

Methane production from CO₂ over Ni-Hydrotalcite derived catalysts

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KEYWORDS

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ABSTRACT

Hydrogenation of carbon dioxide to methane has been reported as one of the most favorable option for the reduction of CO₂ emissions. In the literature, different metal based catalysts have been studied for this reaction being Ni based catalysts the most widely investigated one. The properties of mixed oxides derived from hydrotalcites are interesting for catalytic applications such as CO₂ methanation. In this work, Ni-hydrotalcite derived catalysts (Ni, Mg, Al mixed oxides) with different Ni content and x ratios ($x = \text{Al}/(\text{Al} + \text{Mg} + \text{Ni})$) were prepared by co-precipitation method, characterized by Fourier Transform-Infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA), X-Ray diffraction (XRD), Low temperature nitrogen sorption, Hydrogen temperature programmed reduction (H₂-TPR), H₂ and CO₂ Temperature programmed desorption and Scanning Electron Microscopy (SEM). Samples were finally tested to evaluate their catalytic performances in terms of CO₂ conversion and CH₄ selectivity. All samples synthesized in the present work revealed interesting catalytic performances towards CO₂ methanation. Ni content seemed to slightly favour both conversion and selectivity probably due to the enhancement of the Ni species reducibility and x ratio did not have strong influence in the catalytic results. Samples remained stable after 24h test and more active for CO₂ methanation than a commercial catalyst containing similar Ni amount over Al₂O₃.

1. Introduction

Growing environmental concern regarding the increasing levels of CO₂ has resulted in the renewed interest for CO₂ methanation reaction. Between the different alternatives for converting CO₂ to chemicals and fuels, CO₂ methanation is the more favorable alternative in terms of thermodynamics [1].

Furthermore, methane is easier to handle and store and can be used as feedstock for producing various industrially important chemicals. Although CO₂ methanation is advantageous when compared to other options, a good catalyst is still needed to overcome the kinetic barrier of the reaction and activate the stable CO₂ molecules

increasing at the same time the selectivity to the desired product [1].

Due to the high efficiency and lower cost, Ni supported catalysts have been widely investigated for methanation reaction. Hydrotalcite, because of its thermal stability, is widely studied as a favorable support for exothermic reactions [2]. In addition, due to its basic properties, it was referred as advantageous for CO₂ activation [2].

$$x = \frac{\text{mol of Al}^{3+}}{\text{mol of Al}^{3+} + \text{mol of Mg}^{2+} + \text{mol of Ni}^{2+}}$$

This work involves the study of CO₂ methanation over Ni-Hydrotalcite derived catalysts. The effects of Ni content and Al/(Mg+Ni+Al) ratio (x) were evaluated.

2. Experimental

2.1. Catalysts preparation

Hydrotalcite – like catalysts containing trivalent metal (Al) and divalent metals (Mg, Ni) with different ratios of x and different Ni content were prepared by co-precipitation method at constant pH (**Table 1**). For the synthesis two aqueous solutions, one containing sodium hydroxide (1 M) and the second containing mixed nitrates of divalent and trivalent metals, were added drop-wise into a flask containing an aqueous solution of sodium carbonate and kept under vigorous stirring at 65°C and constant pH of 9.5–10. The mixture was subjected to aging for 24 h and then filtered and washed with deionized water. Then it was dried overnight at 80°C and calcined under air flow at 500°C for 5 hours at the heating rate of 10°C/min. A pure sample of Mg-Al hydrotalcite (without Ni) was also prepared by the same method.

Table 1. Catalysts prepared in the present study and compositions determined by ICP analysis.

Catalyst	Ni	Mg	Al	x
HT _{0.26}	0.0	33.5	13.0	0.26
13%Ni/HT _{0.26}	13.0	23.0	11.0	0.26
17%Ni/HT _{0.26}	17.0	21.5	11.0	0.26
20%Ni/HT _{0.26}	20.0	20.0	11.0	0.26
20% Ni/HT _{0.20}	20.0	22.0	8.5	0.20

2.2. Catalysts characterization

The prepared catalysts were characterized by ICP analysis, FTIR, thermogravimetric analysis (TGA), X-ray diffraction (XRD), N₂ adsorption, H₂ temperature programmed reduction, H₂ and CO₂ temperature programmed desorption and scanning electronic microscopy (SEM).

ICP analyses were performed in *Laboratório de Análises do IST* (LAIST) in Lisbon.

Fourier transform-infrared spectra were obtained for fresh catalysts with a PerkinElmer FT-IR spectrometer. Thirty-two scans were taken for each spectrum for wave numbers from 400 cm⁻¹ to 4000 cm⁻¹ registered with a resolution of 4 cm⁻¹. The hydrotalcite samples were mixed with KBr at 1:100 ratio and pressed into disks.

TGA measurements were carried out in a SETARAM TGA92 analyser and the samples were heated from the room temperature to 900°C under air flow at a heating rate of 10° C/min.

XRD diffractograms were obtained using in a Bruker AXS Advance D8 diffractometer, using Cu Ka radiation, and operating at 40 kV and 40 mA. XRD data were collected between 3 and 90° (2θ) with a step size of 0.03°/16s.

N₂ adsorption experiments were performed in a Quantachrome Autosorb iQ station at -196°C. The samples were outgassed at 90°C for 1h and then at 300°C for 4h in flowing nitrogen.

H₂-TPR profiles were obtained in a Micromeritics AutoChem II. Prior to TPR, samples were pre-treated under Ar flow at 250°C and then cooled down to the room temperature. After that, TPR was carried out over a H₂/Ar mixture and raising the temperature till 900°C.

H₂-TPD experiments were also carried out in a Micromeritics AutoChem II using 150 mg of catalyst. Samples were pre-reduced at 800°C under pure H₂ flow and then the flow was switched to Ar and the temperature was kept at 810°C for 1h. After that, samples were cooled down overnight and 4h under pure H₂ flow. The physisorbed H₂ was removed with Ar flow during, at least, 3h. Finally, desorption was carried out by raising the temperature till 900°C. From the area of TCD signal, the metal surface area, crystallite size and dispersion were calculated.

CO₂-TPD was carried out in a fixed-bed flow reactor. The catalyst, previously reduced ex-situ at 800°C, was reduced again in-situ at 470 °C for 1 h under H₂/Ar flow. After that, sample was cooled down till room temperature and the gas mixture was changed to CO₂/Ar for 1 h. After that, the excess adsorptive gas was purged with Ar flow. Finally, TPD was carried out and the catalyst was heated up to 500°C. The desorbed species were analysed using ABB EL3020 CO_x analyzer.

2.3. Catalytic tests

The prepared samples were tested in a fixed bed reactor under atmospheric pressure. The reactor was heated using a TermoLab *Fornos Eléctricos* oven with a temperature controller. A

thermocouple was placed outside and close to the reactor bed to follow the reaction temperature during the tests. All gases used throughout the tests were supplied by Air Liquid and had purity above 99.999%. Flows were controlled by Brooks controllers and the mass of the catalyst was kept constant (0.1744g) for all the tests.

Prior to catalytic tests, samples were reduced ex-situ at 800°C during 1h under pure H₂ flow. All samples were again treated in-situ at 470°C for 1h using 300 ml/min flow of 5% H₂/Argon stream. They were then cooled down to 200°C and the feed was switched to H₂:CO₂:Ar at a molar ratio of 4:1:95 and a total flow of 300 ml/min. The reaction was then carried out in the temperature range of 200°C to 450°C in steps of 50°C with the heating rate of 5°C/min. In each step the temperature was kept constant for 45 minutes. The amounts of CO, CO₂ and CH₄ at the reactor outlet were analyzed using an ABB EL3020 NO_x, CO_x and CH₄ analyzers. CO, CO₂ and CH₄ are measured every 5 seconds and at each temperature, after the stabilization of the signal an average value was calculated.

3. Results and discussion

The present work will be divided into three main topics:

- **Ni content effect**
- **Structure (x) effect**
- **Comparison with commercial catalyst**
- **Long term test**

For all cases the main results obtained from characterization techniques will be discussed and correlated with the catalytic performances calculated from the tests performed.

3.1. Ni content effect

3.1.1. Catalysts characterization

Fresh samples prepared keeping the structure parameter x constant and varying the amount of Ni were analyzed by FTIR, TG and XRD.

Regarding FTIR spectra of non-calcined samples (Figure 1), the same bands were obtained for the different catalysts. The first band around 3500-3600 cm⁻¹ can be attributed to the H-bonding stretching vibrations of the OH group in the brucite-like layer [3]. In addition, a shoulder can be observed around 3000 cm⁻¹. This has been

attributed to hydrogen bonding between H₂O and the anion in the interlayer [3] being an additional band of H₂O bending vibration present at 1600 cm⁻¹. Furthermore, the main absorption bands of the anions are observed between 1000 and 1800 cm⁻¹ being reported carbonate bands at 1350-1380 cm⁻¹, 850-880 cm⁻¹ and 670-690 cm⁻¹ [3]. As a conclusion, FTIR studies confirm that hydrotalcite materials were synthesized by the

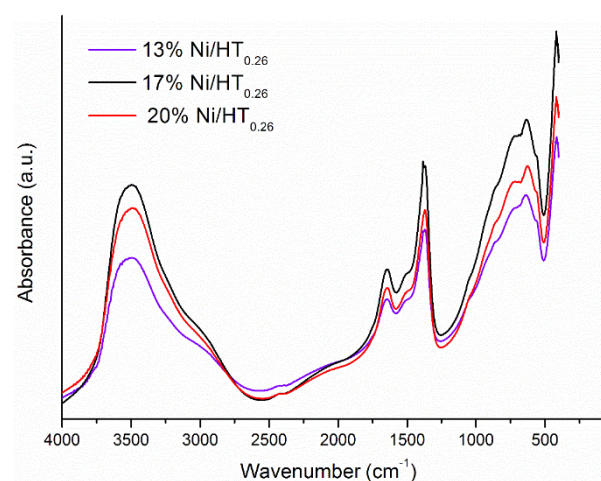


Figure 1: FTIR spectra obtained for non-calcined samples with different Ni content.

experimental procedure carried out.

Regarding TGA experiments of non-calcined samples (not shown) HT_{0.26} as well as the samples with different Ni contents present two main transitions: the first below 350°C and the second above 350°C. The first one corresponds to the reversible loss of interlayer water, without collapse of the structure [3]. The second step is due to the loss of hydroxyl groups from the brucite-like layers, as well as of the anions [3]. Furthermore, results showed that a temperature of 500°C should be used for the calcination treatment in order to complete all the decomposition processes.

In terms of XRD diffraction patterns, results are shown in Figure 2. As it can be observed, three relatively narrow reflection are present at low 2θ values (2θ = 11.6°, 23.2°, 34.8°) corresponding to the (0 0 3), (0 0 6) and (0 1 2) planes of hydrotalcite structure. Regarding the calcined samples, the post-synthesis treatment completely destroys the layered structure of the hydrotalcite, resulting in a high surface area mixed oxides with peaks indicating the presence of NiO, NiAl₂O₄,

MgO and solid solutions of NiO/MgO indicated as $\text{Ni}_x\text{Mg}_{1-x}\text{O}_2$.

Type IV isotherms characteristic of mesoporous materials were obtained for all samples by N_2 adsorption. The main textural properties of the different samples were determined (Table 2). As it can be observed, BET surface areas were not strongly affected by the Ni content and the values are in accordance with the literature [4]. In terms

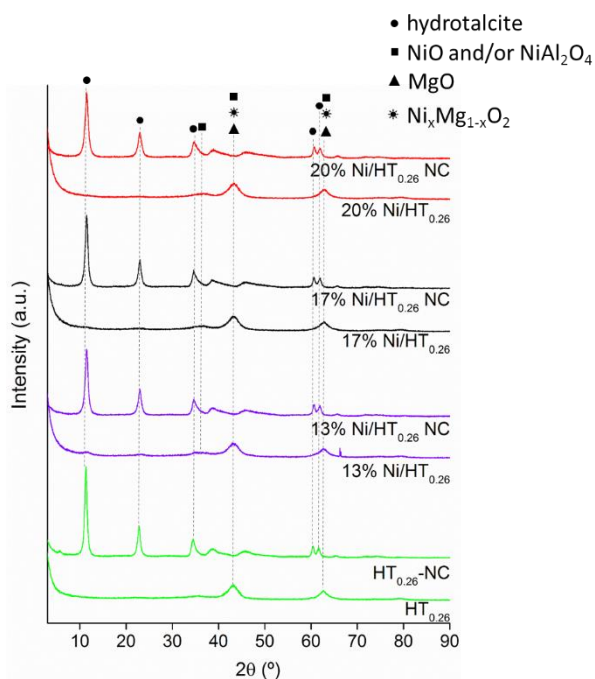


Figure 2: XRD patterns of Ni-HT derived samples. NC denotes sample is not calcined

of average pore diameter a decrease with Ni incorporation was observed. Regarding $V_{\text{mesopores}}$ no trend was observed.

Table 2. Textural properties obtained for samples with different Ni content.

Catalyst	S_{BET} (m ² /g)	D_p (nm)	V_{meso} (cm ³ /g)
HT _{0.26}	238	32	0.896
13% Ni/HT _{0.26}	236	20	0.681
17% Ni/HT _{0.26}	223	19	0.721
20% Ni/HT _{0.26}	236	16	0.654

The H_2 -TPR profiles (Figure 3) display peaks around 160, 390 and 860°C, corresponding to NiO associated with the reduction of segregated NiO as well as NiO weakly interacting with MgO [5] and Ni strongly interacting with the MgO lattice (bulk NiO from NiO/MgO mixed oxides) [5] as well as Ni from NiAl_2O_4 [6]. The maximum

temperature and the area of the peak at temperatures close to 850°C changes with Ni content. The higher the Ni content the lower the maximum temperature [5].

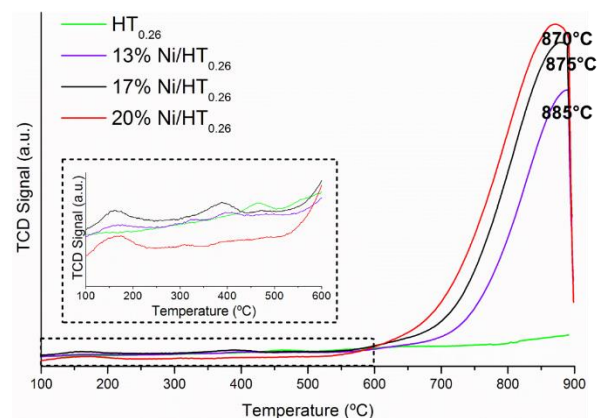


Figure 3: H_2 -TPR profiles of samples with different Ni content.

Furthermore, from H_2 -TPD technique it was observed that higher Ni content seems to produce larger metallic particles.

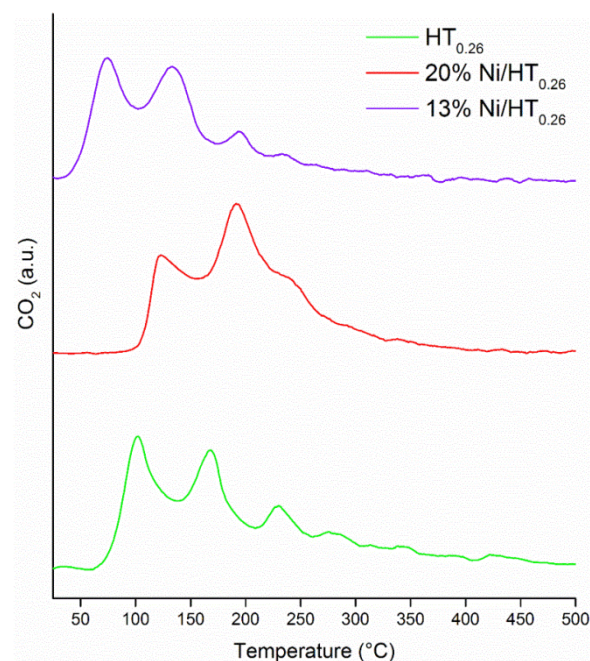


Figure 4: CO_2 -TPD profiles for samples with different Ni content

CO₂ desorption profiles (Figure 4) presented three main peaks attributed to weak, medium and strong basic sites associated with surface OH-groups, Mg²⁺-O²⁻ and Al³⁺-O²⁻ acid-base pairs and low coordinated O²⁻ [7]. However, the maxima temperatures for the peaks related to the three types of basic sites are different for different catalysts.

3.1.2. Catalytic tests

The catalytic performances of the samples containing different amounts of Ni can be found in Figure 6. As it can be observed, the HT_{0.26} which is used as reference presents activity towards CO₂ methanation even without Ni. For catalysts containing increasing amounts of Ni, it can be observed that both CO₂ conversion and CH₄ selectivity slightly increase with Ni content, probably due to the enhancement of Ni reducibility (Figure 3).

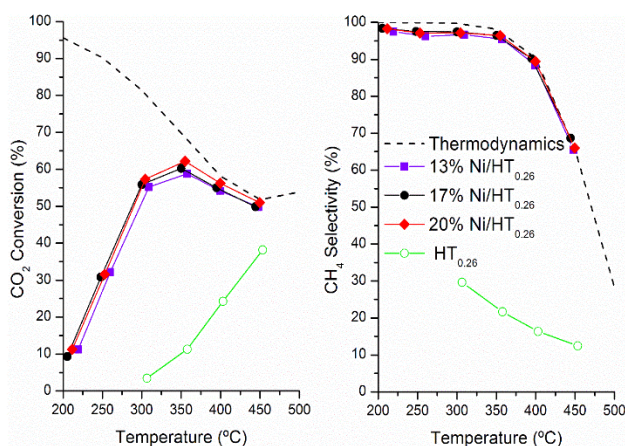


Figure 6: CO₂ conversion and CH₄ selectivity of samples with different Ni content

3.2. Structure (x) effect

3.2.1. Catalysts characterization

The spectra obtained from FTIR studies and used for the comparison of the structural effect (Figure 5) are similar to those of the Ni content effect with different bands corresponding to H-bonding stretching vibrations of the OH group in the brucite like layer, hydrogen bonding between H₂O and the anion in the interlayer, vibrations of anion, etc. It can be observed from the graph that there is a shift to higher wavenumbers for some bands with the decreasing x. This shift is in accordance with the literature findings [3] and

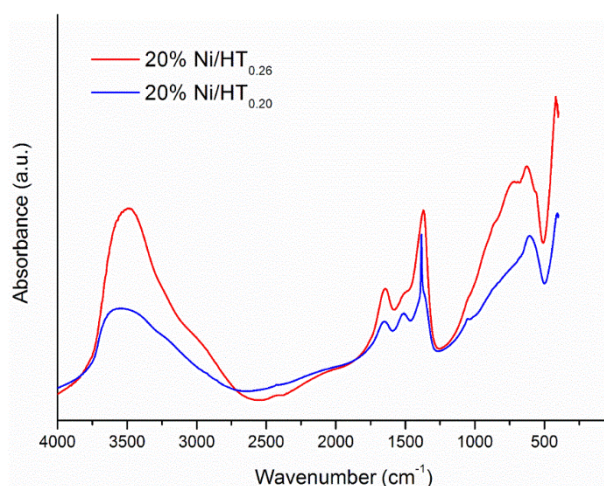


Figure 5: FTIR spectra for samples with different structure composition.

has been attributed to the modification in the interlayer spacing.

The reflections observed in the different XRD patterns (figure not shown) confirm the synthesis of hydroxalcalite like materials. No significant changes are observed in the patterns obtained for the samples with the different x. As obtained previously for the samples containing different Ni amount, the calcined samples of Ni-HT catalysts with different x displayed the peaks at 2θ ~ 43.5 and 63° corresponding to (2 0 0) and (2 2 0) planes of the periclase-like structure [4].

The textural properties of the samples with different x were determined from low-temperature nitrogen sorption isotherms and are of IUPAC type IV, characteristic of mesoporous materials. The textural properties obtained by the analysis of data from N₂ - sorption are displayed in the Table 3.

Table 3 Textural properties obtained for samples with different x factor.

Catalyst	S _{BET} (m ² /g)	D _p (nm)	V _{meso} (cm ³ /g)
HT _{0.26}	238	32	0.896
20% Ni/HT _{0.26}	236	16	0.654
20% Ni/HT _{0.20}	226	12	0.474

It can be seen that pore diameters and mesoporous volumes slightly increases with x value, as observed in the literature [8]. Higher x factor implies more Al in the structure. As

explained in the Literature review, the presence of Al generates positive charges in the structure which is compensated by CO_3^{2-} anions in the interlayer. During calcination these carbonates are decomposed generating porosity in the material [8]. A higher amount of carbonates (higher x) in the non-calcined sample leads to higher pore volumes and pore sizes after calcination, in accordance with the results obtained in the present study.

Regarding H_2 -TPR studies (Figure 7), lower x in the catalyst leads to a shift of the temperature of the maximum of the main Ni reduction peak. In addition, the sample with lower x shows a peak around 330°C which could be attributed to the presence of a higher amount of NiO particles dispersed in the surface of the catalyst.

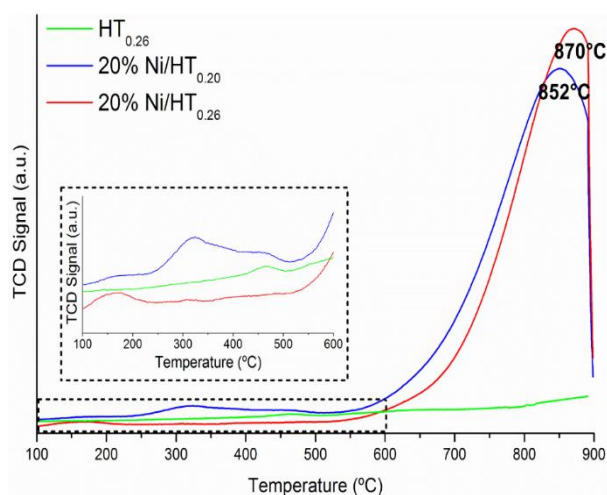


Figure 7: H_2 -TPR profiles of samples with different x

Concerning H_2 -TPD studies, the H_2 desorption profiles (figure not shown) obtained for the samples with different x are considerably similar where the temperature of maximum is concerned. The only difference is a slightly higher H_2 desorption below 88°C for the sample with $x=0.26$. From the analysis of H_2 uptake, it is found that higher x leads to lower dispersion and, as a result, bigger average size for Ni^0 particles.

Regarding CO_2 -TPD experiments three types of adsorption sites can be observed, similarly as in the previous study. When comparing the profiles of samples with different x (figure not shown), it can be noticed that higher x leads to slightly higher CO_2 uptake. The presence of higher

amount of Al species in the Mg-based structure (higher x) leads to the generation of additional surface O^{2-} ions suitable for CO_2 adsorption [8] justifying the increase in the CO_2 uptake.

3.2.2. Catalytic tests

The results obtained from the catalytic tests of the samples with different x values are presented in the Figure 8. Both in terms of conversion and selectivity, the results are quite similar for both samples. This could be attributed to the similar CO_2 adsorption capacities for the samples and the results already very close to the thermodynamic values. However, at some temperatures (300°C and 350°C), the sample with lower x seems to have slightly higher performance, probably due to the higher dispersion of Ni^0 particles as well as for the favored reducibility of NiO species at lower temperature according to H_2 -TPR results. The close resemblance in the performance of these catalysts could also be due to experimental error.

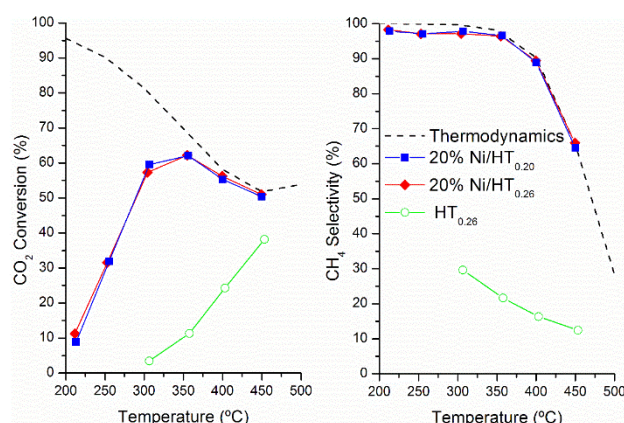


Figure 8: CO_2 conversion and CH_4 selectivity for samples with different x.

3.3. Comparison with commercial catalyst

In order to compare the catalytic results obtained by the Ni-hydrotalcite derived materials from the present study with commercially available catalyst, a commercial $\text{Ni}/\text{Al}_2\text{O}_3$ with a similar Ni content was tested under the same conditions. As it can be seen, Figure 9 shows the comparison of commercial catalyst and 20% $\text{Ni}/\text{HT}_{0.26}$. From the figure it may be derived that the Ni based catalyst of the present study has better catalytic performances than the

commercial one. The enhanced CO₂ adsorption capacity of the hydrotalcite derived catalyst could be responsible for the better catalytic performance of this type of material.

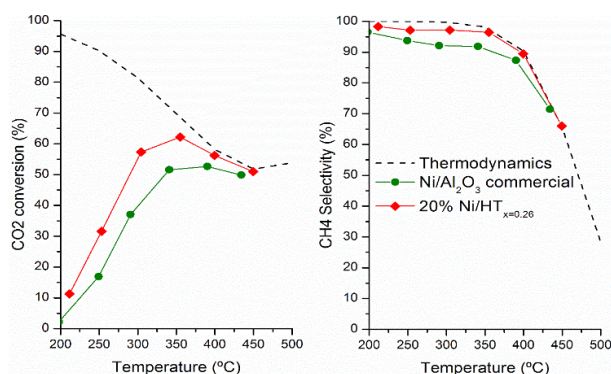


Figure 9: The comparison of commercial catalyst and 20%Ni/HT_{0.26}

3.4. Long term test

A catalytic test of 24h at a reaction temperature of around 350°C was carried out in order to evaluate the stability of one of the samples under study with time. The 20 Ni%/HT_{0.26} sample was chosen because of being the one leading to better performances in the catalytic test. The results are shown in the Figure 10 and, as observed, the CO₂ conversion remained at around 57% and CH₄ selectivity at around 95% all throughout the test without any obvious decline of activity. This good stability of Ni-hydrotalcite derived catalysts provides a potential for its usage in industrial applications.

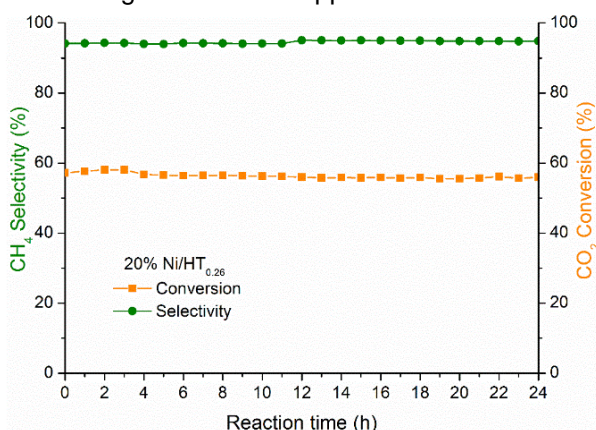


Figure 10: Long-term test results for catalyst 20%Ni/HT_{0.26}.

4. Conclusions

The structure of the synthesized Ni-hydrotalcite derived catalysts were verified by FT-IR and XRD characterizations. The calcination of the sample leads to the formation of mixed oxides. The calcined samples have high specific surface area in the range of 220-240 m²/g. All materials showed a high CO₂ adsorption capacity below 300°C. The percentage of strong basic sites increased both with increase in the Ni content and x value. In terms of catalytic performances, no important differences between catalysts were detected. However, higher Ni content led to a slight increase in CO₂ conversion and CH₄ selectivity. The prepared Ni-hydrotalcite derived catalyst was compared with a similar Ni content commercial catalyst. According to the results, Ni-hydrotalcite derived catalyst showed better performance both in CO₂ conversion CH₄ selectivity than the commercial catalyst. A catalyst of the present study was active during 24h stability test at a reaction temperature of 350°C without any significant loss of catalytic performance.

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