

# Novel bimetallic La-Ni and Ba-Ni ceramic foams for dry reforming of methane

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### Significance and Relevance

Dry reforming of methane (DRM) represents a technology for the valorization of  $CO_2$  and the decarbonization of industrial processes. The resulting syngas that is widely utilized in Fischer-Tropsch synthesis and ammonia production, among others. The most active catalyst for this reaction is Ni supported on alumina. The implementation of DRM requires the use of structured catalysts capable of processing large flow rates of  $CH_4$  and  $CO_2$ . Furthermore, the design of active and stable nickel catalysts with a high resistance to coke formation and sintering of the active particles is essential.

Preferred and  $2^{nd}$  choice for the topic: CO<sub>2</sub> utilization and recycling; H<sub>2</sub> storage and transportation, green H<sub>2</sub> production, hydrogen vectors.

Preferred presentation: Oral preferred or short oral

## **Introduction and Motivations**

Climate change represents a significant challenge for contemporary society, prompting governments and institutions to pursue the decarbonization of energy sources<sup>1</sup>. An alternative solution is the valorization of CO<sub>2</sub> and CH<sub>4</sub> through DRM which generates syngas, one of the main intermediate products<sup>2</sup>. This process typically operates at elevated temperatures between 650 and 850 °C and high flowrates in the presence of a Ni-based catalyst<sup>3</sup>. This demands the use of structural catalysts with lower pressure drop, as well as efficiently performs in terms of resistance to deactivation by coking and sintering. However, under these conditions, catalysts frequently undergo deactivation due to the formation of coke and sintering of active metal crystallites<sup>4</sup>. To mitigate coke formation, the addition of a ceramic foam as a support and a second metal which promotes its gasification, such as lanthanum or barium. Lanthanum is known for its coke-gasification property and barium for its basicity. Adding these to the bare catalyst can improve its stability. This study proposes a characterization and performance evaluation of the two promoters in DRM.

### **Materials and Methods**

Modified NiAl<sub>2</sub>O<sub>4</sub> precursors with a promoter/Ni molar ratio of 0.06 and Ni/Al molar ratio of 0.5 were synthesized by Solution Combustion Synthesis (SCS) from a Ni(NO<sub>3</sub>)<sub>2</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, and La(NO<sub>3</sub>)<sub>3</sub> or Ba(NO<sub>3</sub>)<sub>2</sub> solution and glycine as fuel. The open-cell foam was dipped into this gel several times with an intermediate calcination step at 300 °C until a 10wt% loading was achieved. The resulting structured ceramic foam was stabilized at 850 °C for 4 h. The physico-chemical characterization of the samples was carried out using N<sub>2</sub> physisorption, XRD, H<sub>2</sub>-TPR and CO<sub>2</sub>-TPD. Catalytic performance was assessed at 700 °C, and a space velocity of 96,000 h<sup>-1</sup> using a 10%CH<sub>4</sub>/10%CO<sub>2</sub>/80%N<sub>2</sub> feed stream for 72 h at a total flow rate of 800 cm<sup>3</sup> min<sup>-1</sup>. Prior to the reaction, the ceramic foams were reduced at 850 °C for 2 h with a 5%H<sub>2</sub>/N<sub>2</sub> gas stream. The used catalysts were characterized via DTG.

## **Results and Discussion**

X-ray diffractograms of the calcined foams revealed the presence of signals indicative of NiAl<sub>2</sub>O<sub>4</sub> spinel, as well as mullite, cordierite and cristobalite, which can be attributed to the constitutional oxides of the foam substrate. No promoters were identified due to their low concentration and high dispersion. The crystallite size of the NiAl<sub>2</sub>O<sub>4</sub> phase was estimated using the Scherrer equation, obtaining 22 nm



Figure 1. Catalytic lanthanum, barium and non-promoted catalysts.

and 30 nm for Ni-La and Ni-Ba precursors, respectively. Reduced catalysts have been characterized via N<sub>2</sub> physisorption presenting a BET area of 4.8 and 2 m<sup>2</sup> g<sup>-1</sup> for the Ni-La and Ni-Ba samples, respectively. This low area is due to the BET area of the ceramic foam, which is only 0.2 m<sup>2</sup> g<sup>-1</sup>, and the catalyst constitutes only 10% of the total mass. DRX analysis also revealed the crystallite size following reduction, which was 9 nm for the La foam and 12 nm for the Ni-Ba counterpart. No NiAl<sub>2</sub>O<sub>4</sub> was identified, validating the reduction method employed for the ceramic foams. H<sub>2</sub>-TPR analysis revealed two distinct reduction events: one for temperatures below 600 °C for segregated performance of the NiO and other above 600  $^\circ C$  for NiAl\_2O\_4 spinel reduction. The integration and quantification of the reduction profiles demonstrated that over 88% of

the nickel incorporated in the Ni-La foam was in the form of NiAl<sub>2</sub>O<sub>4</sub>, whereas this fraction in the Ni-Ba sample was only 67%. This evidences that barium prevents the reaction between nickel and alumina, while lanthanum limits the formation of the undesired NiO. CO<sub>2</sub>-TPD was conducted to estimate the basic sites of the reduced foams, thereby obtaining the total basicity of the foams and their classification as weak (0-200 °C), medium (200-500 °C) or strong (> 400 °C) basicity. The Ni-La foam exhibited a total basicity of 0.06 mmol CO<sub>2</sub> g<sup>-1</sup> and displayed 86% of strong basicity, whereas the Ni-Ba foam presented a higher total basicity (0.14 mmol  $CO_2 g^{-1}$ ) with a 91% of strong basicity.

The catalytic performance was evaluated in terms of CH<sub>4</sub> and CO<sub>2</sub> conversions and H<sub>2</sub>/CO ratio and compared with the non-promoted ceramic foam with Ni/Al molar ratio of 0.5. Ni-La sample obtained a high conversion, reaching approximately 60%, and exhibited a remarkable stability. In contrast, the bare NiAl foam achieved a similar conversion but began to show signs of deactivation after 48 h. This behavior was assigned to a better coke-gasification properties and a smaller crystallite size for the active phase in Ni-La catalyst. The Ba-promoted catalyst displayed a comparatively lower conversion rate, potentially due to the low nickel spinel formation, yet it demonstrated a more stable conversion than the NiAl foam. The H<sub>2</sub>/CO ratio showed a different tendency as the conversion, with 1.5, 1.2 and 1 molar ratios for the Ba, La and NiAl catalysts, respectively.

Lastly, coke formation was evaluated via TGA resulting in 0.02, 0.106 and 0.77 mg<sub>coke</sub> mg<sub>foam</sub><sup>-1</sup> for the Ni-La, Ni-Ba and NiAl foams, respectively. This indicates a reduction in coke formation in the promoted catalysts and, thereby enhancing their stability.

### References

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