with distilled water until reaching neutral pH and then was washed using 150 mL of ethanol to eliminate the sodium ions. The obtained precipitate was dried at 75 °C for 12 h. The precursors of La2CuO4 and La16Ba04CuO38 oxides were calcined in air for 4 h at 650 °C and 700 °C, respectively. Calcination temperatures were determined according to the thermogravimetric analysis results. The catalysts were subjected to thermal treatment at 900 °C for 4 h, in order to evaluate their thermal stability. The fresh catalysts were named LaCu and LaBaCu and the catalysts submitted to the thermal treatment, LaCu900 and LaBaCu900.

The chemical composition of the solids was measured by inductively

coupled plasma optical emission spectrometry (ICP-OES) technique, performed using a Spectro brand equipament, model Arcos. The surface area of the samples was determined using a Micromeritics ASAP 2020 analyzer. Prior to the analysis, the samples were degassed under 50 mTorr vacuum at 300 °C for 2 h. X-ray diffraction patterns were obtained by the powder method and collected on a Rigaku Miniflex II equipment, using Cu K $\alpha$  radiation (30 kV/15 mA), step size of 0.05° step<sup>-1</sup> with step time of 2.0 s step<sup>-1</sup>, collected in a 2 $\theta$  range from 10 to 80°.

O<sub>2</sub> temperature programmed desorption (O<sub>2</sub>-TPD) measurements were carried out in a multipurpose unit AutoChem 2920 Micromeritics coupled to a mass spectrometer Pfeiffer Vacuum OmniStar, following the masses 18, 28, 32 and 44. Initially, 50 mg of the catalyst was pretreated at 300 °C for 40 min under He flow at a rate of 10 °C min  $^{-1}$ . The sample was cooled down to room temperature (RT) and then performed the oxygen adsorption under 5 %  $O_2$ /He at a rate of 10 °C min<sup>-1</sup> from room temperature to 800 °C, kept at this temperature for 30 min. Subsequently, the sample was cooled down under the same gas mixture flow. Upon reaching room temperature, the catalyst was purged with He for 30 min. Finally, the sample was heated under He flow at a rate of 10 °C min<sup>-1</sup> up to 1000 °C to record the TPD spectra. The desorbed O<sub>2</sub> quantification was carried out considering a prior calibration with the mixture containing 5% O<sub>2</sub>/He, using a known volume loop. H<sub>2</sub> temperature-programmed reduction (H2-TPR) analyses were also performed in the multipurpose unit AutoChem 2920 Micromeritics. Initially, 100 mg of sample was pretreated in argon flow at 300 °C for 60 min. After cooling down to room temperature, a catalyst reduction was performed with a mixture 10 %  $H_2$ /Ar flowing at 30 mL min<sup>-1</sup>, at a heating rate of 10 °C min<sup>-1</sup> up to 500 °C.

X-ray absorption near edge structure (XANES) spectra were measured at the D06A-DXAS beamline of the National Synchrotron Light Laboratory (LNLS) in order to determine the copper oxidation state under the reaction conditions. A Si (111) monochromator was used to select the X-ray beam from the synchrotron light produced by the 1.37 GeV electron storage ring with a maximum stored current of 200 mA. The Cu K-edge absorption spectra were recorded in the transmission mode, in a range of photon energy from 8950 to 9150 eV, using a CCD camera. The reactor consisted of a quartz tube, where the pellet was placed in a sample holder, positioned perpendicular to the gas flow but not necessarily percolated by it. The reaction was carried out with a stoichiometric gas mixture (NO (1%), CO (1%), balance in He); from room temperature to 500 °C at a heating rate of 5 °C min<sup>-1</sup>. A pretreatment at 150 °C under He stream for 1 h was performed to remove

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the physisorbed water in the catalysts. For LaBaCu sample, an experiment using a reducing pretreatment (H $_2$  flow, 500 °C, 1 h) was also conducted.

XANES spectra were normalized using Athena software from the IFEFFIT software package [41]. Some spectra obtained at intermediate reaction temperatures were chosen and a linear combination was performed using the initial and final spectra as standards. Thereafter, XANES spectrum obtained at the end of the reaction was quantified using the initial spectrum and the standards (CuO, Cu<sub>2</sub>O and metallic Cu), in order to determine the quantities of copper species and initial oxide present in the catalysts at the end of the reaction.

Catalytic tests were carried out in a fixed-bed flow reactor with a vertical furnace (PID temperature control) and a HP6890 chromatograph coupled. External and internal diffusion limitations were experimentally evaluated with one of the most active catalysts available in our laboratory. Regarding the internal diffusion effects, catalyst activities were measured for several catalyst particle sizes which allowed us to define a granulometric range free from internal diffusion limitations. For external diffusion limitations, the conversion was measured for different flowrates at the same space time, which provided us a flowrate that ensured the absence of external diffusion problems. The size of the catalyst particles and the flow rates used in the catalytic test of the present work were chosen in order to guarantee that diffusion problems did not limit the catalytic processes.

The tests were accomplished with 120 mg of the sample, previously sieved (40–60 mesh size fraction). The catalysts, in the selected granulometry, were diluted in silicon carbide in a mass ratio of 1:3. This procedure minimizes the formation of hot spots inside the reactor and contributes to the reproducibility of the tests. Prior to the catalytic activity tests, the catalysts were either pretreated under He stream at 150 °C for 1 h to remove the physisorbed water or subjected to a reduction pretreatment (H<sub>2</sub> flow, 500 °C, 1 h). The catalytic activity evaluation was carried out using a mixture containing 1% CO and 1% NO in He, under 225 mL min<sup>-1</sup> flow and temperature ramp of 2 °C min<sup>-1</sup> from room temperature to 500 °C.

#### 3. Results and discussion

Table 1

#### 3.1. Characterization of the catalysts

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The chemical analysis of the solids by ICP-OES is presented in Table 1. In addition to the mass percentages of each element, the molar ratios are also presented. For LaCu sample, the La/Cu molar ratio is equal to 1.40, below the desired value of 2 (for La<sub>2</sub>CuO<sub>4</sub>). Almost the same ratio (La/Cu) was obtained for LaBaCu sample, but in this case, the Ba incorporation increased the (La + Ba)/Cu molar ratio, which reached the value of 1.8. The Ba/La molar ratio was 0.2 instead 0.40 (the nominal value). From these molar ratios and considering oxidation state for La, Ba and Cu as +3, +2 and +2, respectively, it was proposed a formula for each solid, showed in Table 1. The results indicated that larger atoms (La e Ba) are more difficult to incorporate from the solution to the solid during the coprecipitation process.

The BET surface area values for the fresh samples were less than 10 m<sup>2</sup> g<sup>-1</sup> as observed in Table 2. Thermal aged samples presented negligible area. Previous studies shown that perovskite or perovskite-like oxides calcined in the temperature range of 650–950 °C present surface

 Table 2

 Amount of desorbed oxygen and surface areas of the catalysts.

Catalyst	Amount of desorbed	Surface area (m <sup>2</sup> /g)	
	$\alpha$ (T < 600 °C)	$\beta$ (T > 600 °C)	
LaCu LaBaCu LaCu900 LaBaCu900	- 45 - 146	870 327 948 432	2.5 2.2 0 0

area values generally lower than 10 m<sup>2</sup> g<sup>-1</sup> [23,40]. The partial replacement of La by Ba did not cause significant changes in the surface area values that remained very low or negligible.

The diffractograms of the perovskite-type mixed oxides are shown in Fig. 2. For the LaCu sample, only the presence of the orthorhombic La<sub>2</sub>CuO<sub>4</sub> phase is verified (ICSD 56528). According to the literature, although La<sub>2</sub>CuO<sub>4</sub> with a K<sub>2</sub>NiF<sub>4</sub> structure exhibit a tetragonal symmetry, a structural distortion may occur, which means that an orthorhombic and not tetragonal structure can be obtained [24]. After thermal aging, the LaCu900 sample remained showing a characteristic diffractogram of the orthorhombic La<sub>2</sub>CuO<sub>4</sub>, but it also exhibits small peaks at 35.4, 38.9 and 48.9° (20) belonging to CuO (ICSD 291393). It indicates that occurs a segregation of CuO crystalline phase after catalyst exposure to more severe conditions. The chemical analysis and XRD results suggest that LaCu900 is a mixture of La<sub>2</sub>CuO<sub>4</sub> and CuO. According to the stoichiometry proposed in Eq. (1), the La<sub>2</sub>CuO<sub>4</sub>/CuO ratio is 2.3 (0.7/0.3). Therefore, it is possible that these two phases are already present in the fresh LaCu catalyst, but in this case, CuO would be amorphous or with crystalline fractions undetectable by XRD.

$$La_{1,4}CuO_{3,1} \rightarrow 0.7 La_2CuO_4 + 0.3 CuO$$
 (1)

The LaBaCu diffractogram shows that the partial substitution of La by Ba induced a small change in the crystalline phases present in the mixed oxide. Although the diffractogram remains predominantly characteristic of orthorhombic La<sub>2</sub>CuO<sub>4</sub> perovskite-type mixed oxide, different peaks are observed in 23.8, 27.6, 34.6 and 46.9° (20) characteristic of BaCO<sub>3</sub> (ICSD 15196).

After thermal aging of LaBaCu, the characteristic peaks of BaCO<sub>3</sub> practically disappeared, but new diffraction peaks appear at  $2\theta$  values of 22.7, 32.4, 39.9, 46.4 and 57.6°, indicating that the thermal aging promoted the formation of a new phase. This phase was identified as the tetragonal La<sub>1.5</sub>Ba<sub>1.5</sub>Cu<sub>2.94</sub>O<sub>6.84</sub> phase (ICSD 62923), with a tetragonal YBa2Cu3O7 structure, that has triple layers of perovskite with defects, especially oxygen vacancies [42]. These results indicate that up to 700 °C part of the Ba was not inserted into the mixed oxide structure, but with the thermal aging at 900 °C, the Ba atoms from BaCO<sub>3</sub> underwent a solid-state reaction giving rise to a La-Ba-Cu mixed oxide. Therefore, in the LaBaCu900 sample a mixture of the orthorhombic La2CuO4 and tetragonal LaxBa3-xCu3O7 phases was obtained. Even though the XRD results showed the La1,5Ba1,5Cu2,94O6,84 phase, this formula does not necessarily represent the composition of the phase, but certainly indicates that this crystalline phase corresponds to the structure YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>.

As previously mentioned, the transport of oxygen ions is of great importance for catalytic performance of perovskite related materials and can be associated with the presence of oxygen vacancies [29–31].

	Composition	Composition (% w/w)		Molar ratio	Molar ratio		Proposed formula	
	La	Cu	Ва	La/Cu	Ba/La	(La + Ba)/Cu		
LaCu LaBaCu	63.6 57.4	20.8 17.5	- 10.1	1.4 1.5	- 0.2	1.4 1.8	La <sub>1.4</sub> CuO <sub>3.1</sub> La <sub>1.5</sub> Ba <sub>0.3</sub> CuO <sub>3.55</sub>	



Fig. 2. X-ray diffractograms of the fresh and thermal aged catalysts and patterns. At the botton, stick representation shows the orthorhombic  $La_2CuO_4$  pattern (ICSD 56528). \* is CuO (ICSD 291393), + is BaCO<sub>3</sub> (ICSD 15196) and o is  $La_{1.5}Ba_{1.5}Cu_{2.94}O_{6.84}$  (ICSD 62923) phases.

Studies related to oxygen adsorption and desorption (O<sub>2</sub>-TPD) are used for this purpose. In general, two types of peaks are exhibited in the desorption curves, the peak at low temperature is attributed to oxygen adsorbed on surface vacancies ( $\alpha$ -oxygen), and the one observed at higher temperature ( $\beta$ -oxygen), is related to lattice oxygen or oxygen species that occupy the inner vacancies originated from cation substitution in the perovskite [43–46].

According to Fig. 3, LaCu catalyst presented only an intense peak at 850 °C attributed to  $\beta$ -oxygen desorption, adsorbed on vacancies in the bulk structure. This result is in agreement with those obtained by Zhu et al. [47] in which the perovskite type La<sub>2</sub>CuO<sub>4</sub> mixed oxide did not show  $\alpha$ -oxygen desorption. However, the partial substitution by Ba in LaCu caused structural changes, creating oxygen vacancies on the surface of the catalyst. A peak in the range of 200-400 °C, characteristic of  $\alpha$ -oxygen desorption, is observed in LaCuBa, indicating that the Ba addition led to the formation of vacancies on the catalyst surface. Seiyama et al. [48] also used O2-TPD technique to characterize defects on the surface and in the bulk of the La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub> type perovskite catalysts (obtained from isostructural substitutions of lanthanum by strontium). For x equal to 0.4, a large increase in  $\alpha$ -oxygen desorption was observed. The authors suggested that the partial substitution of  ${\rm La}^{3\, +}$  by a low valence cation (+2) leads to the creation of surface vacancies in the perovskites by a charge compensation effect.

From Fig. 3, it can still be seen that the partial replacement of La by Ba was unfavorable to the formation of oxygen vacancies in the bulk, with a decrease of desorption peak at 850 °C for LaBaCu sample. Studies involving O<sub>2</sub>-TPD in perovskite-type mixed oxides have indicated that  $\beta$ -oxygen desorption peak might be more associated with B-site cation. However, the A-site partial replacement might interfere with B-site electronic configuration and consequently have an influence on  $\beta$ oxygen desorption [46,49]. In order to verify the influence of the B cations nature on the  $\beta$ -oxygen desorption, Seiyama et al. [48] performed O<sub>2</sub>-TPD experiments with LaMO<sub>3</sub> perovskites (M = Ni, Cr, Fe, Mn and Co). LaCoO<sub>3</sub>, LaMnO<sub>3</sub> and LaNiO<sub>3</sub> presented wide peaks attributed to large amounts of  $\beta$ -oxygen desorption, while LaCrO<sub>3</sub> and



Fig. 3. O2-TPD profiles of the catalysts.

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LaFeO<sub>3</sub> showed no desorption peak. According to the authors, the oxygen desorption associated with vacancies creation in the bulk is related to the partial reduction of the B cations, on the surface and within the perovskite crystalline lattice. Thus, the oxygen desorption from perovskite mixed oxides might depend on many factors, as the crystalline structure, oxygen deficiency and reducibility of the B-site cation [46].

For the aged samples, the thermal treatment did not cause significant changes in the unsubstituted LaCu sample (LaCu900), which maintained the same desorption profile with a single peak at approximately 850 °C, characteristic of desorbed oxygen of vacancies in the bulk. However, thermal aging promoted changes in the desorption profile of the Ba-containing sample. Oxygen desorption peaks are present at low (around 400 °C) and high (around 1000 °C) temperature, related to the formation of both surface and bulk vacancies, respectively. The  $\beta$ -oxygen peak (above 900 °C) can be associated with both, the oxygen adsorbed in the bulk that desorbed, and the oxygen output from the crystalline lattice. The thermal aging of LaBaCu sample (LaBaCu900) favored the formation of tetragonal La<sub>x</sub>Ba<sub>3-x</sub>Cu<sub>3</sub>O<sub>7</sub> phase, as observed by XRD (Fig. 2). The presence of this new crystalline phase might have contributed to increase the oxygen mobility, since in YBaCu<sub>3</sub>O<sub>7</sub> structure type the oxygen content easily changes with temperature [50].

The oxygen quantification in these desorption stages is presented in Table 2. With thermal aging, the samples showed an increase in the amount of  $\alpha$ - and/or  $\beta$ -oxygen desorbed. Probably, the high temperatures reorganized oxygen atoms in the structure, including the possibility of generating new crystalline phases, in which the surface oxygen atoms would migrate, releasing vacancies in the surface region. It is noteworthy that the catalyst LaCu after aging (LaCu900) presented a 9 percent increase in bulk oxygen vacancies. Besides, the barium addition proved essential for the formation of surface vacancies.

Temperature programmed reduction results are shown in Fig. 4. For LaCu and LaBaCu samples, the TPR profiles showed H<sub>2</sub> consumptions between 170 and 350 °C and a less intense consumption starting at approximately 410 °C, remaining to 500 °C, the TPR final temperature. The most intense H<sub>2</sub> consumption for LaCu sample occurred in a single step, with a single peak attributed to the reduction of  $Cu^{2+}$  species to  $Cu^+$ . The last peak at 470 °C is related to the reduction of  $Cu^+$  to  $Cu^\circ$  [51]. However, H<sub>2</sub> consumption relative to the second peak is much



lower than that of the first one. Probably,  $Cu^+$  species are very stable even at high temperature and under H<sub>2</sub> atmosphere [47,52–54].

According to Velasquez et al. [51], the H<sub>2</sub> consumption relative to the first reduction stage, between 230 and 320 °C, might be associated with other possibilities (eq. 2–6). Thus, in addition to the reduction of  $Cu^{2+}$  to  $Cu^{1+}$  and the reduction of a possible CuO segregated, formed during the preparation, a partial reduction of La<sub>2</sub>CuO<sub>4</sub> to a delafossite-type phase (LaCuO<sub>2</sub>) may be occurring (eq. 2). The second peak at 470 °C might be also relative to the delafossite-type phase to Cu° [51].

$$2La_2CuO_4 + H_2 \rightarrow 2LaCuO_2 + La_2O_3 + H_2O(230 \,\mathrm{a}\,320\,^{\circ}\mathrm{C})$$
(2)

 $2La_2CuO_4 + H_2 \rightarrow Cu_2O + 2La_2O_3 + H_2O (230 \text{ a} 320 \,^{\circ}\text{C})$ (3)

$$CuO + H_2 \rightarrow Cu^0 + H_2 (230 \,\mathrm{a}\, 320 \,^\circ\mathrm{C})$$
 (4)

$$Cu_2O + H_2 \rightarrow 2Cu^0 + H_2O (420 \,\mathrm{a}\,550\,^\circ\mathrm{C})$$
 (5)

$$2LaCuO_2 + H_2 \to 2Cu^0 + La_2O_3 + H_2O (420 a 550 \,^\circ\text{C}) \tag{6}$$

For LaBaCu catalyst, in addition to the high temperature peak interpreted previously, are observed two other H<sub>2</sub> consumption peaks in the first reduction stage, below 350 °C. Clearly, different reducible species might have been formed in the catalyst. As well as for La<sub>2</sub>CuO<sub>4</sub> sample, it is likely that extra-framework Cu species are also present in LaBaCu, probably as CuO. These species are reduced at higher temperatures and apparently contribute to the formation of the second peak of reduction, at around 300 °C. The presence of BaCO<sub>3</sub> verified by XRD indicates that not all barium has been incorporated into the perovskitetype mixed oxide structure. ICP results showed a molar ratio (La + Ba)/ Cu equal to 1.8 (lower than the theoretical ratio equal to 2) confirming Ba segregation. Thus, the change in the reduction profile is possibly due to the different Cu species, including those dispersed and in the perovskite-type mixed oxide structure. This differentiated behavior is related to the Ba addition that also provided a decrease in the initial temperature of the reduction. This might indicate that the barium presence promoted the formation of oxygen vacancies at lower temperatures, as verified by O2-TPD, improving the catalyst redox properties. Therefore, the partial substitution of lanthanum by barium appears to increase the surface mobility of lattice oxygens favoring the LaBaCu surface reducibility, but this effect did not reach the bulk.

The H<sub>2</sub> consumption during the reduction of the catalysts are presented in Table 3. When comparing the H<sub>2</sub> consumption corresponding to the first peak of LaCu sample (2794 µmol g<sup>-1</sup>) with that of the La-BaCu sample (2091 µmol g<sup>-1</sup>), a consumption decrease is observed, which is in agreement with the chemical analysis that presented a higher Cu content for LaCu sample. It is possible to verify that for both samples, mainly for LaBaCu, the TPR hydrogen consumption is lower than the theoretical consumption required to reduce all Cu present (3265 µmol g<sup>-1</sup> for LaCu and 2751 µmol g<sup>-1</sup> for LaBaCu, calculated according to the results of ICP-OES). The reduction percentage at the end of the TPR was 94 % for the LaCu catalyst and 86 % for LaCuBa. Possibly not all Cu present in the samples is reduced to metallic copper. Cu<sup>2+</sup> in the CuO form is generally reduced to the metallic state by H<sub>2</sub> below 500 °C, however in the case of perovskite-type mixed oxides, as

Table 3	
Quantitative results of H <sub>2</sub> -TPR experiments.	

Catalyst	Maximum temperature (°C)		Consum	ption of I	Η <sub>2</sub> (μmo	l g <sup>-1</sup> )	
	Peak 1	Peak 2	Peak 1	Peak 2	Total	Theoretical	% red
LaCu LaCu900 LaBaCu LaBaCu900	268 329 <sup>a</sup> 242 292 <sup>a</sup>	468 477	2794 2314 2091 2345	283 277	3077 2314 2368 2345	3265 3265 2751 2751	94 71 86 85

<sup>a</sup> Despite showing more peaks, the program identified only the main peak for both aged samples.



Fig. 5. CuK-edge XANES spectra of the LaBaCu under H<sub>2</sub> treatment at the temperature range of 30 to 500 °C.

mentioned above,  $Cu^+$  may be stable even under high temperatures [47,53,54].

In order to corroborate the TPR results, the reducing treatment was performed and monitored through Cu-K edge XANES for LaBaCu sample, whose spectra are presented in Fig. 5. It is observed that Cu only begins to be reduced from 380 °C and the significant reduction occurs in the temperature range between 380 and 500 °C. This discrepancy in relation to the conventional TPR results is probably due to the different flow dynamics, since in the TPR reactor the reagents flow crosses the catalytic bed, whereas in XANES experiments, not all the flow crosses the pellet, in which the catalyst is diluted with boron nitride. Thus, it is reasonable to expect changes in the reduction kinetics. Anyway, the evolution of copper oxidation state is clearly observed. A detailed analysis of the spectra obtained during the reduction process shows a more intense decrease of the peak at 8999 eV, called peak A. The wider and less intense peak at 9013 eV, called peak B undergoes minor changes. According to the literature, these two peaks are related to the Cu<sup>2+</sup> [11,55,56].

As the reduction temperature increases, the peak at approximately 8983 eV appears, called peak C, which is attributed to  $Cu^+$  and/or  $Cu^0$  species [58].

Aiming for a better understanding of the copper species evolution, the first spectrum (at room temperature) and the last one (at 500 °C) were analyzed separately. The sample spectra in the presence of H<sub>2</sub> at room temperature and at 500 °C were plotted together with CuO, Cu<sub>2</sub>O and Cu foil standard spectra. These spectra are shown in Figs. S1 and S2 of the Supplementary Information. It is possible to note through the normalized and derivative spectra that the position of the main peak is the same for CuO and for the sample at room temperature and does not match with the other two standards (Cu<sub>2</sub>O and Cu foil). Our results were compared with the ones of Tranquada et al. [55], who carried out an exhaustive XAS studies in order to verify the copper valence in compounds with K<sub>2</sub>NiF<sub>4</sub> type structure, such as La<sub>2-x</sub>(Ba,Sr)<sub>x</sub>CuO<sub>4-v</sub> (being x from 0 to 0.3). The XANES profiles obtained for these samples are similar to the LaBaCu of our work. Tranquada et al. [55] compared the XANES spectra of their samples with calculations and experimental standards and concluded that the lack of variation in the main peak position(in c.a. 8999 eV) of the CuO, Cu<sup>2+</sup> ion (CuCl<sub>2</sub> solution) standards and La2-x(Ba,Sr)xCuO4-y samples, was sufficient evidence for confirming the 3d<sup>9</sup> configuration of Cu<sup>2+</sup> in the samples. The shoulder in approximately 8987 eV, being stronger in CuO standard than LaBaCu sample, is a feature of the fine structure, that depends on the radial distances of neighboring atoms. In CuO and LaCuO<sub>4</sub> structures, the copper is in distorted octahedral coordination, but in CuO the distortion is higher, inducing this small difference in the XANES profiles.

At 500 °C, however, the Cu reduction can be more easily observed

through the derivative of the absorption curves (see Fig. S2). It can be seen the peak at 8983 eV include mainly the peak corresponding to  $Cu_2O$  and a very small part of metallic Cu. In the 8985 – 8999 eV region a CuO contribution also appears. Therefore, it can be concluded that at 500 °C the spectrum is mainly composed of Cu<sup>+</sup> species and in minor proportion, of Cu<sup>2+</sup> and Cu<sup>o</sup> ones.

The XANES results also provided an assessment of copper oxidation state present in the samples after preparation. It is known that the replacement of lanthanum by a lower valence element induces the formation of oxygen vacancies [57], which can change the oxidation state of one of the metals involved. However, there is also a consensus that the surface oxygen binding energy is of great importance, because oxygen with weaker bond strength (labile oxygen) favors the formation of vacancies [58].

In fact, the introduction of barium in the LaCu catalyst generates an unbalanced charge in the solid since lanthanum (3+) is replaced by barium (2+). The XANES spectra of LaBaCu catalyst at room temperature (Fig. S1) are quite similar to the CuO pattern, indicating that copper is mainly in the 2+ oxidation state. Thus, in the case of this perovskite-type material, barium promoted the generation of more labile oxygen species (as observed by the results of TPD-O<sub>2</sub>), which also contributes to the reduction of LaBaCu, as observed by the TPR results.

#### 3.2. Catalytic performance

Catalytic performance results are presented in Fig. 6. The behavior of CO conversion curves was similar to the NO conversion curves for all catalysts (the light-off curves for CO conversion are shown in Supplementary Information, Fig. S3), indicating that CO and NO react with each other and are converted into N2 and CO2. It was verified that fresh catalysts (LaCu and LaCuBa) have similar activities. The variations observed are very small and practically within the experimental error margin. However, LaCu900 sample reached only 59 % of NO conversion at 500 °C, indicating that it loses activity after thermal aging. The LaBaCu900 sample showed to be slightly more active at lower temperatures, which can be attributed to the presence of surface vacancies that provides easily accessible adsorption sites, facilitating the reaction, as observed by O2-TPD results. This behavior is also consistent with that observed by the H2-TPR data. LaBaCu900 catalyst has been reduced at lower temperatures than the LaCu900. Thus, although the partial substitution by Ba did not promote an increase in the catalytic activity of the fresh sample, the Ba addition improved thermal stability as evidenced by the LaBaCu900 catalytic behavior, which reached 97 % of NO conversion, compared to 56 % of barium-free catalyst (LaCu900).

In order to explain the catalysts performance in the reduction reaction of NO by CO, X-ray absorption near edge structure studies were



**Fig. 6.** (a) Light-off curves for NO conversion and (b) N<sub>2</sub>O yield of fresh and thermal aged catalysts. Pretreatment: He flow at 150 °C for 1 h. Catalytic test: 1% CO and 1% NO in He,  $225 \,\mathrm{mL\,min^{-1}}$ , 2 °C min<sup>-1</sup> from RT to 500 °C. Reactor: fixed bed where the sample is in power form.

carried out on freshly prepared and thermal aged samples. The Cu-K edge XANES spectra obtained at the beginning and at the end of the reaction, following a temperature ramp of 5 °C min<sup>-1</sup> up to 500 °C, are shown in Fig. S4 of Supplementary Information. All XANES spectra show similar profiles at room temperature, exhibiting a sharp increase of absorption, giving an intense and narrow peak at 8999 eV and a less intense peak at 9013 eV, related to the  $Cu^{2+}$  [11,55,56]. At the end of the reaction, (500 °C), the samples had their profile changed, except the LaCu900 catalyst whose profiles at 500 °C showed little changes. The intensity of peak A decreased and one shoulder began to appear in the region of 8982-8985 eV (peak C) [56]. The decrease in peak A indicates a change in the copper electron density, maintaining the same structural arrangement. This behavior, togetherwith the appearance of the peak C, is characteristic of the copper species reduction to Cu<sup>+</sup> and/ or Cu° [11,55]. These results are in agreement with the H2-TPR data, which indicated that Cu<sup>+</sup> can be stable even under high temperatures in the presence of reducing agent.

The quantification results acquired by linear combination of the CuO, Cu<sub>2</sub>O, metallic Cu and the initial catalyst species are shown in Fig. 7. As explained before (H<sub>2</sub> reduction monitored by XANES), the K<sub>2</sub>NiF<sub>4</sub> type structure has particular features slightly different from the CuO, and for this reason, the initial catalyst (at room temperature) was included in the linear combination.

According to Fig. 7, LaBaCu activity starts at lower temperature, around 250 °C, while LaCu only at around 350 °C. By increasing the temperature, the distribution of copper species in these catalysts differs significantly. For LaCu catalyst, only Cu° is formed, whereas Cu<sup>+</sup> is additionally formed in LaBaCu. As the catalytic performance of both catalysts compared at high temperatures are similar (Fig. 6), this might indicate that Cu° promotes the reaction.

Some changes in the spectra (Fig. 7) were also observed when comparing the catalysts before and after thermal aging. The biggest difference is between LaCu and LaCu900 catalysts, with the latter not being reduced during the reaction. This means that for LaCu900, the copper species present in the beginning of the reaction (practically only  $Cu^{2+}$ ) were maintained up to 500 °C. As the reduced copper species are more active, the poor performance of LaCu900 is explained by the

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**Fig. 7.** Distribution of copper species (Cu<sup>2+</sup>, Cu<sup>+</sup> and Cu<sup>°</sup>) in fresh and thermal aged samples. Pretreatment: He flow at 150 °C for 1 h. Catalytic test: stoichiometric gas mixture 1:1 of NO and CO in He, samples in pellet form, 5 °C min<sup>-1</sup> from RT to 500 °C. Reactor: tube where the sample in a pellet form is arranged in a sample holder.

absence of these species during the reaction. According to Fig. 6(a), the LaBaCu900 catalytic behavior is completely different from that observed for LaCu900, reaching 97 % of NO conversion at 500 °C even after thermal aging. In relation to the fresh catalyst (LaBaCu), it also performs well.

Regarding the formation of reduced species during the reaction (Fig. 7), the reduction of copper species in LaCuBa900 occurs, but at higher temperatures compared to LaBaCu, explaining the differences observed in the catalytic performance of these catalysts. This result is in accordance with the TPR profiles (Fig. 4). For LaBaCu900, its reduction starts at temperatures slightly below those of the fresh sample, however, it stabilizes between 200 and 270 °C and advances only at higher temperatures (above 270 °C) compared to the reduction profile of the LaBaCu sample.

The better performance of LaBaCu900 catalyst in comparison with LaCu900 might be associated with the presence of  $YBa_2Cu_3O_7$  type structure in the phase  $La_{1.5}Ba_{1.5}Cu_{2.94}O_{6.84}$  (proposed formula), which has higher Ba content than LaBaCu, besides the presence of oxygen vacancies.

In order to evaluate the nitrous oxide formation during the NO reduction by CO, in Fig. 6(b) are shown the N<sub>2</sub>O yield curves of fresh and thermal aged catalysts. All catalysts exhibited a low N<sub>2</sub>O yield with a maximum of 10 % at 405 °C for LaCu catalyst. The fresh catalysts have N<sub>2</sub>O production initiated as soon as the NO conversion starts; it reaches a maximum yield that decreases until N<sub>2</sub>O is no longer produced. For thermal aged samples, N<sub>2</sub>O is still produced even at 500 °C, but the yield values are lower than the fresh samples.

The *in-situ* XANES results showed that during the reaction, between 320 and 420 °C, the fresh samples exhibit mainly the reduction of  $Cu^{2+}$  to  $Cu^{+}$  and  $Cu^{\circ}$ , which corresponds to the temperature range where N<sub>2</sub>O is formed. Above this range, copper is predominantly present in the



**Fig. 8.** (a) Light-off curves for NO conversion and (b) N<sub>2</sub>O yield of the fresh and thermal aged catalysts. Pretreatment: H<sub>2</sub> flow at 500 °C for 1 h. Catalytic test: 1% CO and 1% NO in He, 225 ml min<sup>-1</sup>, 2 °C min<sup>-1</sup> from RT to 500 °C. Reactor: fixed bed where the sample is in power form.

reduced form, and the N2O yield decreases.

Regarding to the thermal aged samples, for LaCu900, N<sub>2</sub>O continues to be produced even at 500 °C (Fig. 6(b)), but the yield values are much lower than the fresh samples as well as the NO conversions obtained by the catalysts.

#### 3.3. Effect of reducing treatment on catalytic performance

Previous *in situ* XANES results had already shown that  $Cu^+/Cu^0$  species are formed during the NO reduction by CO reaction and remain present even under high temperatures working as an active site for the reaction. Therefore, the presence of reduced copper species might be contributing to the better catalytic performance of the samples, especially at lower temperatures. Thus, it was decided to carry out a reducing pretreatment prior to the reaction and evaluate the catalyst performance under these conditions.

Fig. 8(a) shows the results of NO conversion to the catalysts with reducing pretreatment (the light-off curves for CO conversion are shown in Supplementary Information, Fig. S5). Comparing Figs. 6 and 8, the previously reduced samples were more active throughout the temperature range investigated. In this condition, the fresh catalyst partially replaced with Ba presented better performance, being active at lower temperature, just after 100 °C. The most of Cu species in this catalyst were reduced to metallic copper after the pretreatment with H<sub>2</sub> (Fig. S2), leading to a collapse of the perovskite-type mixed oxide structure. Thus, the higher activity of the previously reduced LaBaCu catalyst, even at lower temperatures, is related to the Cu species present in the material. At higher temperatures, above 250 °C, these catalysts showed similar behavior, probably due to the formation of the same copper species in both samples during the reaction.

The thermal aged catalysts also showed a conversion improvement, since, as in the fresh samples,  $Cu^+$  and  $Cu^\circ$  were formed after the reducing treatment, working as active sites for the reaction. A more significant improvement in catalytic activity was observed for the LaCu900 catalyst, whose NO conversion starts at lower temperature than LaBaCu900 and at 500 °C it jumped from 59 to 85 %. According to the XANES spectra, LaCu900 sample lost its reduction capacity under

the reaction conditions, but with the reducing pretreatment, active sites were generated, justifying the significant improvement in the activity of the LaCu900 after pretreatment with  $H_2$ .

Concerning to the  $N_2O$  generation, when catalysts are subjected to reducing pretreatment,  $N_2O$  appears at lower temperatures, whereas the NO conversion is also anticipated. Even so, the yield values remain low (maximum of 13 % for LaCu catalyst) and much lower compared to those obtained in catalysts based on noble metals. Except for the LaCu900 sample, all catalysts had nitrogen production finished before 500 °C. Considering that  $N_2O$  is an intermediate in the NO reduction by CO, its formation will depend on the adsorption equilibria on the different copper species as well as on the relative rates of formation and decomposition to  $N_2$ .

A simplified kinetic study was also carried out using the conversion results of the light-off curves and are described in detail in the Supplementary Information. A pseudo-first order reaction rate model was used, which can be a good approximation considering that the experiments were performed at low partial pressures of NO and CO, as well as under a fixed NO/CO molar ratio [59]. Although we are aware that the light-off curves may be affected by eventual changes in the catalyst over the temperature domain, a good consistency of the results was verified, indicating that the first order model is a reasonable approximation. The results regarding the kinetic constant calculated for each catalyst confirm the conclusions obtained by the light-off curves for both pretreatments performed. For aged catalysts, the barium-containing catalyst is more active; it has undergone less deactivation which confirms its stabilizing role. For the catalysts pretreated in H<sub>2</sub>, there is a decrease in the activation energy (Fig. S7(b) and S7(d), and Table S1) and an increase in the activity of the catalysts after a pretreatment under H\_2, when compared with the pretreated catalysts at 150  $^\circ\text{C}$  in helium. This indicate a change in the nature of the active sites after treatment with hydrogen, with the formation of reduced copper species since the beginning of the reaction.

### 4. Conclusions

LaCu and LaBaCu fresh catalysts showed good activity in the NO reduction by CO reaction. The Ba addition caused structural changes creating oxygen vacancies on the surface and in the bulk of the catalyst that promoted the reducibility and activity of the fresh catalysts mainly at low temperatures. Another important role of barium was the improvement of the catalyst thermal resistance, maintaining their reducibility even after thermal aging. Based on *in-situ* XANES results, LaBaCu900 presented the higher reducibility with Cu<sup>+</sup> and Cu<sup>°</sup> formation during the reaction. The use of a reducing pretreatment provided active sites formation, justifying the significant improvement in catalytic activity. The N<sub>2</sub>O generation was also observed in all catalysts (fresh and aged) but in lower yields when compared with noble metal-based catalysts. The decrease in the activation energy of the pretreated catalysts at 500 °C under H<sub>2</sub> flow indicates a change in the active sites (presence of reduced copper species since the beginning of the reaction)

#### Author statement

All authors declare that they have seen and approved the content of the submitted manuscript. The paper presents original work not previously published in similar form and not currently under consideration by another Journal.

The conception and design of study, acquisition of data, analysis and/or interpretation of data, drafting the manuscript and critical revision had the participation of all the authors

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial

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interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2020.06.052.

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