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# A comparative study of dry reforming of methane over nickel catalysts supported on perovskite-type $\text{LaAlO}_3$ and commercial $\alpha\text{-Al}_2\text{O}_3$

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## ABSTRACT

A systematic and comparative study was made to determine the influence of perovskite-type  $\text{LaAlO}_3$  and commercial  $\alpha\text{-Al}_2\text{O}_3$  on the performance of nickel-based catalysts in dry reforming of methane (DRM). The perovskite-type  $\text{LaAlO}_3$  was selected due to its characteristics of solid state semiconductor with oxygen vacancies and high structural stability. The catalysts were characterized by X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF),  $\text{N}_2$  adsorption-desorption, temperature programmed reduction (TPR- $\text{H}_2$ ), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The catalyst performance was evaluated based on activity tests (600–800 °C) and short- and long-term stability (10 and 20 h) at 700 °C at a GHSV (Gas Hourly Space Velocity) of 18 and 72  $\text{L g}^{-1} \text{h}^{-1}$ . The TPR- $\text{H}_2$  profiles indicate that the oxygen vacancies on the perovskite surface exerted a strong effect on the reduction temperature and reducibility of the NiO nanoparticles, resulting in weak Ni<sup>0</sup>/support interaction. The results of the tests after 10 h under GHSV of 18  $\text{L g}^{-1} \text{h}^{-1}$  indicate that the Ni/ $\text{LaAlO}_3$  catalyst is 7.8 and 11.5% more stable than Ni/ $\alpha\text{-Al}_2\text{O}_3$  in the conversions of  $\text{CH}_4$  and  $\text{CO}_2$ , respectively. The higher stability and activity of Ni/ $\text{LaAlO}_3$  is directly ascribed to the presence of NiO (3.38 wt%) after activation, which promoted the formation of carbon nanotubes (CNT) and increased the dispersion of the metallic phase. Even under severe conditions of activation and reaction (high GHSV), as in the long-term test, the Ni/ $\text{LaAlO}_3$  catalyst showed a 37.2% higher  $\text{H}_2$  yield than the Ni/ $\alpha\text{-Al}_2\text{O}_3$ . Analyses by TEM indicate that the Ni/ $\alpha\text{-Al}_2\text{O}_3$

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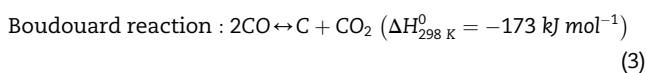
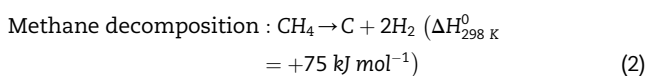
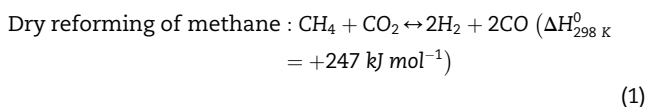
catalyst exhibited deactivation problems associated with sintering effects. Thus, the presence of structural defects and surfaces rich in oxygen vacancies makes LaAlO<sub>3</sub> perovskite a potential support for application in methane catalytic reforming processes.

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## Introduction

The high concentrations of CO<sub>2</sub> in the atmosphere resulting from increasing energy consumption and mainly from burning fossil fuels have generated initiatives for the production of renewable energy and clean technologies for CO<sub>2</sub> capture and conversion [1–4]. Dry reforming of methane (DRM) stands out as a technology for the conversion of CH<sub>4</sub> and CO<sub>2</sub> using fuels as the natural gas or renewable gas (biogas) for the production of H<sub>2</sub> and CO, which are the basis of the chemical and energy industries [5,6]. Hydrogen is considered the main energy source of the future and its production has attracted attention in recent years due to the new technologies and materials for its safe storage [7–10], as well as its use in fuel cells [11–13].

The DRM reaction catalyzed by metal supports (Eq. (1)) is endothermic and spontaneous starting from 640 °C [14]. The noble metals (Ru, Rh, Pd, Ir and Pt) exhibit the highest catalytic activities and stabilities for this reaction [15], but their high cost make them unfeasible for large-scale use. Different metals have been proposed as substitutes for noble metals, with special attention focusing on Ni, Fe and Co [5,16,17]. Nickel stands out for its good performance and relatively low cost compared to the noble metals [18,19], but studies indicate that its catalytic stability is still limited due to sintering and the carbon deposits that cover the active sites [20]. Thus, several researches have focused on the development of nickel catalysts and on the optimization of process conditions that eliminate accumulated carbon by inhibiting certain parallel reactions (Eqs. (2) and (3)) [21]. However, recent studies indicate that certain types of carbon may produce positive effects on the catalytic reaction [22], and may increase nickel activity and stability in DRM [23], although it is not yet clear which set of factors lead to this behavior. Once the interactions between metal and support influence the type of carbon, the development and optimization of support synthesis has become a promising strategy [24,25].



Several studies have been carried out using different ceramic materials as supports for nickel catalysts [5,18,19,21]. In these studies, special attention has focused on alumina due to its relative abundance and low cost. Alpha (α) and Gamma (γ) phases of Al<sub>2</sub>O<sub>3</sub> have been used most frequently because of their differentiated structural and textural properties [26,27]. A critical aspect of the synthesis of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts is the control of metal/support interaction, as well as the formation of NiAl<sub>2</sub>O<sub>4</sub> secondary phases. Ni<sup>2+</sup> species dispersed on the surface of γ-Al<sub>2</sub>O<sub>3</sub> diffuse readily, forming NiAl<sub>2</sub>O<sub>4</sub> after calcination above 600 °C [28]. The formation of NiAl<sub>2</sub>O<sub>4</sub> for the DRM reaction should be avoided due to its low reducibility and sintering problems [29,30]. The high thermal and chemical stability of α-Al<sub>2</sub>O<sub>3</sub> prevents the formation of NiAl<sub>2</sub>O<sub>4</sub> [24] and may favor the production of free NiO on its surface.

For catalytic applications, the properties of the aluminum oxides are improved by adding metals to their structure, forming spinels and perovskites [16,28]. The addition of lanthanum stabilizes the structure and changes the acid-base properties of γ-Al<sub>2</sub>O<sub>3</sub> due to the formation of perovskite-type LaAlO<sub>3</sub> [31,32]. The typical synthesis of LaAlO<sub>3</sub> powders is via solid state reaction by mixing the oxides and calcinating at high temperatures (usually above 1500 °C) [33,34]. However, this method has some disadvantages, such as the introduction of impurities during the milling process of the precursors, low chemical homogeneity, high reaction temperatures and large particle size of the resulting powders. In recent years, several low-temperature chemical routes have been used to synthesize homogeneous LaAlO<sub>3</sub> powders, including the sol-gel [35], Pechini [36], combustion [37], hydrothermal [38], coprecipitation [39], solvothermal [40], combined EDTA-glycine process [41] and sucrose methods [42]. In addition to these methods, the synthesis of monophasic and homogeneous ceramic materials via microwave assisted combustion reaction has been considered simple, fast and inexpensive [43], and was used here to obtain the LaAlO<sub>3</sub> structure.

The stable LaAlO<sub>3</sub>, SrTiO<sub>3</sub> and BaTiO<sub>3</sub> perovskites have been evaluated as catalytic supports [35], but dry reforming of methane studies using nickel as active metal and LaAlO<sub>3</sub> as support are reduced in the literature [28,44]. In almost a century of research on DRM [14] barely is known about the phenomenological behavior of the Ni/LaAlO<sub>3</sub> catalyst. In this context, the purpose of the present study was to synthesize and evaluate the LaAlO<sub>3</sub> support in dry reforming of methane using nickel as an active metal. The performance and formation of carbon of the Ni/LaAlO<sub>3</sub> catalyst was systematically compared to the Ni catalyst supported on commercial α-Al<sub>2</sub>O<sub>3</sub>.

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