



Full Length Article

La-promoted Ni-hydroxalcite-derived catalysts for dry reforming of methane at low temperatures



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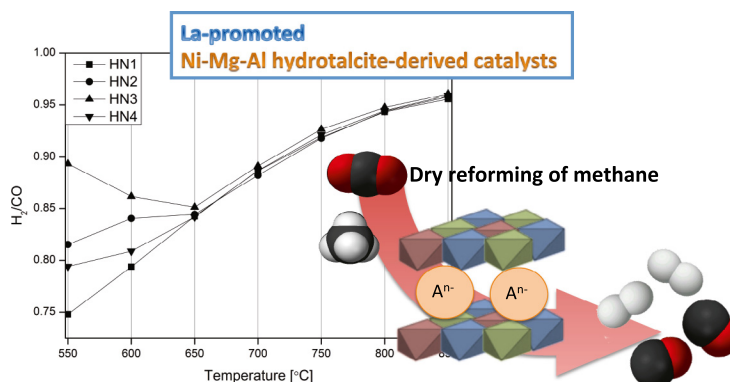
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HIGHLIGHTS

- La-promoted Ni–Mg–Al hydroxalcite-derived catalysts for methane dry reforming.
- La increases weak and medium strength basicity.
- La improves the reducibility of Ni-species.
- La enhances the catalytic activity.
- La contributes to the gasification of carbon deposits.

GRAPHICAL ABSTRACT



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ABSTRACT

La-promoted Ni-containing hydroxalcite-derived catalysts were prepared and tested in dry methane reforming at low-moderate temperatures. The prepared materials were characterized by means of X-ray diffraction (XRD), temperature programmed reduction (H₂-TPR) and CO₂-temperature programmed desorption (TPD). The presence of lanthanum was found to enhance the reforming reaction, but also direct methane decomposition at low reaction temperatures. This fact was assigned to an increased presence of Ni⁰ sites as a consequence of improved reducibility of Ni-species in the La-promoted catalysts. Lanthanum can well contribute to the gasification of amorphous carbon deposits, resulting in lower overall carbon deposition at 550 °C.

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1. Introduction

Dry reforming of methane (DRM), the reforming of methane with CO₂: CH₄(g) + CO₂(g) = 2CO(g) + 2H₂(g), ΔH₀ (298 K) = + 247 kJ mol⁻¹, is nowadays considered as a perspective alternative

for the production of syngas, H₂ + CO, involving the valorization of CO₂, coming either from capture or naturally present in the reactant gas, i.e. such in biogas. Furthermore, the H₂/CO molar ratio in DRM-syngas, equal to 1, makes it applicable for Fischer-Tropsch synthesis [1–4]. There are, however, several important drawbacks that hinder the practical application of DRM, such as its high endothermicity, and different issues related to the selectivity and stability of the DRM catalyst under operation conditions [5,6].

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The co-existence of parallel reactions, such as direct methane decomposition and the reverse water gas shift reaction results in low yields and in catalyst deactivation through carbon deposition, especially at low reaction temperatures. Increasing the temperature favors DRM thermodynamics, but Ni particles tend to sinter leading to a dramatic decrease in the catalytic performance.

Different active metals, e.g. Ru, Pt, Pd, Ni or Rh, supported on different materials, have been proposed as DRM catalysts [7–17,19]. Among them, nickel shows comparable activity to noble metals, being much cheaper and more readily available. Current research efforts focus on finding support materials and promoters that improve the selectivity of the process and that contribute to enhanced catalytic stability. As an example, Vergyios [20] showed that the incorporation of Ni onto La_2O_3 support notably improved the catalysts stability in comparison to Ni– Al_2O_3 , through the formation of oxy-carbonate species ($\text{La}_2\text{O}_2\text{CO}_3$) that were further able to gasify the already formed carbon deposits.

Also known as layered double hydroxides, hydrotalcites are mixed hydroxide materials having the general formula: $[\text{M}_{1-x}^{\text{II}}\text{M}_x^{\text{III}}(\text{OH})_2][\text{A}_{x/n}^{n-}] \cdot m\text{H}_2\text{O}$, where $\text{M}^{\text{II}}/\text{M}^{\text{III}}$ represent divalent and trivalent metal ions and A^{n-} hydrated anion. Their composition can be easily modified through the substitution of different divalent and trivalent cations in the brucite layers, i.e. substituting Mg^{2+} by Ni^{2+} . The works of Cavani et al. show that even monovalent and tetravalent cations such as Li^+ , Zr^{4+} , Ti^{4+} and Sn^{4+} can be as well introduced into these hydrotalcite-layers [21]. Therefore, the acid-base and redox properties of hydrotalcite-derived oxides can be properly tailored to fit any particular catalytic application [22,23]. Moreover, the materials obtained after calcination of the hydrotalcite matrix offer other interesting properties, such as adequate porosity, and a random and homogeneous distribution of the different cations on the resulting mixed-oxide structure. As a consequence, Ni-containing hydrotalcite-derived materials have been recently considered as promising catalysts for DRM [18,24–26].

The addition of promoters can positively influence activity, selectivity and/or stability of hydrotalcite-derived catalysts. Among them, the incorporation of rare earth oxides can help controlling DRM selectivity, through the inhibition of carbon formation reactions, or strengthened CO_2 adsorption on the support [17,26–28]. Debek et al. [26,29] found that incorporation of Ce into Ni-containing hydrotalcite-derived catalysts resulted in an increased reducibility of nickel species, and led to the formation of new strong basic sites, which improved the long-term stability of these catalysts in DRM reaction. However, CO_2 and CH_4 conversion became somewhat lower. Lanthanum has also been considered as a promoter of Ni-containing hydrotalcite-derived catalysts for DRM. Previous published papers just evidence the promotion effect of La, or its promoting effect in combination with noble metals or other promoters [18,30,31]. Serrano-Lotina et al. [30] studied the influence of calcination temperature on the activity of a Ni (2.3 wt.%) catalyst containing La (1.3 wt.%). Lucredio et al. [31] prepared several hydrotalcite-derived catalysts containing 10 wt.% of Ni and 10 wt.% of La and/or 1 wt.% of Rh. La-promotion did not lead to improvement of activity but increased the stability in the DRM reaction. It should be taken into account that the activity of Ni-containing hydrotalcite-derived catalysts strongly depends on the amount of Ni-cations introduced in the pristine hydrotalcite structure [32]. The best performance was observed for the catalysts containing ca. 20 wt.% of Ni (i.e. 25% of exchanged Mg in the catalysts). There is still no clear understanding of the effect of lanthanum incorporated to hydrotalcites containing a constant amount of nickel. Moreover, so far and to the best of our knowledge, only the work of Yu and co-workers takes into consideration the incorporation of different amounts of La, however, La-loadings employed (3–10 wt.%) were much higher

than the ones used in the preparation of the catalysts presented herein.

Thus, the present work considers the addition of lanthanum (1–4 wt.%) to 15 wt.% Ni-containing hydrotalcite-derived catalysts for dry reforming of methane. Special attention has been paid to the influence of La-promotion on the physico-chemical properties of the hydrotalcite-derived catalysts, as studied by means of XRD, H_2 TPR and CO_2 TPD, and its consequences in terms of activity, selectivity and stability in the DRM reaction.

2. Experimental

2.1. Synthesis of the hydrotalcite-derived catalysts

Hydrotalcites containing M(III) trivalent and M(II) divalent metals (Al, La, Mg, Ni,) with M(III)/M(II) molar ratio of 0.33, were prepared by a co-precipitation method at constant pH (from 9.5 to 10). Two aqueous solutions, one containing the mixed nitrates of divalent and trivalent metals, and a second one containing sodium hydroxide (1 M), were added dropwise into a flask containing an aqueous solution of sodium carbonate, and subsequently kept under vigorous stirring at 65 °C and constant pH. This mixture aged for 24 h and then filtered, carefully washed with deionized water and finally dried overnight at 80 °C. The nominal (assumed) concentration of the different components in each hydrotalcite prepared (un-promoted and La-promoted), as well as their labeling, is listed in Table 1. In order to obtain the corresponding hydrotalcite-derived catalysts, each hydrotalcite was calcined under air at 550 °C for 4 h.

2.2. Physico-chemical characterization

X-ray diffraction (XRD) patterns were acquired in a PANalytical-Empyrean diffractometer, equipped with Cu $K\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation source, within 2θ range from 3° to 90°, with a step size of 0.02°/min. The Scherrer equation was used for calculating the Ni crystal size on the reduced HT-derived catalysts. Temperature programmed reduction (H_2 -TPR) profiles were obtained in a BELCAT-M (BEL Japan) device, equipped with a thermal conductivity detector (TCD). The calcined hydrotalcites were first outgassed at 100 °C for 2 h and then reduced using 5 vol.% H_2 -Ar at a heating rate of 7.5 °C/min, from 100 °C to 900 °C. Temperature programmed desorption (CO_2 -TPD) was performed using the same apparatus (BELCAT-M). The catalysts were first degassed for 2 h at 500 °C and then cooled to 80 °C. Subsequently, a mixture of 10 vol.% CO_2 -He was fed for 1 h in order to saturate their surface with CO_2 , followed by the desorption of weakly (physically) adsorbed CO_2 under a flow of pure He for 15 min. Then, the catalysts were heated up from 80 °C to 900 °C under He, at 10 °C/min and the evolution of CO_2 was followed with the aid of a TCD detector. The amount of carbon deposited on the surface of each catalyst upon the DRM reaction was measured by means of its thermogravimetric oxidation in a SDT Q600 apparatus (TA Instruments), under air flow (100 mL/min), heating from ambient temperature to 900 °C at a rate of 10 °C/min. The resulting materials were grinded and sieved keeping the solid fraction corresponding to a particle size distribution between 100 and 300 μm .

2.3. Dry reforming of methane (DRM) activity tests

The activity of the different HT-derived catalysts was assayed in an experimental set-up consisting of a tubular quartz reactor (8 mm internal diameter) heated inside the catalytic fixed bed was measured with the aid of a K-type thermocouple. A series of mass-flow meters (Brooks) allowed the fed of 100 mL/min of a

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