



# Dry reforming of methane over Ni/La<sub>2</sub>O<sub>3</sub> nanorod catalysts with stabilized Ni nanoparticles



Xinyu Li<sup>a,b</sup>, Di Li<sup>a,b</sup>, Hao Tian<sup>a,b</sup>, Liang Zeng<sup>a,b</sup>, Zhi-Jian Zhao<sup>a,b</sup>, Jinlong Gong<sup>a,b,\*</sup>

<sup>a</sup> Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

<sup>b</sup> Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, China

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## ABSTRACT

This paper describes the design of a Ni/La<sub>2</sub>O<sub>3</sub> catalyst using La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> nanorod as a support precursor (denoted as Ni/La<sub>2</sub>O<sub>3</sub>-LOC) via a wet impregnation method for dry reforming of methane (DRM). The results showed that La<sub>2</sub>O<sub>3</sub> derived from the La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> precursor maintained its initial morphology upon thermal treatment and could highly disperse Ni particles on it. Additionally, the nanorod-shaped support could provide more medium-strength basic sites to facilitate CO<sub>2</sub> adsorption and activation on its surface. Consequently, the Ni/La<sub>2</sub>O<sub>3</sub>-LOC catalyst reached 70% of CH<sub>4</sub> conversion and 75% of CO<sub>2</sub> conversion at 700 °C after 50 h DRM reaction with a H<sub>2</sub>/CO ratio of 0.87. The enhanced metal-support interaction restricted the sintering of nickel particles under harsh reaction conditions. Coke evolution on the catalysts was also investigated to understand coke formation mechanism and the role of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> in coke elimination. It has been found that nickel dispersion can affect distribution of coke and La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> on the surface of catalyst, both of which have a close relation with catalytic performance.

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## 1. Introduction

With the rapid development of human society, people rely on energy more than ever before. As one of the three primary fossil fuels (coal, oil and natural gas), the exploitation of natural gas is increasing, which requires clean and efficient utilization of methane. Simultaneously, discoveries of abundant shale gas reserves are expected to reduce dependence on crude oil [1]. At present, industrial-scale hydrogen generation is still dependent on the conversion of natural gas or shale gas [2], and methane reforming processes have been extensively investigated [3–5], such as steam reforming of methane (SRM) [6], partial oxidation of methane (POM) [7–9], autothermal reforming of methane (ATR) [10], and dry reforming of methane (DRM) [11]. DRM has many intriguing advantages attracting considerable attention [3]. DRM (Eq. (1)) uses CH<sub>4</sub> and CO<sub>2</sub> as feedstocks to produce syngas (CO + H<sub>2</sub>) so that DRM can mitigate the adverse effect resulting from global warming problems, since both CH<sub>4</sub> and CO<sub>2</sub> are major greenhouse gases. On the other hand, the obtained syngas via DRM process has a moderate ratio of H<sub>2</sub> to CO (1:1), which is lower than the syngas

obtained via SRM process (H<sub>2</sub>/CO = 3:1), and then the mixture of the above two syngases can be applied in liquid fuel production through the Fischer-Tropsch synthesis (H<sub>2</sub>/CO = 2:1) [10,12,13]. Moreover, CO<sub>2</sub> is an undesirable impurity in natural gas and sometimes its concentration is as high as 70% [14,15]. The raw natural gas can be directly used as DRM feedstock to produce syngas so that subsequent gas separation and purification can be cut to save equipment investment. However, the obtained syngas via DRM process generally has a ratio of H<sub>2</sub>/CO lower than 1 due to the occurrence of reverse water gas shift (RWGS) reaction (Eq. (2)) [3], which is harmful for H<sub>2</sub> production since a part of H<sub>2</sub> reacts with the reactant CO<sub>2</sub> to produce water [16]. RWGS is thermodynamically favored at low temperatures (<600 °C) [17,18], thus DRM is typically operated at 700–800 °C to suppress RWGS and coke from the Boudouard reaction (Eq. (3)) for attaining industrial relevant conversions [19–21]. Moreover, when temperature reaches beyond 800 °C, sintering occurs significantly and the process is highly energy-consuming [19].



\* Corresponding author at: 92 Weijin Road, Nankai District, School of Chem. Eng. & Technol., Tianjin University, China.

E-mail address: [jl.gong@tju.edu.cn](mailto:jl.gong@tju.edu.cn) (J. Gong).

Active metals of catalysts used in DRM can be generally divided into noble metals [3] and base metals [4]. Noble metals primarily comprise Pt [22], Rh [11], Ru [23], etc., which have superior capacity to cleave the C–H bond and suppress carbon deposition. However, their industrial application is restricted due to their high costs. Simultaneously, nickel-based catalysts have been extensively investigated in the DRM process on account of their high catalytic activity and availability. Nickel-based catalysts have two intrinsic drawbacks which can result in deactivation: they are prone to sinter under elevated temperatures and suffer from severe coke deposition. Coke deposition mainly originates from the Boudouard reaction (Eq. (3)) and CH<sub>4</sub> decomposition (Eq. (4)) [24]. There are various mechanisms to suppress sintering and coke deposition [4]. Our group recently summarized encapsulated group VIII metal catalysts exhibiting excellent anti-sintering performance [25]. In addition, Liu et al. concluded various types of carbon deposition and respective carbon growth mechanism on nickel-based catalysts used in the DRM process [5].

The reaction mechanism of DRM depends on the properties of both active metals and supports. Iglesia et al. extensively studied the mechanism of CH<sub>4</sub> reforming reactions on the basis of isotopic and kinetic assessment [26–28]. Up till now, many oxides have been investigated in DRM to support nickel nanoparticles, such as Ni/SiO<sub>2</sub> [29,30], Ni/Al<sub>2</sub>O<sub>3</sub> [31], and Ni/La<sub>2</sub>O<sub>3</sub> [7–9,32,33]. For Ni/SiO<sub>2</sub>, both CH<sub>4</sub> and CO<sub>2</sub> are activated on metal active sites [4], where the monofunctional mechanism will cause two reactants to compete for metal active sites thus leading to the decrease of reaction rates. With regard to Ni/La<sub>2</sub>O<sub>3</sub>, it follows a bifunctional mechanism: methane dissociation occurs on Ni nanoparticles, which is typically considered as the rate determining step, and CO<sub>2</sub> activation occurs on La<sub>2</sub>O<sub>3</sub> support [34–36]. Generally, supports with acidity are more inclined to cause coke deposition [4], while La<sub>2</sub>O<sub>3</sub> as a basic support can promote CO<sub>2</sub> adsorption and activation on its surface since CO<sub>2</sub> has mild acidity [37]. Indeed, La<sub>2</sub>O<sub>3</sub> is applied in DRM for its basicity and its capacity to react with CO<sub>2</sub> to form La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, both of which are advantageous to suppress carbon deposition. La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> can react with coke on the surface of nearby Ni nanoparticles (NPs) to form CO and regenerate La<sub>2</sub>O<sub>3</sub> [34–36,38]. Recently, Müller and co-workers reported that the addition of Co on Ni/La<sub>2</sub>O<sub>3</sub> can increase the rate of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> formation and bring about improvements in catalytic activity and stability [33]. Therefore, La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> is regarded as a good intermediate species to eliminate deposited coke.

Poor dispersion of active metal on La<sub>2</sub>O<sub>3</sub> is the main problem for Ni/La<sub>2</sub>O<sub>3</sub>-based catalysts due to the limited surface area [39]. In order to improve this problem, mineral-type precursors are introduced in this system, such as perovskite [39,40], spinel [41], pyrochlore [11,15]. LaNiO<sub>3</sub> perovskite derived Ni/La<sub>2</sub>O<sub>3</sub> has been studied extensively [42], on which Ni dispersion gained prominent improvement. Additionally, a method of nanocasting using SBA-15 as a hard template was adopted to prepare high-surface-area LaNiO<sub>3</sub> perovskite precursor, which could further disperse Ni particles on La<sub>2</sub>O<sub>3</sub> support after reduction [37]. However, a common drawback of this method is that the introduced template is hard to remove completely [43]. Mo et al. adopted oleic acid in the impregnated solution to disperse Ni particles on La<sub>2</sub>O<sub>3</sub> doped SiO<sub>2</sub> support via a self-assembled core-shell precursor route [44]. Besides, La<sub>2</sub>O<sub>3</sub> is usually used as promoter due to the fact that La<sub>2</sub>O<sub>3</sub> can improve catalyst properties including surface basicity of supports and metal-support interaction. Montero et al. used La<sub>2</sub>O<sub>3</sub> as promoter to investigate coke formation mechanism during the deactivation of a Ni/La<sub>2</sub>O<sub>3</sub>- $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst in ethanol steam reforming (ESR) process, since La<sub>2</sub>O<sub>3</sub> can tune surface basicity of support to suppress the formation of C<sub>2</sub>H<sub>4</sub> as coke precursor [45]. Our group found La-modifiers enhanced the basicity of ordered mesoporous Ni-based catalysts, suppressed carbon deposition and

improved catalyst stability [46]. However, on account of intrinsic hydrophilic nature of La<sub>2</sub>O<sub>3</sub>, La species may partially cover the Ni catalytic surface via the migration of La species and then lead to the deactivation of catalysts [47]. Therefore, the amount of La<sub>2</sub>O<sub>3</sub> addition should be controlled.

La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> as an active intermediate of La<sub>2</sub>O<sub>3</sub> to suppress deposited coke can be easily prepared with different shapes, such as nanorods, nanoplates, nanosheets, nanoparticles, nanoflowers [43]. Among nanoshaped La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> nanorods have been applied in steam reforming of glycerol [48] and oxidative coupling of methane [49], which can enhance interaction with metals thus exhibiting excellent anti-sintering performance [50,51]. Recently, Singh et al. found that Ni/La<sub>2</sub>O<sub>3</sub> highly depends on shape and structure of parent nanoparticles [32]. Moreover, they reported that high-aspect ratio parent shapes (e.g. rods) may prove to be an ideal structure [32].

This paper describes the synthesis of Ni/La<sub>2</sub>O<sub>3</sub> nanorod catalyst with stabilized Ni nanoparticles for the DRM process. We expect that nanorod-shaped La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> as a support precursor could enhance Ni dispersion on La<sub>2</sub>O<sub>3</sub> support and contribute to obtain robust DRM performance. Coke evolution was investigated to understand coke mechanism on Ni/La<sub>2</sub>O<sub>3</sub> catalyst and the role of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> in coke elimination. The physical-chemical properties of the catalysts were investigated by X-ray diffraction (XRD), N<sub>2</sub>-adsorption, transmission electron microscopy (TEM), H<sub>2</sub> pulse chemisorption, thermogravimetric analysis (TGA), H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR), temperature-programmed oxidation (TPO), and Raman spectra. Catalytic tests were conducted to differentiate the performance of the two catalysts. The stabilities of the both catalysts were characterized under high gas hourly space velocity (GHSV), while low GHSV was adopted to investigate the coke evolution on the catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

Analytical grade Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were obtained from Aladdin Industrial Corporation (Shanghai, China). De-ionized water (18.0 M $\Omega$ ) was prepared from Ulupure water purifier machine (Chengdu, China). Anhydrous ethanol (99.8 wt.%) and analytical grade aqueous ammonia (25 wt.%) were supplied by Guangfu Fine Chemical Research Institute (Tianjin, China). Guaranteed grade urea was gained from Kermel Chemical Reagent (Tianjin, China).

The synthesis routes of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> are modified according to the preparation method reported by Huang et al. [48]. 2.6 g of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was dissolved in 160 mL of de-ionized water, and 7.2 g of urea was dissolved in another 240 mL of de-ionized water. Once dissolved, the two solutions were mixed with continuously stirring, and then 1.6 mL of aqueous ammonia was added into the mixture. After heating in a water bath at 90 °C for 3 h with agitation, the obtained white suspension was naturally cooled to room temperature. Then the white suspension was centrifuged, and the precipitate was washed twice with absolute ethanol. After drying at 80 °C overnight and calcination at 500 °C for 2 h, nanorod-shaped La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> was obtained.

Ni/La<sub>2</sub>O<sub>3</sub> catalysts were prepared by a wet impregnation method. The loading was fixed to 5 wt% for all the reduced samples to be investigated. The supported Ni/La<sub>2</sub>O<sub>3</sub> catalyst was prepared by impregnating 0.95 g of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> with an aqueous solution containing 0.25 g of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O dissolved in 40 mL of de-ionized water. After stirring at 80 °C for 3 h, vacuum evaporation was carried out until the solvent was completely removed. Then the sample was ground and calcined at 600 °C for 2 h.

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