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Non-noble metal doped perovskite as a promising catalyst for ammonia borane dehydrogenation

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Graphical abstract



Highlights

- Lanthanum Strontium Cobalt (LSC) perovskites were prepared by sol-gel method.
- Doped-LSC perovskites were assessed in ammonia borane decomposition.
- The closer interaction Cu-Co might be favoring the catalytic activity.
- Cu doping was found to be a good alternative to boost the catalytic activity.

Abstract

Lanthanum Strontium Cobalt (LSC) perovskite-based catalysts were prepared and evaluated in the ammonia borane dehydrogenation reaction. Doping with additional non-noble metals, such as Ni or Cu greatly enhanced the catalytic performance, especially in the case of Cu. In order to evaluate

the effect of the Cu loading, catalysts with various Cu contents ranging from 0.82 to 5.42 wt.% were synthesized. It was found that the Cu-doped sample with a nominal formula of $La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O_3$ containing 2.72 wt.% of Cu displayed the highest catalytic activity among investigated, which outperformed the counterpart Cu-supported catalyst (Cu/La_{0.7}Sr_{0.3}CoO₃). $La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O_3$ showed good durability during five consecutive reaction runs, confirming the suitability of perovskite-type catalysts in stabilizing the catalytic active phase. The present catalytic system provides a cost-effective alternative to the noble-metal-based catalysts commonly used to catalyze the ammonia borane dehydrogenation reaction.

Keywords: hydrogen production, ammonia borane, perovskite, non-noble metals

1. Introduction

One of the most important challenges for researchers over the last decades has been to find an effective, abundant and green supply of energy. At this point, hydrogen could play a pivotal role as an energy carrier because of its high gravimetric energy density (120 kJ g^{-1}) as well as its use in high-performing energy production from fuel cells. However, hydrogen storage and handling remain serious drawbacks for its use in energy applications [1]. For this reason, many efforts have been focused on the hydrogen storage strategies, and today it is still a huge challenge that must be overcome in the field of energy materials. Within the traditional chemical and physical ways of hydrogen storage, chemical approaches could fulfil requirements related to efficiency, safety or lightweight that physical storage alternatives are not able to achieve yet [2]. Regarding chemical strategies, hydrogen can be stored in molecular carriers such as covalent hydrides, metallic hydrides, formic acid, hydrazine, and so on [2–6]. These molecular carriers can generate hydrogen by means of thermal or catalytic decomposition [7,8]. Among molecular carriers, ammonia borane (NH₃BH₃, AB) has properties that make it a promising candidate for hydrogen storage, such as high gravimetric hydrogen capacity (19.6 wt.%), low molecular weight (30.87 g mol⁻¹), nontoxicity and high stability in solid form under ambient conditions [2,9]. The importance of chemical hydrogen storage by means of AB has been reflected in a large number of studies to design and optimize both homogeneous and heterogeneous systems to catalyze its decomposition [10–12], being the heterogeneous catalysts preferred because of their advantages from the practical point of view. The majority of the studied heterogeneous catalysts to boost the AB dehydrogenation is based on supported noble-metals nanoparticles (NPs) (e.g. Ru, Pd, Pt and Rh) [11–15]. Bearing in mind the high cost of the noble-metals used, the design of catalysts based on non-noble metals with good catalytic activity and high chemical stability has been one of the hurdles that researchers have had to tackle recently. In this context, Cu or Co-based NPs have

attracted particular attention because they have shown good catalytic ability for the AB dehydrogenation [16-18]. A general shortcoming of non-noble metal is their poor stability in the metallic state, which is often the most active species for this application. Then, the hydrogen evolution profiles obtained by such systems tend to show long induction time, after which the metal species are reduced to form active phase and initiate the AB dehydrogenation reaction. However, a different behavior was observed for Cu-based catalysts, which were reported to be catalytically active in their oxidized forms [19,20]. Additionally, NPs sintering under experimental conditions and accumulation of metaborate in the reaction medium are known reasons for catalytic activity decay in this reaction [13,21,22]. In order to avoid such drawbacks, diverse approaches have been extensively studied to stabilize NPs by means of nanoconfinement, thin films, capping agents, "click" chemistry, and so on [12,14,23-27]. However, some of them use expensive techniques or are performed following a multi-step and time-consuming approaches. The stability of NPs also depends on the natures of supports, in which surface area, porosity and metal-support interaction might influence the final catalytic activity. A wide range of solids has been studied as support of catalysts for AB dehydrogenation, such as carbon materials [10], oxides [11], zeolites [15], metal organic frameworks (MOFs) [16,28], hydroxyapatites [29], etc. However, the search for alternative catalysts that fulfil cost-effectiveness, stability and reusability is still a hot topic. In this sense, although perovskites (ABO₃) have been widely studied in several catalytic reactions [30-32], they have hardly been assessed in AB dehydrogenation [33]. The broad family of perovskite oxides together with the range of possible substitutions of A or B cations make them materials with high tunability from the physicochemical point of view. Therefore, this versatility of perovskite composition, which in turn influences in the electronic structure, can lead to the enhancement of catalytic performance. It has already been observed that B sites play a pivotal role

in controlling the electronic structure [34,35], while A sites are responsible for the acid-base catalytic properties [36]. To date, lanthanum-based perovskite oxides have been widely studied in different catalytic systems [37–39], showing outstanding catalytic performances in the hydrogen production from water splitting [40,41], autothermal reforming of ethanol [42] and catalytic thermal decomposition of hydrogen sulfide [43].

Herein, we report the synthesis of non-noble metal doped perovskite-type catalysts based on La_{0.7}Sr_{0.3}CoO₃ perovskite (LSC). The chemical composition of La_{0.7}Sr_{0.3}CoO₃ perovskite is fitted to replace some Co atoms with Cu or Ni. Doped perovskite-type catalysts were studied in AB dehydrogenation to evaluate the non-noble metal doping effect towards hydrogen production ability. It was observed that such doping greatly enhanced the catalytic performance in the AB dehydrogenation reaction, being particularly marked in the case of Cu. In order to assess the optimum doping level, Cu-doped LSC catalysts with various Cu contents ranging from 0.82 to 5.42 wt.% were prepared. The best-performing catalyst among investigated was found to be La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O₃, which displayed good catalytic ability and stability during five consecutive reaction runs.

2. Experimental

2.1 Synthesis of non-noble metal doped perovskite

Lanthanum-based perovskite oxides were prepared by the sol-gel method. In the case of La_{0.7}Sr_{0.3}CoO₃ perovskite, fixed amounts of La(NO₃)₃·6H₂O, Sr(NO₃)₂ and Co(NO₃)₂·6H₂O were first dissolved in water under mechanical stirring. Then, citric acid (CA) and ethylene diamine tetraacetic acid (EDTA) were added to the previous solution with an equimolar ratio of CA:EDTA:metal. Subsequently, the solution was heated up to 80 °C for 4 h. The transparent pinkish solution was evaporated under vacuum at 80 °C and the resulting purple solid was dried at

100 °C overnight. Finally, the obtained solid was heated at 5 °C min⁻¹ up to 700 °C in air and kept at the same temperature for 6 h to yield a final perovskite solid. Regarding the non-noble metal doped perovskite ($La_{0.7}Sr_{0.3}Co_{1-y}X_yO_3$, X= Cu or Ni), they were prepared using the same method except for the addition of designated amounts of nitrate salts of Cu(II) or Ni(II). For comparison purpose, a Cu-supported perovskite catalyst was prepared by impregnation of $La_{0.7}Sr_{0.3}CoO_3$ with an aqueous solution of Cu(NO₃)₂·3H₂O and subsequent reduction with NaBH₄. This sample was denoted as Cu/La_{0.7}Sr_{0.3}CoO₃ and had the same Cu content as the best-performing Cu-doped counterpart ($La_{0.7}Sr_{0.3}CoO_{.90}Cu_{0.10}O_3$, *vide infra*). Furthermore, three additional reference samples were synthesized by supporting Co (2.72 wt.%), Cu (2.72 wt.%) and Cu+Co (total of 2.72 wt. %; Cu: 0.3 wt.%; Co: 2.42 wt.%) on fumed silica (Sigma-Aldrich) by the same procedure (samples denoted as Co/SiO₂, Cu/SiO₂ and CuCo/SiO₂).

2.2 Characterization of the catalysts

The X-ray diffraction (XRD) analysis was performed by using a Rigaku Ultima IV diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å). The characterization of the porous texture of the perovskites was carried out by means of adsorption of N₂ at -196 °C by using a BELSORP-max system (MicrotracBEL, Corp.). All samples were outgassed under vacuum at 250 °C for 4 h to remove any adsorbed impurities. Transmission Electron Microscopy (TEM) analysis was conducted to check the morphology of the samples by using a Hitachi H-800 electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) data were recorded using a Shimadzu ESCA 3400 Electron Spectrometer, which is dotted with a Mg K α radiation (1253.6 eV) X-ray source located at a low-pressure chamber. Furthermore, X-ray Auger spectra were also measured to discriminate Cu species. The binding energy of all spectra was calibrated using the C1s line (284.6 eV).

2.3 Catalytic test

The evaluation of catalytic performance in AB dehydrogenation was performed as follows; 20 mg of La-based perovskite catalyst was dispersed into 10 mL of distilled water and it was placed into a Schlenk-type reaction vessel (30 mL) connected with a gas burette that was purged with nitrogen gas several times. To start the reaction test, 1.0 mL of an aqueous solution of 1.5 mol/L AB was injected into the reaction vessel under mechanical stirring and the evolved gas (H₂) was measured by using a graduated burette system until the AB dehydrogenation is completed. The temperature was held at 30 °C throughout the reaction by using an oil bath. Reusability tests were performed by injecting a fresh AB solution (1.5 mol/L) into the reaction vessel that contained the spent catalyst. Five consecutive runs were performed and the released gases were monitored using the same experimental condition as for the 1st reaction cycle.

TOF values (h⁻¹) were calculated using the following equation:

$$TOF(h^{-1}) = \frac{P_{atm} V_{H_2}}{R T t N_m} (Eq. 1)$$

where P_{atm} is the atmospheric pressure, V_{H2} (L) is the produced volume of H₂, *R* is the perfect gas constant, *T* is the reaction temperature (303 K), N_{m} is the Cu amount (mole), and *t* (h) is the reaction time.

3. Results and discussion

The catalytic performances of bare LSC and Cu and Ni-doped counterparts were assessed and the results are shown in Figure 1. It can be observed that the non-doped catalyst showed a long induction time of ~25 min, time after which the reaction proceeded gradually and reached 100% of conversion after 180 min of reaction (which corresponds to approximately 112 mL of H₂). As

can be seen, both Cu and Ni-doped catalysts showed better performances than bare LSC, since shorter induction times were needed in both cases. As shown in Figure 1, the reaction was much faster in the case of the Cu-doped catalyst than those of bare LSC and Ni-doped LSC catalysts. This observation confirmed the beneficial effect of the substitution of B sites by the second nonnoble metal on the catalytic performance of the present system, which is particularly pronounced in the case of copper.



Figure 1. Reaction time profiles of La-based perovskite catalysts in the AB dehydrogenation reaction at 30 °C.

To get further insight into the Cu-doping effect, lanthanum-based perovskite catalysts with Cu content ranging from 0.82 to 5.42 wt.% were prepared, characterized and their catalytic abilities in the AB dehydrogenation were evaluated. The details of the composition of the catalysts are listed in Table 1.

| Sample | Cu content ^a (wt.%) | BET surface area ^b (m ² /g) |
|---|--------------------------------|---|
| $La_{0.7}Sr_{0.3}CoO_3$ | - | 16 |
| $La_{0.7}Sr_{0.3}Co_{0.97}Cu_{0.03}O_{3}$ | 0.82 | 10 |
| $La_{0.7}Sr_{0.3}Co_{0.94}Cu_{0.06}O_3$ | 1.63 | 13 |
| $La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O_3$ | 2.72 | 9.0 |
| $La_{0.7}Sr_{0.3}Co_{0.85}Cu_{0.15}O_3$ | 4.07 | 15 |
| $La_{0.7}Sr_{0.3}Co_{0.80}Cu_{0.20}O_3$ | 5.42 | 13 |

Table 1. Copper content and BET surface area of the series of Cu-doped LSC perovskite

catalysts.

^a Theoretical value assumed from the composition of initial synthetic solution. ^b Determined by BET (Brunauer– Emmett–Teller) method using the N₂ adsorption isotherm data.

From the XRD patterns (Figure 2a), it can be observed that the increase of the substitution of B-sites by copper did not cause any clear crystallographic changes in the main phase of LSC catalysts. All samples displayed the peaks ascribed to the perovskite phase (2θ =23, 32.9, 40.6, 47.3, 58.8, 69.3 and 79.0°). The diffractograms did not show relevant peaks between 36° and 39° that would be ascribed to CuO and Cu₂O [44], respectively. However, the diffraction peak located between 32° and 34° showed a progressive shift to lower degrees as the copper amount increased (see Figure 2b). This change in the peak position is due to the lattice expansion after substitution of Co³⁺ cations by Cu²⁺, which has a large ionic diameter, and indicated the effective substitution of B-sites of the LSC lattice. This effect has been observed in LSC catalysts for other applications after the substitution of B sites of Co³⁺ by Pd²⁺ [45].



Figure 2. a) XRD patterns and b) Magnified XRD peak around 33° for $La_{0.7}Sr_{0.3}Co_{1-y}Cu_yO_3$ catalysts with different Cu contents (y = 0 – 0.20).

Cu-doped catalysts were also characterized by means of nitrogen adsorption at -196 °C and the results indicated that the Cu-doping did not cause specific surface area change of the perovskite; The specific surface area values for Cu-doped catalysts ranges from 9 to 16 m² g⁻¹, which is in agreement with those obtained from La-based perovskites prepared by a sol-gel method using citric acid and EDTA [45].

As for the morphology of the samples, Figure 3 shows representative TEM micrographs of the bare LSC, $La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O_3$ and $Cu/La_{0.7}Sr_{0.3}CoO_3$. It can be seen that the perovskite exhibited characteristic irregular and rounded aggregated nodules, which are particularly visible in the case of bare LSC and $La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O_3$ samples (Figure 3a and 3b) [36]. It should be mentioned that while the Cu-doping did not change the morphology of bare LSC, sample $Cu/La_{0.7}Sr_{0.3}CoO_3$ is composed of more loose aggregates corresponding to the perovskite phase and a new phase that might be ascribed to the copper oxide particles.



Figure 3. TEM micrographs of a) bare LSC, b) $La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O_3$ and c) $Cu/La_{0.7}Sr_{0.3}CoO_{3.}$

Regarding the electronic features of Cu species, XPS measurements were performed for $La_{0.7}Sr_{0.3}Co_{1-y}Cu_yO_3$ catalysts as well as Cu-supported perovskite. Figure 4 shows the XPS spectra for the $La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O_3$ catalyst, as a representative example of $La_{0.7}Sr_{0.3}Co_{1-y}Cu_yO_3$ samples, and Cu/La_{0.7}Sr_{0.3}CoCuO₃. The Cu 2p XPS spectrum of $La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O_3$ catalyst showed two peaks located at around 933.5 and 953.6 eV, which are attributed to Cu (II) species [20,46]. Four different peaks can be distinguished in the case of the Cu-supported catalyst, which correspond to the same peaks as in $La_{0.7}Sr_{0.3}Co_{0.9}Cu_{0.1}O_3$ catalyst related to Cu (II) species and their shake-up satellite peaks centered at 943.5 and 962.3 eV. The presence of these shake-up satellites, associated with a charge transfer process between oxygen and copper, supported the presence of Cu (II) species [47]. Nevertheless, the higher intensity of the Cu 2p peaks observed for Cu/La_{0.7}Sr_{0.3}CoCuO₃ might be indicative of the higher concentration of Cu (II) on the surface of this catalyst as compared to that of the doped sample, in which Cu (II) is expected to be placed within the lattice of the perovskite structure. As Cu (I) cannot be identified by the analysis of Cu 2p XPS spectra, Auger region was also analyzed for La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O₃ and

Cu/La_{0.7}Sr_{0.3}CoO₃. According to the kinetic energy of the Cu (L₃VV) Auger transition, it was observed that La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O₃ contained Cu (I), besides the aforementioned Cu (II) species, while the presence of Cu (I) was not confirmed in sample Cu/La_{0.7}Sr_{0.3}CoO₃.



Figure 4. Cu 2p XPS spectra of La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O₃ and Cu/La_{0.7}Sr_{0.3}CoO₃ (fresh catalysts).

As for the catalytic performances, the results of the hydrogen evolution profiles from AB dehydrogenation for all $La_{0.7}Sr_{0.3}Co_{1-y}Cu_yO_3$ catalysts are depicted in Figure 5. The hydrogen evolution rates in the presence of Cu-doped catalysts are markedly improved with respect to the Cu-free perovskite (Figure 1). It can be seen that the catalytic activity is strongly depended on the Cu-doping level and that it enhanced gradually while increasing the Cu content until reaching the best performance among investigated for sample $La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O_3$. Further increase of Cu content showed a detrimental effect in the catalytic performance, which resulted in more sluggish hydrogen evolution profiles obtained for $La_{0.7}Sr_{0.3}Co_{0.85}Cu_{0.15}O_3$ and $La_{0.7}Sr_{0.3}Co_{0.8}Cu_{0.2}O_3$.



Figure 5. Reaction time profiles of $La_{0.7}Sr_{0.3}Co_{1-y}Cu_yO_3$ catalysts with different Cu contents (y = 0.03 – 0.20) in the AB dehydrogenation reaction at 30 °C.

The stability of the best performing catalyst was investigated by conducting five consecutive runs at 30 °C and the results are shown in Figure 6a. It can be observed that after the 1st cycle, the spent catalyst lost part of its initial activity, and showed a slightly reduced reaction rate from the 2nd catalytic run. Nevertheless, after the 2nd run, the sample showed the almost same hydrogen evolution profiles from 2nd to 5th run and reached 100% of AB conversion for all the cycles. Such activity decay in the AB dehydrogenation reaction after the 1st run has been previously observed for several systems and has been attributed to changes in the features of the active phase, e.g. poisoning of the active sites by boron-based byproducts, accumulated metaborate in the reaction medium or leaching of the active phase during the reaction [48]. Taking into account that the activity of the catalyst was preserved after the 2nd run, the activity loss might be mainly ascribed to changes in the active phase features rather than accumulated species in the reaction medium. It

is important to mention that, even though the reusability of the catalysts is a vital aspect to be considered, the catalytic activity is not always preserved in the systems found in the literature as catalysts for the AB dehydrogenation reaction. For instance, it has been reported that Ru/C catalysts prepared from tri(2,2-bipyridyl) ruthenium (II) chloride lose about 40% of its initial activity after 5 consecutive runs [10]. Shuren et al. also reported an important deactivation of the catalysts with the consecutive AB dehydrogenation reaction runs while using Ru₁Ni₁@MIL-53(Al), Ru₁Ni₁@MIL-53(Al) and Ru₁Cu₁@MIL-53(Al) [49]. The gradual loss of the catalytic performance in the AB dehydrogenation was also observed by Özkar et al. who studied on hydroxyapatite-supported cobalt(0) nanoclusters [29]. The relatively high stability displayed by the catalytic system herein studied indicates its suitability for the present application. This property, together with the easy synthesis and cost-effectiveness, make this catalyst a promising candidate for the AB dehydrogenation.

For comparison purpose, the performance and stability of Cu-supported catalyst, $Cu/La_{0.7}Sr_{0.3}CoO_3$, were also investigated by monitoring the reaction under the same experimental conditions (Figure 6b). Both $La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O_3$ and $Cu/La_{0.7}Sr_{0.3}CoO_3$ showed nearly constant values of AB conversion along the five consecutive reaction cycles. It should be noticed that 100 % of conversion was achieved with Cu-doped catalysts in every catalytic runs, while for the Cu-supported counterpart the hydrogen generation ceased when only 85-87 % of the theoretical maximum conversion was achieved. Furthermore, the Cu-loaded sample showed a continuous activity reduction in terms of reaction rate, which is in contrast to the high stability displayed by $La_{0.7}Sr_{0.3}CoO_3$, which was confirmed by following the hydrogen generation with the filtrate obtained after removing the solid catalyst from the reaction medium; ca. 10 mL of H₂ was

generated from the filtrate of $Cu/La_{0.7}Sr_{0.3}CoO_3$ after 1 h of reaction, while H₂ generated from the filtrate of La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O₃ was negligible under the same experimental conditions. Such observation confirmed the beneficial effect of the perovskite framework in stabilizing Cu species and achieving durable catalysts rather than the loading of Cu by a conventional synthetic strategy based on impregnation followed by a subsequent reduction, in which Cu species are loaded on the surface of the catalysts, thus being more prone to suffer from deactivation and leaching. It should be also mentioned that TEM analysis did not show any aggregated Cu species in the used La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O₃ catalyst, confirming the stability of Cu species embedded in the perovskite structure. The better performance of Cu-doped catalytic system might not be only ascribed to the better stability of Cu species but also to the presence of well-distributed Cu species as well as closer Cu-Co interaction within the perovskite structure. It should be noted that in sample Cu/La_{0.7}Sr_{0.3}CoO₃, aggregates of Cu oxide species were detected by TEM analysis, while such species were not observed for the doped sample as mentioned above. This fact suggests that in La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O₃ catalyst Cu atoms are incorporated within the perovskite framework so that a closer interaction Cu-Co is favored in this case. The important synergistic effect of Co-Cu for the present application has already been pointed out in the literature for other catalytic systems, such as Cu_xCo_{1-x}O nanoparticles supported on graphene oxide (GO) [50], GO supported Cu@Co core-shell nanoparticles [51], Cu nanoparticles supported on nanosized Co₃O₄ (Cu/Co₃O₄) [20], self-supported Cu(OH)₂@Co₂CO₃(OH)₂ core-shell nanowire [52], etc. It was shown in those investigations that both Cu and Co species can be active in catalyzing the AB dehydrogenation reaction. Particularly, Jagirdar et al. observed that the presence of Cu (I) in the catalysts can greatly contribute to enhancing the performance by strongly interacting with AB molecules so that the formation of an activated complex is favored. Such metal complex formed upon adsorption of AB

on the catalysts will be further attacked by water molecules to release H₂ [53]. In our case, the presence of Cu (I) was confirmed only for $La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O_3$ catalysts, which might be another reason for the improved catalytic performance compared with Cu-loaded counterpart.



Figure 5. Hydrogen generation profiles obtained in five consecutive reaction runs in the AB dehydrogenation reaction at 30 °C from: a) La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O₃, b) Cu/La_{0.7}Sr_{0.3}CoO₃.

Herein the evaluation of Cu/SiO₂, Co/SiO₂ and CuCo/SiO₂ as reference samples suggested the important contribution of Cu species as main responsible for the catalytic activity and the synergistic effect for Cu-Co herein observed (the volume of H₂ generated after 2 h of reaction was 42, 2.0 and 48 mL for Cu/SiO₂, Co/SiO₂ and CuCo/SiO₂, respectively) as well as the suitability of the perovskite-base catalysts for the hydrogen production from AB.

In the present study, a TOF number of 843 h^{-1} (calculated on the basis of Cu) was obtained, which is comparable to the value achieved by other more complex non-noble metal catalysts previously reported in the literature (501.6, 1110 and 1693 h^{-1} for Cu@Co/rGO NPs [51], PEI–GO_{3D}/Co [54] and Cu/MIL-101[55], respectively). The catalytic system herein investigated constitutes a new approach in the design of non-noble metal catalysts for the AB dehydrogenation reaction that encompasses the exceptional performance of copper oxide species while avoiding the

deactivation commonly caused by their sintering or aggregation under reducing condition [19,20,53].

4. Conclusion

LSC perovskite-based catalysts were assessed in ammonia borane dehydrogenation reaction. It was observed that doping with additional non-noble metals such as Ni or Cu greatly enhanced the catalytic performance, with a particularly marked effect in the case of Cu. The impact of Cu-doping was investigated by preparing samples with Cu contents ranging from 0.82 to 5.42 wt.%. The hydrogen production was strongly composition-dependent and, among investigated, sample La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O₃ with a 2.72 wt.% of Cu was the best-performing sample, displaying a better catalytic performance than the Cu-supported catalyst counterpart. La_{0.7}Sr_{0.3}Co_{0.90}Cu_{0.10}O₃ catalyst showed good durability during five consecutive reaction runs and no leaching was observed, confirming the suitability of perovskite-type catalysts in stabilizing the catalytic active phase. It is demonstrated that the composition-controlled catalysts for a certain application. In this case, the easy and scaled up synthesis, high stability and cost-effectiveness of the catalysts endow the present system with potential application in the hydrogen production from ammonia borane.

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