

# Effect of composition and thermal pretreatment on properties of Ni–Mg–Al catalysts for CO<sub>2</sub> reforming of methane

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## Abstract

Ni–Mg–Al catalysts prepared by continuous coprecipitation were evaluated for carbon dioxide reforming of methane carried out between 500 and 700 °C. The mixed oxides obtained after calcination exhibit higher surface area values and lower crystallinity. The activity results obtained with different samples demonstrated that the catalytic properties of Ni–Mg–Al catalysts are more affected by the M<sup>II</sup>/M<sup>III</sup> ratio than the Ni/Mg ratio. For samples with constant M<sup>II</sup>/M<sup>III</sup> ratio the best results were obtained for  $5 \geq \text{Ni/Mg} > 1$  ratios. Among the thermal pretreatment effects, the reduction temperature was revealed as a strong influence on the activity and selectivity for the CO<sub>2</sub> reforming of methane. In contrast, the catalytic properties can be considered practically independent from the calcination temperature, and the influence of this parameter is restricted to the decrease of the surface area values with the increase of the calcination temperature.

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## 1. Introduction

Mixed oxides resulting from thermal treatment of hydrotalcites present several interesting properties [1]. Hydrotalcite-like compounds are layered double hydroxides. The general formula of these compounds can be represented as  $[M_{1-x}^{(II)}M_x^{(III)}(\text{OH})_2]^{x+} [A_{x/n}^{n-}]_m \text{H}_2\text{O}$  where M<sup>(II)</sup> and M<sup>(III)</sup> are divalent and trivalent cations and A is the compensation anion. The structure can accommodate a wide variation in the different M<sup>(II)</sup> and M<sup>(III)</sup> metals, leading to different properties. Thermal decomposition of these materials by calcination results in the formation of mixed oxides with a high thermal stability and a large surface area. In addition, well-dispersed metallic particles are usually obtained after a reduction treatment [1,2].

Ni–Al-mixed oxides obtained from hydrotalcite compounds are among the most investigated materials. However, little was known about ternary mixed oxides before Fornasari et al. [3] presented a detailed study of the reactivity of Ni–Mg–Al-mixed oxides with high surface area. Later studies carried out by Tichit et al. [4] demonstrated that the thermal stability of Ni–Mg–Al samples increases with the Mg content for calcination

up to 700 °C while the reducibility decreases when both calcination temperature and Mg and Al contents increase. On the other hand, it is very well known that the acid–base character of the surface influences the catalytic properties of mixed oxides [1]. Casenave et al. [5] studied the acid–base character of Ni–Mg–Al-mixed oxides using adsorption calorimetry and their results indicate an increase in the acid sites with the nickel content. However, at the same time, the highest concentration of basic sites was observed in the sample with low magnesium and high nickel contents. According to the authors, this fact evidences the synergetic effect of these metals for the basic properties [5].

The particular properties of Ni–Mg–Al-mixed oxides have been applied to several reactions such as hydrogenation of acetonitrile [6], CO<sub>2</sub> reforming of methane [7–10], partial oxidation of methane [11–13] or light paraffins [14], and oxidative dehydrogenation of hydrocarbons [15,16].

In previous works related to CO<sub>2</sub> reforming of methane Bhattacharyya et al. [7] compared clay-derived Ni–Mg–Al catalysts with supported Ni/Al<sub>2</sub>O<sub>3</sub> or Ni/MgAl<sub>2</sub>O<sub>4</sub> catalysts, and they concluded that the clay-derived catalysts exhibited superior activity and stability under severe operating conditions. Later studies conducted on Ni-supported catalyst prepared by solid phase crystallization method, starting from hydrotalcite anionic clay [8], verified that Ni cation can well

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replace the Mg cation, resulting in the formation of highly dispersed Ni metal particles. These catalysts showed higher activity than those prepared by the conventional impregnation method in the CO<sub>2</sub> reforming of methane. Recently, Hou and Yashima [10] showed that Ni existed mainly in NiAl<sub>2</sub>O<sub>4</sub> and/or Ni–Mg–O solid solution on mesoporous Ni–Mg–Al catalysts. According to the authors, the higher surface area of the catalysts allowed a stronger interaction between Ni and Al–Mg, which improved the dispersion of Ni and retarded the sintering of Ni during the reforming process. The highly dispersed Ni exhibited higher reforming activity, lower coke formation and higher stability. With respect to the pretreatment influence on the catalytic properties of Ni–Mg–Al catalysts, Lee and Lee [12] have reported that the catalyst performance was strongly related to the Ni particle size and calcination temperature in the partial oxidation of methane.

Nevertheless, in some of these previous works, the results were obtained using catalysts with a fixed composition of Ni [10,12,13] or fixed Ni/Mg ratio [8]. In some cases, studies were conducted to evaluate the influence of the pretreatment [9,12]. Although Ni–Mg–Al catalysts samples with different compositions were used in some works [6,16], in one of them [16] the M<sup>II</sup>/M<sup>III</sup> ratio was maintained constant. Cabello et al. [6] found that an optimal Ni/Mg ratio maximizes the selectivity in the hydrogenation of acetonitrile. The occurrence of this optimum is related to a compromise between the reducibility of Ni and the acidity–basicity of material.

As can be seen, several parameters influence the catalytic properties of Ni–Mg–Al-mixed oxides. In the catalyst formulation, the content of the active phase (Ni), the Ni/Mg ratio, and the M<sup>II</sup>/M<sup>III</sup> ratio is essential [1,3]. Keeping in mind that the literature revision indicates that the studies concerning the CO<sub>2</sub> reforming of methane on Ni–Mg–Al catalysts were carried out without taking into account all these parameters simultaneously, this work will evaluate the influence of the catalyst composition as well as the influence of the thermal treatment on the properties of Ni–Mg–Al to CO<sub>2</sub> reforming of methane.

Carbon dioxide or dry reforming of methane is more endothermic and produces a more adequate CO/H<sub>2</sub> ratio for the synthesis of the valuable oxygenated chemicals than Steam methane reforming, which is the conventional route to transform natural gas into synthesis gas. In recent years, renewed interest in the CO<sub>2</sub> reforming reaction has arisen from an environmental viewpoint since both CH<sub>4</sub> and CO<sub>2</sub> are greenhouse gases. This reaction has attracted interest as carbon dioxide consuming process.

Different catalysts have been evaluated in this reaction containing Ni and noble metals, amongst others, as the active phase. Noble metal catalysts, belonging to Group VIII, are less sensitive to coke deposition than Ni catalysts [17–20]. However, the high cost and the difficulty in producing noble metals [21] have led to the development of nickel catalysts resistant to coke deposition and to extended time on stream.

The main cause of nickel catalyst deactivation in catalytic reforming processes is coke deposition [20,22,23–25]. It has been more frequently observed in the CO<sub>2</sub> reforming due to the low H/C ratio of the system. Carbon deposition can occur

through the CO disproportionation or by methane cracking reactions.

Some authors [22,26,27] reported a reduction of coke deposition through the addition of alkaline oxides, with the intent of increasing the basicity of the catalyst. Another way to decrease deactivation by coke deposition is to prepare a catalyst with adequate alkaline properties through simultaneous coprecipitation with a metal of basic properties. Considering that mixed oxides obtained from hydrotalcites-like compounds exhibit basic properties as well as a higher dispersion of the active phase [3], these materials have proved themselves interesting catalysts for the reforming of methane. In addition, these materials allow great flexibility in the molar ratio between divalent and trivalent cations.

In this context, the objective of this work is to study the influence of the catalyst composition and the influence of both calcination and reduction temperatures on the catalytic properties of Ni–Mg–Al for CO<sub>2</sub> reforming of methane.

## 2. Experimental

The Ni–Mg–Al catalysts were prepared by a continuous coprecipitation from two aqueous solutions. The first solution contained nitrates of the metals and the second solution contained potassium carbonate as precipitant. The coprecipitation was carried out under constant agitation at 60 °C, maintaining the pH constant (8 ± 0.1) by adjusting the flow rate of solutions. The precipitated was submitted to crystallization for 1 h and then vacuum filtered and washed thoroughly with distilled and deionized water, until the pH value of the filtrate was equal to that of the washing water. The resulting slurry was later dried overnight at 90 °C in an oven. The oxides were obtained by thermal treatment with synthetic air (80 cm<sup>3</sup>/min) at 600 °C for a period of 6 h and using a heating rate of 10 °C/min. To study the influence of calcination temperature, some samples were also calcined at different temperatures (400, 600, and 800 °C).

The samples were characterized by surface area measurements (*S*<sub>BET</sub>), X-ray diffraction (XRD) analysis, temperature-programmed reduction (TPR) and temperature-programmed oxidation coupled with differential thermal analysis (TPO/DTA). For surface area and pore volume measures, the samples were previously outgassed under vacuum at 300 °C. The adsorption isotherms were carried out on a Quantachrome Nova-1200 surface area analyzer by N<sub>2</sub> adsorption at liquid nitrogen temperature. The X-ray diffraction patterns were collected by the powder method with a D-500 Siemens diffractometer using Cu K $\alpha$  radiation. The crystallite sizes of Ni<sup>0</sup> after reduction and before reaction (fresh samples) were determined by Scherrer equation [28] from the (1 1 1) reflection. For thermogravimetry analysis, TG, TPR, and TPO/DTA profiles were recorded on a TA thermobalance (model SDTQ600). For TPR profiles the samples were heated at 10 °C/min with a H<sub>2</sub>/N<sub>2</sub> mixture (30% H<sub>2</sub>) at a total flow of 150 cm<sup>3</sup>/min. For TG and TPO/DTA profiles the following conditions were used: air flow (100 cm<sup>3</sup>/min), heating rate of 10 °C/min from room temperature to 800 °C and sapphire as reference compound.

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