

# Ammonia as a carrier for hydrogen production by using Perovskites

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**Keywords:** ammonia, perovskites, nickel, cobalt, hydrogen

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## 1. Introduction

A great deal of effort is made by the scientific community to identify new energy sources and vectors to replace the fossil fuels. Hydrogen seems to be a good candidate to make up for the global energy demand but the use of this compound as an energy carrier is limited by its storage and transportation problems. In this restrictive scenario, ammonia ( $\text{NH}_3$ ) provides some advantages associated to its low production cost and high availability. Chemically, it includes 17% in weight of H and it is a carbon-free vector. Thus, ammonia could be used as “energy vector” carrying out its decomposition when clean hydrogen needs to be produced. Most of the catalyst requires high reaction temperatures ( $>500\text{ }^\circ\text{C}$ ) to achieve complete conversion. The Ni and Co metals have attracted much interest as alternative active phase owing to its low cost and the high activity for ammonia decomposition among non-noble metals. Moreover, the rare-earth oxides were effective as the support materials although their surface areas were significantly small (Okura et al. 2018).

In this work, we focused on the perovskites-type oxide ( $\text{LaBO}_3$ ) in order to develop highly active catalysts. Interesting catalytic properties are published for these materials for different reactions. In this study, the effective species in perovskite-type oxides for ammonia decomposition were discussed by systematically changing the B-site elements for nickel and cobalt. Moreover, calcination temperature of the perovskites was studied.

## 2. Experimental

Catalysts were prepared by combustion synthesis. This method takes advantage of an exothermic, fast and self-sustaining chemical reaction between  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NiO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a suitable organic fuel (citric acid). The mixture is slowly heated to evaporate the solvent forming a gel and further heat treatment causes the gel to swell as gasses evolves before finally auto-combusting at a temperature in the range of  $200\text{--}300\text{ }^\circ\text{C}$ . All the catalysts were dried at  $80\text{ }^\circ\text{C}$  overnight and calcined in static air at  $700\text{ }^\circ\text{C}$  for 4 h or  $750\text{ }^\circ\text{C}$  for 2 h. Usually, high calcination temperature ( $>900\text{ }^\circ\text{C}$ ) is needed to obtain the perovskite structure (Zhu et al. 2014) but the combustion synthesis method requires lower calcination temperature (around  $700\text{ }^\circ\text{C}$ ) to achieve a convenient structure. The catalytic tests were carried out in a fixed-bed reactor at atmospheric pressure. Catalysts were in situ reduced by flowing  $50\%$   $\text{H}_2/\text{Ar}$  mixed gas at  $550\text{ }^\circ\text{C}$  for 1 h. After cooling down to  $250\text{ }^\circ\text{C}$  under He flow, a  $5\%$  of  $\text{NH}_3$  ( $100\text{ mL}\cdot\text{min}^{-1}$ ) was fed into the reactor.

## 3. Results

Table 1 shows the specific area of the  $\text{LaNiO}_3$  and  $\text{LaCoO}_3$  calcined at  $700$  and  $750\text{ }^\circ\text{C}$ . The samples calcined at  $750\text{ }^\circ\text{C}$  showed lower specific area ( $S_{\text{BET}}$ ) and pore volume ( $V_p$ ) which is in agreement with the literature (Kucharczyk et al. 2019). In addition, the  $\text{LaCoO}_3$  presents higher  $S_{\text{BET}}$  and  $V_p$  than  $\text{LaNiO}_3$  perovskite.

Table 1. Specific surface area and pore volume of Ni and Co perovskites calcined at different temperatures.

	$\text{LaNiO}_3$ 700	$\text{LaNiO}_3$ 750	$\text{LaCoO}_3$ 700	$\text{LaCoO}_3$ 750
$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	9.7	7.8	13.9	13.5
$V_p$ ( $\text{cm}^3/\text{g}$ )	0.059	0.057	0.094	0.077

Figure 1 (A y B) and Figure 2 (A y B) show XRD and TPR profiles respectively of the catalysts. The diffraction XRD patterns of all the prepared materials are similar to each other. Samples showed peaks characteristic of  $\text{LaNiO}_3$  and  $\text{LaCoO}_3$ , with perovskite-like structure.

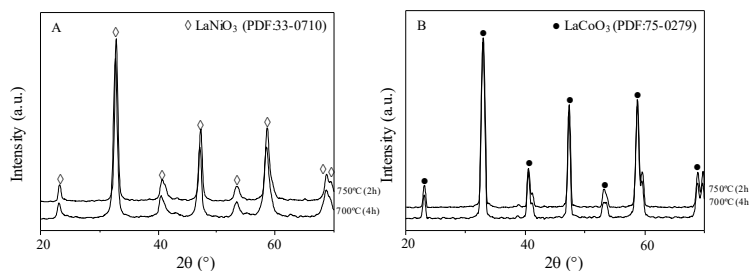


Figure 1: XRD profiles of A)  $\text{LaNiO}_3$  catalysts and B)  $\text{LaCoO}_3$  catalysts.

The reduction profile of the  $\text{LaNiO}_3$  calcined at different temperatures showed two main peaks at temperature ranges of  $200\text{--}400\text{ }^\circ\text{C}$  and  $400\text{--}520\text{ }^\circ\text{C}$ , respectively. The presence of these two phase transition peaks

of  $\text{LaNiO}_3$  perovskite during the reduction is consistent with the literature (Kuras et al. 2008). In the case of  $\text{LaCoO}_3$  perovskite, the reduction profile showed two main peaks at 300-400 °C and 450-550°C attributed to the reduction of  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  to  $\text{Co}^0$ , respectively (Zhao et al. 2017). Therefore, after reduction the active phase of both catalysts are metallic cobalt or metallic nickel deposited on  $\text{La}_2\text{O}_3$ .

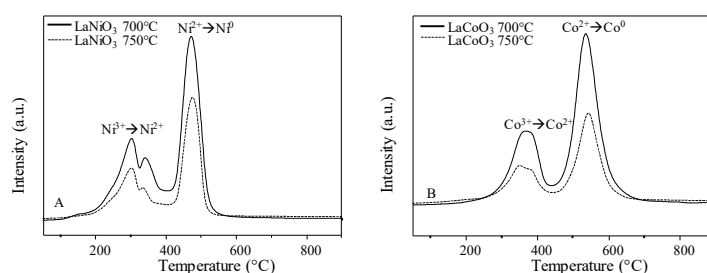


Figure 2:  $\text{H}_2$ -TPR profiles of the A)  $\text{LaNiO}_3$  catalysts and B)  $\text{LaCoO}_3$  catalysts.

Figures 3 and 4 shows the catalytic  $\text{NH}_3$  decomposition over perovskites calcined under different conditions in terms of ammonia conversion at different temperatures. Then,  $\text{LaCoO}_3$  showed better conversion than  $\text{LaNiO}_3$  catalyst when calcination at 700 °C for 4 h is used for the synthesis, reaching an ammonia conversion of 94% at 550 °C with Co perovskite (Figure 3). A better catalytic activity of Co and a higher specific surface as compared with Ni perovskite could explain this result. On the other hand, when the calcination temperature increases at 750 °C (Figure 4), the  $\text{LaCoO}_3$  catalyst achieves a higher ammonia conversion at lower temperature as a consequence of a better dispersion of Co, but the  $\text{LaNiO}_3$  catalysts gets worse the ammonia conversion maybe due to the agglomeration of metallic particles.

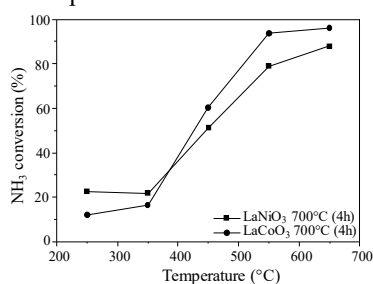


Figure 3: Ammonia conversion versus temperature of catalysts calcined at 700 °C for 4 h.

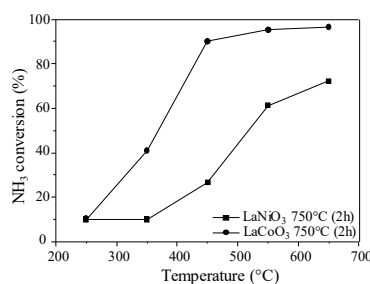


Figure 4: Ammonia conversion versus temperature of catalysts calcined at 750 °C for 2 h.

#### 4. Conclusion

$\text{LaCoO}_3$  are excellent catalyst for the hydrogen production from the ammonia decomposition reaction showing ammonia conversion up to 90% at low temperature (450 °C) when used calcination at 750°C (2h). Temperature calcination in the preparation of perovskites is a crucial parameter that affects differently depending on the metal used.

#### Acknowledgements

This work was supported by the “Junta de Comunidades de Castilla-La Mancha (JCCM)” and European Union [FEDER funds SBPLY/180501/000281].

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