MgO promoted catalysts exhibited higher catalytic activity and lower carbon formation compared to unpromoted catalyst in dry reforming reaction

Effects of alkaline earth promoters on the catalytic performance of the nickel catalysts supported on high surface area mesoporous magnesium silicate in dry reforming reaction

Bahare Ghods¹, Fereshteh Meshkani², Mehran Rezaei^{1, 2*}

Abstract

Nanostructured magnesium silicate nanopowder with high surface area ($619 \text{ m}^2/\text{g}$) synthesized by hydrothermal method and modified by alkaline earth metal oxides (MgO, CaO, and BaO) was used as support for nickel based catalysts in dry reforming of methane. The synthesized catalysts were characterized by N_2 adsorption (BET), X-ray diffraction (XRD) and temperature programmed reduction and oxidation (TPR-TPO) techniques. The results revealed that addition of modifiers decreased the specific surface area and shifted the pore size distributions to smaller sizes. TPR analysis revealed that the reduction temperature decreased by the addition of modifiers to the catalyst. The catalytic results showed that the catalytic performance enhanced by the addition of promoters and modified catalyst by MgO exhibited the highest catalytic performance. Also, Ni/MgSiO₃ catalysts modified by different contents of MgO were prepared and the results showed that the amount of accumulated carbon on the surface of the catalyst decreased with the increase in MgO content.

Keywords: Nanopowder, Magnesium silicate, Alkaline earth modifier, Dry reforming of methane

1. Introduction

In recent years, synthesis gas (a mixture of H₂ and CO) production received more attention because it can be used as feedstock for production of oxygenated hydrocarbons such as methanol and Fischer-Tropsch synthesis [1-5]. Dry reforming of methane is one of the methods to produce extremely valuable syngas with a suitable H₂/CO ratio around 1, by utilization of harmful greenhouse gasses (CO₂ and CH₄)[6, 7]. CO₂ reforming of methane reaction is presented in Eq. (1):

Numerous catalysts including Ni, Co and noble metal-based catalysts with different supports have been employed in dry reforming reaction to achieve high catalytic activity and stability. The main challenge of catalysts in dry reforming reaction is the deposition of carbon on the catalyst surface, which leads to the blocking of active sites and decreasing the catalytic activity. Ni-based catalysts have fascinated because of low costs, high activity and availability [8-10], but the activity decreases with time on stream due to coke formation and active metal sintering [11-16]. On the other hand, noble metal based catalysts show high activity and low carbon formation, but they have limited application because of high cost and less availability [17-21]. Thus, lots of researches have focused on improving the Ni-based catalysts by changing the support, catalyst preparation methods and addition of promoters [22-24]. The effects of various supports such as γ -Al₂O₃, α -Al₂O₃, MgO, SiO₂ on the catalytic performance have been investigated [25-27]. Among the studied supports, MgO shows high thermal strength, low price and can be employed as an effective catalyst support [28-30].

Also, Ni/SiO₂ shows high catalytic performance in reforming reaction but it was deactivated rapidly at high temperature [31].

Bouarab et al. [32] examined the effect of MgO promoter on the catalytic activity and stability of the CO/SiO₂ catalyst in dry reforming reaction. The obtained results showed high stability for the modified catalyst, due to the formation of magnesium silicate phase, which prevents the sintering of cobalt during the reaction. Zhu et al. [33] studied the influence of Ni/SiO₂ catalyst modified by La, Mg, Co and Zn in dry reforming reaction. It was reported that Ni-La/SiO₂ catalyst revealed high activity and stable performance. Two types of carbon were observed on the catalyst surface of the spent catalysts called easily oxidized carbonaceous species and inert carbon. It was reported that inert carbon formed on Ni-Mg/SiO₂ catalyst was the main reason of catalyst deactivation. In other researches alkali elements (K, Ca, Ba or Mg) and rare earth metals (La, Ce or Zr) are added to Ni-based catalysts as promoters to inhibit coke formation [18-22].

The purpose of this research was to synthesize Ni-based catalysts with high catalytic performance in dry reforming reaction. To prepare the stable catalyst, nanostructure mesoporous magnesium silicate with high BET surface area (619 m²/g) synthesized by hydrothermal method and modified by MgO, CaO and BaO was used as catalyst support. The Ni- based catalysts were prepared by impregnation method and the catalytic activity, stability and coke formation were investigated in dry reforming reaction

2. Experimental

2.1. Catalysts preparation

Magnesium silicate with high surface area (619.82 m²/g) was synthesized by hydrothermal method [34]. In order to synthesize magnesium silicate, 0.9 ml sodium silicate, and 1.48g

magnesium nitrate hexahydrate were dissolved in distilled water, separately. Aqueous solutions of sodium silicate and magnesium nitrate were added to a mixture of ethanol and polyethylene glycol (PEG, 400), respectively. The ethanol/PEG ratio was chosen 1/3. Then, the precipitation agent (NaOH: 0.5M) was added drop wise to the solution under stirring by pH adjustment to 10. The resulting sample was transferred into an autoclave and treated at 150°C for 8 h. Then, the sample was vacuum filtered, washed with distilled water and dried at 90°C overnight. The dried sample was calcined at 500°C for 4 h in air atmosphere. The wet impregnation method was employed for the preparation of the catalysts. For the preparation of the catalysts, firstly the desired amount of promoter was dissolved in distilled water and the magnesium silicate powder was impregnated with the prepared solution at room temperature. The suspension was stirred for 3 h, dried at 80°C overnight and calcined at 450°C for 2 h. Afterward, the modified support was impregnated with an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with desired concentration to obtain 10 wt.% Ni with similar method as described above. The prepared catalysts were calcined at 500°C for 3 h.

2.2. Characterization

The specific surface area, pore volume, pore size distribution and N_2 adsorption/desorption isotherms were determined by N_2 adsorption using an automated gas adsorption analyzer (Tristar 3020, Micrometrics). The crystalline structure and phases of the prepared samples were identified by the X-ray diffraction (XRD) analysis using a PANalytical X'Pert-Pro instrument in the range of $2\theta = 10\text{--}80^\circ$. The Micrometrics chemisorb 2750 apparatus was used to study the reduction characteristics of the calcined catalysts by the temperature programmed reduction (TPR) analysis. To perform this analysis, 100 mg catalyst was degassed at 250°C for 1 h in Ar atmosphere. The degassed sample was then subjected to a heat treatment (10°C/min) in a gas flow (30 ml/min) containing a mixture of H_2 :Ar (10:90).

The hydrogen consumption during the analysis was determined by a thermal conductivity detector (TCD). The amount of accumulated carbon on the catalyst surface was determined by the temperature programmed oxidation (TPO) method with the same instrument as described for TPR analysis. In this analysis, a gas mixture (30 ml/min, 5% O₂/He) was passed over the spent catalyst and the temperature increased with a specific ramp rate (10°C/min).

2.3. Catalytic evaluation

The reforming of methane with carbon dioxide in atmospheric pressure was performed in a tubular fixed-bed reactor made of quartz (10-mm-i.d.). For performing the catalytic tests, 100 mg calcined catalyst (35–60 mesh) was loaded into the quartz reactor. The temperature of the catalyst bed was measured and controlled by a K-type thermocouple and thermometer. Before catalytic reaction, the catalysts were reduced at 700°C for 3 h in hydrogen stream (30 ml/min). After reduction process, the temperature was decreased to 550°C and the feed stream containing a mixture of CH₄/CO₂ with the desired ratio was passed through the catalyst bed at a predetermined gas hourly space velocity (GHSV). The reactant conversions were measured at various temperatures in the range of 550 to 700°C in steps of 50°C that were kept for 30 min at each temperature. The product compositions were determined using an online gas chromatograph (Varian 3400, TCD detector, Carboxen 1000 column).

3. Results and discussion

3.1. Structural properties of catalysts

The structural properties of the MgSiO₃, 10%Ni/MgSiO₃ catalyst and modified nickel catalysts with MgO, BaO and CaO are summarized in Table 1. The detailed textural characteristics of the catalyst support were reported in our previous published paper [34]. The catalyst support possessed a high specific surface area and the addition of NiO and promoters reduced the specific surface area. Also, the modified catalysts exhibited lower BET area and

pore volume compared to unmodified catalyst due to deposition of modifiers on the surface of Ni/MgSiO₃ and blockage of pores of the catalyst support. The results showed that the 10%Ni/3%MgO-MgSiO₃ exhibited the lowest specific surface area and pore volume.

The N₂ adsorption/desorption isotherms and the distribution of pores of the synthesized samples are presented in Fig 1a and 1b, respectively. As shown in Fig 1a for all samples, the isotherms can be classified as type IV isotherm with H2 shaped hysteresis loop, which is an important feature for mesoporous materials [35]. This type of hysteresis shows powders containing particles crossed by channels with cylindrical shape [36, 37]. It is obvious that all catalysts illustrated similar isotherms. Fig 1b illustrated that the catalyst support revealed a bimodal pore size distribution and also the prepared catalysts showed a narrow distribution in meso region. The distribution of pores was shifted to smaller sizes by the addition of nickel and promoters.

3.2. TPR analysis

Temperature programmed reduction analysis of Ni/MgSiO₃ catalysts with different modifiers is presented in Fig. 2. As illustrated in this figure, all catalysts illustrated two major reduction peaks at around 700 and 850°C. These reduction peaks are assigned to NiO species with strong interaction with catalyst support. It seems that the addition of modifiers to nickel catalyst changed the position of the T_{max} of the second reduction peak to lower temperature and increased the reducibility of the nickel catalyst.

3.3. Catalytic activity and stability

Fig. 3a and 3b represent the CH₄ and CO₂ conversions of Ni/MgSiO₃ catalysts with different modifiers in dry reforming of methane, respectively. As can be seen, increasing in reaction temperature from 550°C to 700°C, enhanced the catalytic activity, because of the intensely endothermic character of methane reforming with carbon dioxide [38]. Also, CO₂

conversion was higher than the CH₄ conversion because of the occurrence of reverse water gas shift reaction ($\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$). As can be seen in Fig 3a and 3b, compared to the unpromoted catalyst, all the promoted catalysts showed higher catalytic performance. It seems that the MgO promoted catalyst exhibited the highest activity in CO₂ reforming reaction. It can be concluded that the addition of promoters provides adequate Ni active sites for the reactant by increasing the nickel dispersion[39]. Alipour et al. reported that the MgO addition to the Ni/Al₂O₃ catalysts enhanced the methane conversion in dry reforming reaction [40].

The short time stability test of all catalysts at 700°C is plotted in Fig. 3c. It is obvious that all the catalysts possessed high stability during 4 h time on stream. Furthermore, the H₂/CO ratio is shown in Fig. 3d. It is seen that the H₂/CO ratio was less than one, due to the occurrence of reverse water-gas shift reaction.

3.4. TPO analysis

Temperature-programmed oxidation analysis of the spent catalysts is presented in Fig. 4. It is seen that all the samples showed two oxidation peaks. The major fraction of carbon deposited on the catalyst surface oxidized at 500-700°C is attributed to whisker type carbon [35, 41]. Furthermore, unmodified catalyst showed a peak at around 100°C, which is related to superficial carbidic carbon (C α) [42, 43]. It seems that the addition of modifiers did not change the peak intensity and its location at around 850°C but it decreased the intensity of the peak at around 650°C. Also, the peak at around 100°C is disappeared by adding promoter. It can be concluded that the basicity of catalyst is increased by the addition of promoters and led to an increase in CO₂ adsorption capacity, which resulted in inhibiting the boudouard reaction and suppressing the coke formation.

3.5. Effect of MgO loading

3.5.1. Structural properties of the Ni/MgSiO₃ catalysts with different MgO loadings

The structural properties of the synthesized catalysts with different amounts of MgO are summarized in Table 2. The BET analysis illustrated that the BET area of the catalysts reduced by increasing of MgO loading (up to 3 wt.%) due to filling of pores in catalyst support, while further increasing in promoter content increased the BET area. Also, it is obvious that 10%Ni/3%MgSiO₃ had the lowest pore volume and pore size.

The N₂ adsorption/desorption isotherms and pore size distributions of the catalysts with different loadings of modifiers are presented in Fig. 5a and 5b, respectively. The isotherms in Fig. 5a can be categorized as IV type with H2 shaped hysteresis loop, which is significant of mesoporous materials. The results of Fig. 5b reveal the existence of mesoporous structure with pore size distribution in the range of 2-7 nm. It seems that increasing in modifiers loading makes the pore size distribution narrower.

3.5.2. XRD analysis

X- ray diffraction analyses of 10%Ni/MgSiO₃ catalysts with and without modifier are presented in Fig. 6. The diffraction peaks at $2\theta = 37^\circ, 43^\circ, 62^\circ$ and $2\theta = 37.5^\circ, 43.3^\circ, 62.8^\circ, 75.4^\circ$ are related to MgO and NiO (JCPDS. 73-1519), respectively. In modified catalysts, the diffraction peaks of MgO are not detected due to the low percentage of promoters. Also, it can be seen that the intensity of NiO decreased by the addition of promoter to the catalyst and this illustrated that the nickel was highly dispersed on the catalyst surface. Diffraction peaks at $2\theta = 20.3^\circ, 35.1^\circ, 53.7^\circ, 60.9^\circ$ and 72.1° in both samples are related to 2MgO.3SiO₂.2H₂O (JCPDS. 02-1009).

3.5.3. TPR analysis

Temperature- programmed reduction analysis of the synthesized catalysts with various MgO loadings are illustrated in Fig 7. It is obvious that 10%Ni/1%MgO-MgSiO₃ shows two peaks at around 690 and 850°C. By increasing MgO content one peak appeared at around

720°C and its intensity enhanced by increasing in MgO content. This result shows three types of NiO which are different in interaction with catalyst support. The reduction peaks at around 690 and 720°C are assigned to the reduction of NiO with reasonably high interaction with catalyst support, and the peak at around 850°C was recognized to the reduction of nickel with high interaction with support. It seems that by increasing in modifier content, $T_{\max}$ of reduction peaks shifted to a lower temperature, which led to higher reducibility of catalysts.

3.5.4. Catalytic activity

The catalytic performance of modified catalysts with different MgO contents and unmodified catalyst at 550-700°C are shown in Fig. 8. It is seen that the modified catalysts showed higher CH₄ and CO₂ conversions compared to the unmodified catalyst and the catalytic performance improved by the increase in MgO content. It is obvious that 10%Ni/6%MgO-MgSiO₃ catalyst exhibited the highest catalytic performance, due to the formation of more metallic sites and enhancement in contact between metal oxides [44, 45]. Also, the catalytic performance increased by enhancing the reaction temperature because of the endothermic nature of the reaction. It can be seen that the amount of CO₂ conversion is higher than the methane conversion, due to the progress of reverse water gas shift reaction [33, 40].

The short time stability of the prepared catalysts with different MgO contents compared to the unmodified catalyst at 700°C is shown in Fig 9a and 9b. Fig 9a shows that the modified catalysts possessed higher catalytic performance compared to the unmodified catalyst and the catalytic stability remained stable during 4 h time on stream, whereas H₂/CO ratio was not changed in a specific manner, Fig 9b . The long-term stability of 10%Ni/MgO₃ catalyst at 700°C is illustrated in Fig 10. It is obvious that CH₄ and CO₂ conversions are stable after 12 h time on stream. Bouarab et al. reported that the addition of MgO to Co/silica catalyst decreased the coke formation and increased the catalytic stability [32].

The influence of CO_2/CH_4 molar ratio on the catalytic performance of 10%Ni/6%MgO-MgSiO₃ catalyst at 700°C is illustrated in Fig 11. It can be concluded that increasing in CH_4/CO_2 ratio, decreased the CH_4 conversion, whereas CO_2 conversion increased, because of the existence of excess CH_4 in dry reforming reaction.

Fig. 12 represents the influence of GHSV on the catalytic performance of 10%Ni/6%MgO-MgSiO₃ catalyst at 700°C. It is obvious that the increase in GHSV decreased both the CO_2 and CH_4 conversions due to a decrease in the amount of adsorbed reactant and residence time.

3.5.5. TPO analysis

Temperature-programmed oxidation analyses of spent catalysts are shown in Fig 13. The spent catalysts exhibited three peaks at around 100, 700 and 850°C, which are related to three types of carbon formed on the surface of the catalyst. The first peak of the unmodified catalyst at around 100°C is attributed to superficial carbidic carbon (C_α) [42, 43], which is very active and can react with oxygen at low temperature. It is obvious that the first peak is disappeared by the addition of promoter. The oxidation peaks at around 700 and 850°C are related to whisker type carbon [35, 41]. It can be seen that 10%Ni/1%MgO-MgSiO₃ catalyst showed the highest amount of carbon formed on the catalyst surface. The nickel catalyst modified with 6 wt.% MgO exhibited higher carbon deposition compared to the catalyst with 3 wt.% MgO due to higher catalytic performance. Furthermore, TPO analysis of 10%Ni/6%MgO-MgSiO₃ catalyst after 12 h at 700°C is shown in Fig 13. Two observed peaks at around 700 and 850°C are assigned to whisker carbons.

4. Conclusions

In this study, mesoporous nanostructured magnesium silicate with high BET area was synthesized by hydrothermal method and used as support for nickel catalysts in methane reforming with carbon dioxide. The effects of alkaline earth metal oxides (MgO, CaO, and BaO) on the structural properties and the catalytic activity of the synthesized catalysts were studied. The BET analysis of the prepared catalysts indicated that the modified catalysts showed lower specific surface area compared to unmodified one. TPR analysis showed that the addition of modifiers decreased the reduction temperature and improved the reducibility of the nickel catalyst. The obtained results illustrated that the modified catalysts exhibited higher catalytic performance and the MgO modified catalyst possessed the highest activity. This catalyst also showed high stability after 4 h time on stream. According to TPO analysis, coke formation was decreased by the addition of modifiers. The effect of MgO loading on the catalytic performance of the prepared catalysts was studied and the results revealed an improvement in catalytic activity with increasing MgO loading. It can be concluded from TPR analysis that increasing in promoter content shifted $T_{\max}$ of reduction peaks to lower temperature and increased the catalyst reducibility. 10%Ni/MgO-MgSiO₃ catalyst showed high stability after 12 h time on stream and TPO analysis revealed that the addition of promoter decreased the amount of accumulated carbon on the surface of the catalyst.

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Fig. 1. a) Nitrogen adsorption/desorption isotherms and b) pore size distributions of Ni/MgSiO₃ catalysts with different modifiers [27]

Fig. 2. TPR profiles of Ni/MgSiO₃ catalysts with different modifiers

Fig. 3. Catalytic performance of Ni/MgSiO₃ with different modifiers (a) CH₄ conversion, (b) CO₂ conversion, (c) Short time stability of prepared samples at 700°C (d) H₂/CO ratio. Reaction conditions: CH₄/CO₂ = 1:1, GHSV = 18000 ml/gcat. h.

Fig. 4. TPO profiles of spent catalysts with different modifiers

Fig. 5. a) Nitrogen adsorption/desorption isotherms and b) pore size distributions of Ni/MgSiO₃ catalysts with different MgO contents

Fig. 6. XRD patterns of the catalysts with and without promoter

Fig. 7. TPR profiles of Ni/MgSiO₃ catalysts with different MgO contents

Fig. 8. Catalytic performance of 10%Ni/MgO-MgSiO₃ with and without modifiers. (a) CH₄ conversion, (b) CO₂ conversion: Reaction conditions: CH₄/CO₂ = 1:1, GHSV = 18000 ml/gcat. h.

Fig. 9. Short time stability of 10%Ni/MgO-MgSiO₃ catalyst with and without modifier. (a) CH₄ conversion (b) H₂/CO ratio. Reaction conditions: CH₄/CO₂ = 1:1, T = 700°C, GHSV = 18000 ml/gcat. h, T = 700°C

Fig. 10. Long time stability of 10%Ni/6%MgO-MgSiO₃ catalyst with and without modifier. Reaction conditions: CH₄/CO₂ = 1:1, T = 700°C, GHSV = 18000 ml/gcat. h

Fig. 11. Effect of feed ratio on the catalytic performance of 10%Ni/6%MgO-MgSiO₃ catalyst. Reaction conditions: T = 700°C, GHSV = 18000 ml/gcat.h

Fig. 12. Effect of GHSV on the catalytic performance of 10%Ni/6%MgO-MgSiO₃ catalyst.

Reaction conditions: CH₄/CO₂ = 1:1, T = 700°C

Fig. 13. TPO profiles of 10%Ni/MgO-MgSiO₃ spent catalysts with different MgO contents and 10%Ni/6%MgO-MgSiO₃ catalyst after reaction for 12h at 700°C . Reaction conditions:

CH₄/CO₂ = 1:1, GHSV = 18000 ml/g_{cat}. h.

Table 1. Structural properties of the catalysts with and without the addition of modifiers.

Catalyst	Surface area ^a (m ² /g)	Pore volume ^b (cm ³ /g)	Pore size ^c (nm)	Crystalline size ^d (nm)
MgSiO ₃	619	0.73	4.80	7.05
10%Ni/MgSiO ₃	480.2	0.59	4.83	3.6
10%Ni/3%MgO-MgSiO ₃	417.9	0.45	4.42	4.2
10%Ni/3%CaO-MgSiO ₃	436.0	0.51	4.57	4.0
10%Ni/3%BaO-MgSiO ₃	424.5	0.48	4.54	4.0

^a Calculated by the BET equation

^b BJH desorption pore volume.

^c BJH desorption average pore diameter.

^d Average NiO crystalline diameter calculated from NiO (112) plane using Scherrer equation from XRD

Table 2. Structural properties of 10%Ni/XMgO-MgSiO₃ with different MgO contents

Catalyst	Surface area ^a (m ² /g)	Pore volume ^b (cm ³ /g)	Pore size ^c (nm)	Crystalline size ^d (nm)
10%Ni/1%MgO-MgSiO ₃	462.1	0.59	4.8	3.8
10%Ni/3%MgO-MgSiO ₃	417.9	0.45	4.4	4.2
10%Ni/6%Mg-MgSiO ₃	420.6	0.49	4.5	4.1

^a Calculated by the BET equation

^b BJH desorption pore volume.

^c BJH desorption average pore diameter.

^d Average NiO crystalline diameter calculated from NiO (112) plane using Scherrer equation from XRD

Fig. 1. a) Nitrogen adsorption/desorption isotherms and b) pore size distributions of Ni/MgSiO₃ catalysts with different modifiers

Fig. 2. TPR profiles of Ni/MgSiO₃ catalysts with different modifiers

Fig. 3. Catalytic performance of Ni/MgSiO₃ with different modifiers (a) CH₄ conversion, (b) CO₂ conversion, (c) Short time stability of prepared samples at 700°C (d) H₂/CO ratio. Reaction conditions: CH₄/CO₂ = 1:1, GHSV = 18000 ml/gcat. h.

Fig. 4. TPO profiles of spent catalysts with different modifiers

Fig. 5. a) Nitrogen adsorption/desorption isotherms and b) pore size distributions of Ni/MgSiO₃ catalysts with different MgO contents

Fig. 6. XRD patterns of the catalysts with and without promoter

Fig. 7. TPR profiles of Ni/MgSiO₃ catalysts with different MgO contents

Fig. 8. Catalytic performance of 10%Ni/MgO-MgSiO₃ with and without modifiers. (a) CH₄ conversion, (b) CO₂ conversion: Reaction conditions: CH₄/CO₂ = 1:1, GHSV = 18000 ml/gcat. h.

Fig. 9. Short time stability of 10%Ni/MgO-MgSiO₃ catalyst with and without modifier. (a) CH₄ conversion (b) H₂/CO ratio. Reaction conditions: CH₄/CO₂ = 1:1, T = 700°C, GHSV = 18000 ml/gcat. h, T = 700°C

Fig. 10. Long time stability of 10%Ni/6%MgO-MgSiO₃ catalyst with and without modifier.

Reaction conditions: CH₄/CO₂ = 1:1, T = 700°C, GHSV = 18000 ml/g_{cat}·h

Fig. 11. Effect of feed ratio on the catalytic performance of 10%Ni/6%MgO-MgSiO₃ catalyst.

Reaction conditions: T = 700°C, GHSV = 18000 ml/g_{cat}.h

Fig. 12. Effect of GHSV on the catalytic performance of 10%Ni/6%MgO-MgSiO₃ catalyst.

Reaction conditions: CH₄/CO₂ = 1:1, T = 700°C

Fig. 13. TPO profiles of 10%Ni/MgO-MgSiO₃ spent catalysts with different MgO contents and 10%Ni/6%MgO-MgSiO₃ catalyst after reaction for 12h at 700°C . Reaction conditions: CH₄/CO₂ = 1:1, GHSV = 18000 ml/gcat. h.