

# Mesoporous Ni/La<sub>2</sub>O<sub>3</sub> catalyst for highly efficient NH<sub>3</sub> decomposition

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### Significance and Relevance

We report on an advanced synthesis method that combines a complexing agent, a hard template and an exsolution step to produce a high specific surface area catalyst which consists in Ni nanoparticles embedded on  $La_2O_3$ . Our catalyst reaches almost complete conversion at 550 °C in NH<sub>3</sub> decomposition with H<sub>2</sub> production rates similar to those reached with expensive doped Ru catalysts. By increasing Ni nanoparticles dispersion on a mesoporous La oxide-based matrix, our catalyst also succeeds keeping high conversions for long periods (i.e. 72 h) demonstrating its unique stability.

Preferred and 2<sup>nd</sup> choice for the topic: H2 storage and transportation, green H2 production, hydrogen vectors (preferred); Fundamental advances in understanding catalysis (2<sup>nd</sup>) Preferred presentation: (Oral only / **Oral preferred or Short Oral** / Poster)

## Introduction and Motivations

Due to fossil fuels depletion and environmental issues, worldwide societies are looking for new efficient and green energy carriers to replace these carbon-based polluting energy sources.<sup>1</sup> In this regard, hydrogen (H<sub>2</sub>) arises as a plausible alternative, but issues related to its handling and storage have blocked its upscaling and application.<sup>1</sup> Hence, current efforts are focused on developing new technologies to efficiently produce H<sub>2</sub> from non-carbon sources with high H<sub>2</sub> content.<sup>2</sup> The most promising candidate is ammonia (NH<sub>3</sub>) due to its high H<sub>2</sub> density and easy handling andstorage. Nevertheless, the challenge lies in its decomposition into H<sub>2</sub> since this process is carried out at high temperatures (i.e. > 800 °C).<sup>2</sup> So far, Ru catalysts with basic doping agents can perform this reaction at temperatures below 550 °C.<sup>3</sup> However, since Ru is a scarce and expensive noble metal, we have developed a new synthesis method to produce a high specific surface area Ni catalyst capable of reaching high H<sub>2</sub> production yields at low temperatures without using neither critical element nor doping agent to achieve its high performance.

#### **Materials and Methods**

Ni(NO<sub>3</sub>)<sub>2</sub> and La(NO<sub>3</sub>)<sub>3</sub> along with citric acid (1:1:2) were dissolved in a ethanol/H<sub>2</sub>O (3/1) solution under continuous stirring. The complexing agent (i.e. citric acid) chelates Ni and La cations to facilitate the formation of LaNiO<sub>3</sub> perovskite in the following stages. Next, a mesoporous SBA-15 (~900 m<sup>2</sup>/g) was added as hard-template to the mixture, which is heated at 60 °C and rotary evaporated to remove the solvents. Thereby, Ni and La cations diffused inside SBA-15 porosity, where during the subsequent calcination at 750 °C they formed a LaNiO<sub>3</sub> perovskite. Next the SBA-15 hard-template was removed by washing the solid with a 5 mol/L NaOH solution at 90 °C. The resulting mesoporous high specific surface area perovskite obtained after SBA-15 removal was named LaNiO<sub>3</sub>-S. The same protocol was used to synthesize a reference bulk perovskite sample without SBA-15 intervention (LaNiO<sub>3</sub>-B). Samples were all characterized by X-ray diffraction and N<sub>2</sub> physisorption to check the perovskite formation as well as their textural properties. Prior to catalytic tests, samples were exsolved under H<sub>2</sub> atmosphere at 550 °C for 1 h. Ni nanoparticles dispersion was assessed by TEM microscopy along with H<sub>2</sub> chemisorption to correlate the data with the catalytic performances achieved in NH<sub>3</sub> decomposition at a GHSV = 30 000 mLNH<sub>3</sub>/g<sub>cata</sub>.h in a range of 300-650 °C.



#### **Results and Discussion**

LaNiO<sub>3</sub>-B and LaNiO<sub>3</sub>-S show the same characteristic XRD peaks corresponding to lanthanum nickelate confirming that SBA-15 addition (and its subsequent removal) did not alter the formation of the perovskite structure (and its integrity) (Fig 1a). The main difference is observed in their textural properties since LaNiO<sub>3</sub>-S displays 50 times the specific surface area reached by LaNiO<sub>3</sub>-B with a pore size distribution centered on 5 nm (Fig 1c). After exsolution, both samples, now denoted as R-LaNiO<sub>3</sub>-B and R-LaNiO<sub>3</sub>-S, present similar textural properties as before, but XRD revealed their structure changed into Ni nanoparticles (NP) on La<sub>2</sub>O<sub>3</sub> (Fig 1b-c). TEM analyses confirmed the presence of Ni NP and their embedment on the La oxide, as well as the presence of mesopores in R-LaNiO<sub>3</sub>-S (as also revealed by N2 physisorption), while EDS analyses showed a better dispersion of Ni nanoparticles than in the case of R-LaNiO<sub>3</sub>-B (Fig1 d-e). During catalytic tests R-LaNiO<sub>3</sub>-S reached almost complete conversion at 550 °C with a H<sub>2</sub> production rate of 29.9 mmol/g<sub>cat</sub>.min. A gap of 20% in conversion was found amid both catalysts demonstrating that the better Ni dispersion on R-LaNiO<sub>3</sub>-S greatly improved its catalytic performance (Fig1f). Moreover, this catalyst remained active for 72 h when  $NH_3$ decomposition was carried out at 550 °C, which results from the Ni NP embedment achieved thanks to the exsolution approach. Hence, this novel method builds an efficient and active catalyst without using basic doping agents (e.g. Sr, Mg) or noble metals (e.g. Ru) to produce  $H_2$  in  $NH_3$  thermic decomposition at low temperatures.



**Figure 1**. Diffractograms of: a) Perovskites; b) exsolved perovskites; c)  $N_2$  physisorption isotherms; HRTEM and EDS analyses of: d) R-LaNiO<sub>3</sub>-B and e) R-LaNiO<sub>3</sub>-S; f) Catalytic performance of samples at GHSV = 30 000 mLNH<sub>3</sub>/g<sub>cata</sub>.h

#### References

- 1. Züttel, A.; Remhof, A.; Borgschulte, A.; Friedrichs, O. Hydrogen: The future energy carrier. *Philos Trans A Math Phys Eng Sci.* **2010**, 360, 3329–3342.
- 2. Chatterjee, S.; Parsapur, R. K.; & Huang, K. W. Limitations of Ammonia as a Hydrogen Energy Carrier for the Transportation Sector. *ACS Energy Lett.* **2021**, 6(12), 4390–4394.
- 3. Chen, C.; Wu, K.; Ren, H.; Zhou, C.; Luo, Y.; Lin, L.; Au, C.; Jiang, L. Ru-Based Catalysts for Ammonia Decomposition: A Mini-Review. *Energy Fuels*. **2021**, 35, 11693–11706

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