Carbon Dioxide Conversion To Methane Over Nickel Base Catalyst

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Abstract: - Catalytic tests for carbon dioxide hydrogenation are reported over nickel base catalysts, in the temperature range of 350-550°C under atmospheric pressure. The catalysts with Ni loadings ranging from 12 to 22%wt. were prepared by impregnation technique, characterized, and their performances were evaluated in CO_2 conversion. The important parameters namely reaction temperature, H_2/CO_2 molar ratio, GHSV and regeneration procedures were taken into account and optimized. The main experimental results (very high CO_2 conversion together with almost total methane selectivity, obtained up to 400°C) asserted the Ni/Al_2O_3-SiO_2 as a potential catalyst for CO_2 conversion. This method simultaneously possesses the merits of promising methanation performances over a low cost of catalyst and raw material, reusing CO_2 and generating CH_4 fuel as a possible source of energy.

Key-Words: Ni catalysts, catalytic process, impregnation technique, methanation, hydrogenation

1 Introduction

The use of carbon dioxide (CO_2) as either a technological fluid for building complex molecules block or a raw material in chemical processes as a carbon source for fuels or in biotechnological applications, provides the potential to reduce CO_2 emissions [1-4]. Two main solutions are proposed: (i) capturing CO_2 at its source and storing it in the geological subsurface [5, 6], (ii) promoting the transformation of CO_2 in the presence of an adequate catalyst at high temperature [7,8].

Because the introduction of carbon capture and storage processes requires additional costs, more efforts should be dedicated to the possible CO_2 conversion into chemicals or fuel synthesis. The CO_2 conversion process is of interest (i) for the recycling of CO_2 as an energy carrier, thereby reducing its accumulation in the atmosphere, (ii) for the production of renewable hydrocarbon fuels from CO_2, water, and renewable electricity for use as transportation fuels, and (iii) as a convenient means of storing electrical energy in chemical form to level the electrical output from intermittent energy sources such as wind and solar.

This study is a small part of the global challenge regarding the reducing of concentration of the greenhouse emission gas by the catalytic transformation of CO_2 sources, as an essential step for substituting the fuels synthesis. The reaction between CO_2 and hydrogen over heterogeneous catalysts is an issue that has received a great appreciation because of its possibility to manufacture and substitute natural gas, reducing thereby the price of gas obtained from coal.

Many types of catalysts (noble and non-noble metals, oxide supported metals, oxides, etc) were tested and studied in this reaction in relation to their selectivity towards the formation of methane, paraffin, alcohols, especially methanol, and olefins [4-9]. Methane obtaining was receiving a particular attention due to the opportunity regarding technological utilization of CO_2 as a possible source of energy.

The catalytic performance depends on the nature of metals because of their different geometric and electronic proprieties, which influence not only surface reactions but also the adsorption modes of substrates, the latter being key to activate the C═ C and/or C═ O bond. The non-noble metals such as Ni

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generally display lower intrinsic activity as compared with noble metals such as Ru, Pt, Pd,etc. For instance, in the hydrogenation of C− O bond, the following order of activity was obtained:Rh>Ru>Pd>Pt>Ni>Co>>Cu.   To compensate this differences in activity and for economic reasons, the catalyst loading is usually 0.05-0.5% for noble metals and 5-20% for other metals.

Noble metals such as rhodium, ruthenium, platinum and palladium, exhibit promising CO_2/H_2 methanation performance, high stability and less sensitivity to coke deposition [1,9]

Milder and efficient reaction parameters, recently reported in literature, allowed to obtain promising CO_2/H_2 methanation performance as follow: 90% conversion in presence of amorphous alloy Ni–Zr–Sm at 300°C, 43.6% conversion in presence of Pd-Ru-Ni/Al_2O_3 (200°C, 5 h) [11], 90% conversion in presence of Ru (300°C, 2 atm) [12-13], 75% selectivity for CH_4 over Rh/TiO_2 at 400°C [14-15] and 20% conversion over Pt at temperatures higher than 450°C [16], 96% selectivity over Ni/MCM-41, 84.6% conversion on Ni-La/Al_2O_3 [17], 64.1% conversion on Ni/MSN, 42.4% conversion on Ni/SiO_2, 27.6% conversion on Ni/Al_2O_3 at 300°C [18], 89.4% conversion on NiO/SBA-15 [19], 54.2-63.4% conversion over Ni-Mg base or Ni-Fe base catalysts [20].

Even in these cases, either selectivity or conversion was low, or high temperature, or complex catalytic systems or expensive catalysts were required. Nevertheless, nickel remains the favoured catalyst for the reaction by virtue of its life, high activity, selectivity towards methane formation in preference to other hydrocarbons, and it's comparatively low cost. The methanation was studied on Ni catalysts because of the theoretical significance and possble practical application of this reaction. The preferred catalyst for industrial purposes seems to be nickel base catalyst with various materials as support such as Al_2O_3, MCM, SBA-15, ZrO_2, CeO_2, and zeolite. In the chemical processing industry, a catalyst with high selectivity, activity and stability is essential.

To meet these requirements, the catalyst support should provide sufficient surface area, stability and to be composed of a robust material for a high dispersion of the metal. One of the potential candidates for an adequate support for Ni catalysts with different characteristics exhibiting variable performances in terms of selectivity and activity for methanation process, seems to be mesoporous alumina or silica. Previously, the high activity of Ni/alumina was correlated to the existence of both

intra and inter particle porosity and to the high basicity of the catalysts and this led to the high Ni dispersion on the surface of support [18,21]. It has been recently proposed the supported NiO as an efficient catalyst for CO_2 conversion [18, 22-24], but on the other hand, there are only few papers which report specifically NiO/alumina or NiO/silica and no studies exist on Ni/alumina-silica.

In our previous work, Ni-base catalysts supported on alumina-silica was successfully synthesized and tested in a typical hydrogenation reaction [21]. In the current work, the synthesis of the above-mentioned catalysts was extended to their utilization in CO_2 hydrogenation to methane, carrying out the process at 300-550°C and atmospheric pressure. Promising methanation performances were expected due to the optimization of different reaction parameters. These considerations justify the opportunity of the present study aimed to obtain adequate performances as a straightforward method for generating CH_4 fuel as a possible source of energy.

2 Experimental
2.1 Materials
All chemicals required to prepare the Ni base catalysts were purchased: aluminium oxide (Al_2O_3 with 100 Å medium pore diameter, 100 m^2/g Alfa Aesar, used as catalyst support), SiO_2 with 160 Å medium pore diameter Alfa Aesar, used as catalyst support), nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, 98%, Sigma-Aldrich). For the catalytic runs, the hydrogen, argon and carbon dioxide were purchased from Linde Groupe, and were of ultra high purity (UHP).

2.2 Preparation catalysts
The Ni/Al_2O_3-SiO_2 catalysts were prepared by incipient wetness impregnation as follows. The support was obtaining by mixing the Al_2O_3 with SiO_2. The support (dried at 120C for 8 h prior to the impregnation procedure) was impregnated with corresponding aqueous metal nitrate precursors solutions in demineralized water for two hours at T=70°C when heterogeneous catalysts of various Ni content were obtained. After filtration under vacuum the catalysts were dried overnight at 120°C, calcinated under air at 450°C for 4 hours and then kept in a desiccator under vacuum.

2.3 Characterization of the catalysts

The elemental analyses were performed using an atomic absorption spectrophotometer VARIAN AA 240 FS DUO, by solving 0.1 g of every catalyst in a mixture consisting of H_2SO_4, HF and $HClO_4$ in volumes of 2 ml each by using a MicroWave Digestion System Milestone 1200 MEGA. The physical-chemical characteristics of the catalysts obtained by impregnation are given in Table 1.

**Table 1.** The characteristics of the catalysts obtained by impregnation

Catalyst type	Ni/ Al₂O₃ - SiO₂ I	Ni/ Al₂O₃ - SiO₂ II	Ni/ Al₂O₃ - SiO₂ III	Ni/ Al₂O₃ - SiO₂ IV
Ni (%wt.)	12.21	15.14	18.06	21.13
$S_{sp.}$ (m²/g) [a]	136	124	98	92
V_{pores} (%) [b]	49.32	48.96	47.81	47.29
Crystalline size (Å) [c]	78	83	86 (fresh) 95 (used)	98

X-ray powder diffraction patterns of the samples were obtained using a Rigaku Ultima IV diffractometer. The wavelength of Cu-Ko: X-ray radiation used was 1.5418 A while the beam voltage and current were 45 kV and 40 mA, respectively.

The specific surface areas of the samples were determined using the BET method by performing nitrogen sorption measurements using a Micromeritics ASAP 2010 instrument. The adsorption and desorption experiments were done at 77K after initial pre-treatment of the samples by degassing at 120°C for 2h. The surface area was calculated from the linear part of the BET plot. Pore size distribution was estimated using the Barret-Joyner-Halenda (BJH) model.

2.4 Testing of catalysts

The prepared samples were tested in the process of CO_2 conversion to methane. A schematic conducted reaction system is presented in Figure 1. In the reaction system, as can be seen in the figure, three units, comprising a feeding unit, a reaction unit, and a product gas analysis unit, were included.
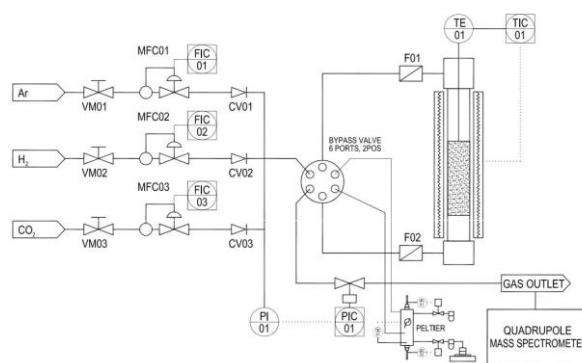
Fig 1. A schematic of the conducted reaction system and experimental procedures

All reactions were carried out in a laboratory-scale, continuous-flow reaction system using a tubular specially stainless steel micro reactor (PID Eng&Tech - MICROACTIVITY- Reference), placed in a cylindrical conventional tubular furnace, equipped with an electrical heater, operated at atmospheric pressure and fully monitored by computer. The temperature was checked with a thermocouple located inside a quartz thermo well fixed into the catalytic bed. During the operation, the product mixture from the reactor outlet was led to an ice-water trap PELTIER, through the tube wrapped by a heating tape, so as to condense the water produced. This water was regularly removed.

The catalytic bed was composed of a layer of inert glass wool on which is placed the powder catalyst. The methanation reactions were performed under atmospheric pressure in the temperature range of 300–500⁰C, with an increment temperature rate of 7˚C. The catalysts used in these reactions were activated prior the reaction by heating at 450˚C reaction temperature in 5% H_2/Ar, under 30 ml/min H_2, for a period of 4 h activation times and then the reactor was heated to the working temperature. Each experiment was repeated twice, and each temperature was maintained for 30 min before the next temperature increment was accomplished. CO_2 and H_2 were continuously fed into reactor together with argon carrier. Mass flow controllers (ALICAT Scientific model) were used to control the flow rates of the feed gases in known proportions prior to reaction.

The compositions of the feed gases were varied by changing the molar ratio of CO_2: H_2 between 1:4 to 1:8, while the total flow rate was maintained at a constant 50 ml min⁻¹. The gas hourly space velocity (GHSV) was varied between 4.000 and 22.000 h⁻¹. GHSV was varied by changing the catalyst mass and keeping the reactant flows constant. The composition of the gaseous phase was measured and continuously monitored by a Hiden HAL VII

quadrupole mass spectrometer. Between the experiments, the entire experimental set-up was flushed with He until the mass spectrometer signals reached practically their respective baseline value. Quantitative calibration of H_2, CH_4 and CO_2 compositions was made based on registered partial pressures signals and using standard calibration gas mixtures.

The conversion of carbon dioxide and selectivity to methane are defined as follows:

$$CO_2\ conversion(\%) = \frac{(Q_{CO_2\_inlet} - Q_{CO_2\_outlet}) \times 100}{Q_{CO_2\_inlet}}$$

$$CH_4\ selectivity(\%) = \frac{(Q_{CH_4\_outlet}) \times 100}{(Q_{CO_2\_inlet} - Q_{CO_2\_outlet})}$$

where Q_{CO2_inlet} and Q_{CO2_outlet} are the molar flow rates of CO_2 (mol s^{-1}) at the inlet and the outlet, respectively.

The used catalysts were washed with various solvents, filtered and dried in a muffle furnace and regenerated in mentioned conditions.

3 Results and discussion

The XRD structural properties of the synthesized catalysts were first estimated by X-ray diffraction measurements (Figure 2). The supported nickel catalysts showed the diffraction peaks corresponding to NiO species (JCPDS65-6920) and phases, Al_2O_3, SiO_2. The reflections at 2 θ of 37.3, 43.3, 62.9 and 75.3 confirm the presence of nickel oxide to the (111), (200), (220), and (311) planes. No distinct nickel aluminate lines are observed. The type of X-ray diffraction spectrum of the catalysts is similar for all prepared catalysts, but it is clear that diffractions peaks of NiO phase become more intense and sharper by increasing the nickel loading from 12 to 21%. These results are consistent with the chemical analysis (atomic absorption spectroscopy). From average of NiO crystallite size corresponding to (200) plane of NiO, estimated using Scherer equation, it can be deduced that crystal structure of Ni catalyst is affected by Ni content, namely the increasing in nickel loading increased the nickel crystallite size, resulting in a decreasing of nickel dispersion.
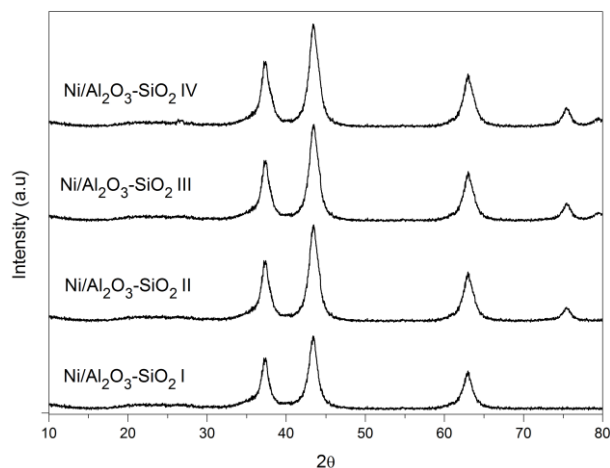
Fig 2. X-ray diffraction spectrum for the prepared samples

The porous structure of the synthesized catalysts was studied by the BET method. The N_2 adsorbtion-desorbtion isotherms of the Ni/Al_2O_3-SiO_2 with H2-type hysteresis loops, indicated a typical hysteresis for mesoporous materials (figure 3). The type of isotherm is similar for all prepared catalysts. The hysteresis loop is narrow, and the adsorption and desorption curves merge at $p/p_0 > 0.42$. It is also noted that the ratio $p/p_0 < 0.05$ the amount of absorbed nitrogen is very small, indicating the existence of small amounts of accessible micropores.

The results of BET are summarized in table 1. As can be seen, the specific surface area of synthesized catalyst are intermediary between silica and alumina, or lower, being known that specific surface area of catalyst should be decreased after impregnation. The pore size of the catalysts is in range 78-98 Å. and has a uniform pore size distribution.
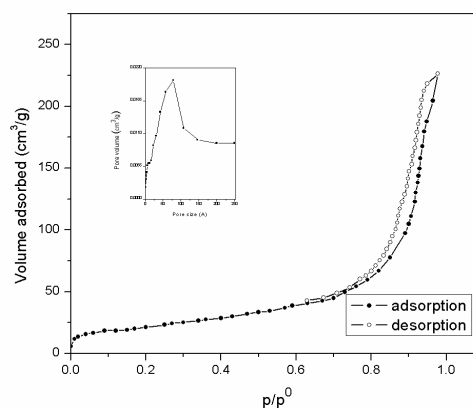

**Fig 3.** N_2 adsorbtion-desorbtion isotherm of Ni/Al_2O_3-SiO_2

The catalytic performance of Ni/Al_2O_3-SiO_2 materials was evaluated in the gaseous phase hydrogenation of CO_2. Figure 4 summarizes the

performances of these catalysts in CO_2 conversion and CH_4 selectivity. In a preliminary optimization study we investigated the effect of metal loading (i.e. 12, 15, 18, 21% wt) for monometallic Ni/Al_2O_3-SiO_2 catalysts, being known the fact that with increasing metal loading, the activity of the hydrogenation catalysts usually reaches a limiting value. Particularly for the methanation, it was observed the following behaviour: an continuous increasing of CO_2 conversion depending of reaction temperature and Ni content (figure 4 a), applying to all prepared catalysts and an increasing in terms of selectivity up to 18%wt Ni, followed by a slightly decreasing (figure 4 b). Increasing the nickel loading above 18% wt. allowed the total CO_2 conversion but resulted in a decreasing of CH_4 selectivity, due to modifying Ni dispersion as a result of bigger crystallite size or blocking of the pore structure at the higher percentage of Ni, preventing the activation (table 1).

Based on these results, the methanation process appears as a benchmark reaction highly sensitive to the properties of supported metallic catalysts. It can be noticed that the methanation process takes place in the presence of all catalysts. The high CH_4 selectivity (close to 100%) was achieved at 400 C on the Ni/Al_2O_3 - SiO_2 III catalyst, containing 18%wt Ni. The high activity of Ni/SiO_2-Al_2O_3 can be related to the observation that methane formation appears to be limited by the dissociation of carbon dioxide to carbon species which further react with hydrogen to produce methane.
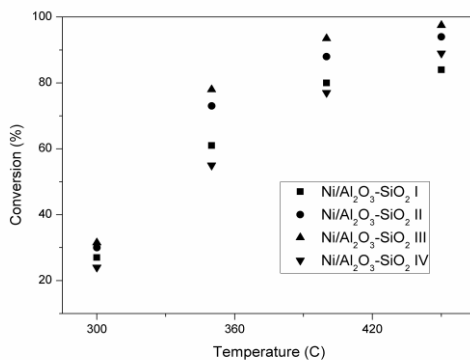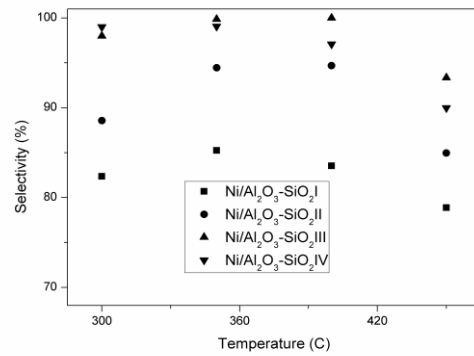

b)

Fig 4. The catalytic performances of Ni/Al_2O_3 - SiO_2 catalysts in methanation reaction *a)* CO_2 conversion; *b)* methane selectivity. The reaction conditions: GHSV=12000 h^{-1}, CO_2:H_2 molar ratio=1:6

Further, the catalyst with the best performances in the methanation process, namely Ni/Al_2O_3 - SiO_2 III was investigated in different reaction conditions to provide a comprehensive observation in the present study. Different amounts of reactants preheated at studied temperatures were introduced into the mass spectrometer through the reactor by-pass for checking the composition of the gaseous mixture. The reactants were then passed into the reactor, by the instrumentality of electro-valve. Depending on the studied reaction conditions the formation of methane was revealed. Temporal distributions of volumetric concentrations for CO_2, H_2 and CH_4 at various reaction temperatures and molar ratios are presented in figure 5. The trends for reactants and products are similar but a comparison suggests that a higher H_2/CO_2 molar ratio leads to a higher obtained CH_4 as a consequence of more CO transformed in methane. For exemplifications, the results obtained at only two temperatures were presented.

a)
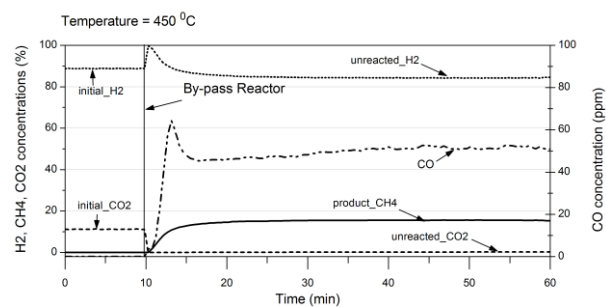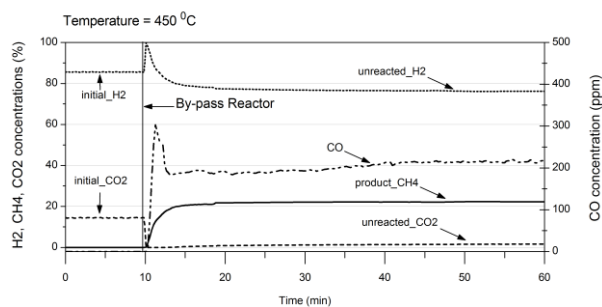
Fig 5. Temporal distributions of volumetric concentrations of CO_2, H_2 and CH_4

Figure 6 presents the effect of gas hourly space velocity (GHSV) in methanation reaction over Ni/Al_2O_3-SiO_2 III. CO_2 conversion was the only catalytic performance discussed as CH_4 selectivity was above 99.8%. In order to determine the catalyst amount to be loaded into the reactor, the GHSV was varied between 4.000 and 22.000 h^{-1}, function of reaction temperature. The conversion increased with temperature, being quite similar at 400 and 450°C, moreover having the same value at GHSV of 4000 h^{-1}. All temperature plots appeared as a similar general profile divided into two regions: the first one is almost abrupt between 4.000 and 16.000 h^{-1}, the second one up to 22.000 h^{-1} was more constant. Working at 400°C as optimal temperature and 12.000 h^{-1} GHSV domain in a linear zone seems to be optimal for CO_2 conversion, meaning the entire catalyst bed works efficiently.
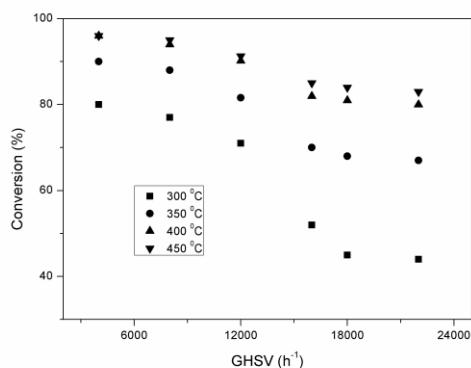

Fig 6. Effect of GHSV on Ni/Al_2O_3-SiO_2 III catalyst performance for CO_2 methanation

The temperature has a significant effect on the CO_2 conversion (Figure 7). The conversion was very low (8%, too slow to be practical) at temperatures below 300°C. When we used higher reaction temperatures, the conversion increased continuously, but CO formation drops over 450°C and by-products appear. This reveals that for methanation known as exothermic reaction, a higher reaction temperature over 450°C disadvantages the formation of CH_4. The optimal agreement for this

type of reaction seems to be between 400 and 430°C, because in this range, methane is the unique hydrocarbon molecule formed, consequently the selectivity is almost 100%.

Many studies focused on the methanation of CO_2 under relevant conditions for methane formation at stoichiometric conditions (H_2:CO_2=4:1). Only few studies dealt with reaction with a high excess of hydrogen [18] and no one was varying reactant ratios on Ni/Al_2O_3-SiO_2.

The effect of CO_2/H_2 molar ratios at different temperatures is also examined in range 1:3.6 to 1:8.0. The CO_2 conversions are growing continuously with the rise of H_2/CO_2 molar ratio, the rise being faster between 350-400°C (Figure 7). The likely reason is that the higher H_2/CO_2 molar ratio shift equilibrium from CO (detected in ppm range) to CO_2. CO is more reactive and leads to product loss by transforming into CH_4. It is emphasized that the CO_2 conversion increase with increasing H_2/CO_2 ratio, without distinction of what the reaction temperature is. This substantiates mechanisms evaluated in recent publications [22, 23].
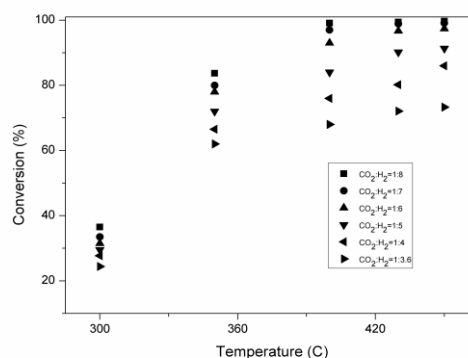

Fig 7. Conversions of CO_2 as a function of temperature and various CO_2/H_2 molar ratios, GHSV=12000 h^{-1}

In order to determine its lifetimes, longer term methanation experiments have been carried on at 400°C, GHSV of 12.000 h^{-1}, CO_2:H_2 molar ratio=1:6, and the Ni/Al_2O_3-SiO_2 was found to be significantly stable providing over 97% CO conversion after 72 h. The performances decay steadily to about 82% after 120 h. The results indicate that the catalysts, whose slowly deactivation was caused by a temporary deactivation or by the sintering of metallic Ni and by the forming of $NiAl_2O_4$ species (used form from figure 8), must be regenerated through a reduction–oxidation method [24, 25].

Different treatments aiming to verify the effectiveness of the regeneration procedure in connection with the reusing the catalyst for

methanation reaction, were applied for regenerating of used catalyst. The used catalysts (reaction conditions: 400˚C reaction temperature, atmospheric pressure, $CO_2:H_2$= 1:6 molar ratio, 120 h) were regenerated by different treatments (table 2). After heating the catalyst in air at 200 and 250˚C for 2-4 h, the reduced Ni was not observed in the XRD spectra. A subsequent repeated reduction with H_2/Ar at 350˚C resulted to the formation of the metallic Ni, which indicates that after the oxidation-reduction treatment, the concentration of the active species increases, reflecting in a higher catalytic activity. The data obtained in this work show that the oxidation at 350˚C seems to be the best procedure to regenerate the used catalyst to NiO more than 90%.
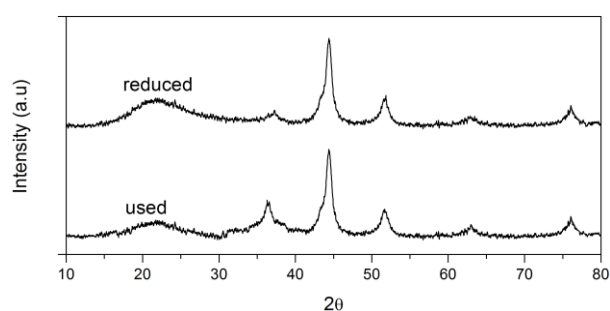
Fig 8. X-ray diffraction spectrum of the reduced and used catalyst

The XRD patterns of the reduced and used samples are presented in figure 8. Typical diffraction peaks corresponding to metallic nickel at 2 θ of 44.8, 52.2, and 76.8 were observed. The Ni crystallite sizes, calculated by Scherer equation using the Ni (111) diffraction peak are indicated in table 1. The Ni crystallite size of used samples after 120 h on lifetime test, compared to those of the reduced catalysts, increased by almost 12%, maybe due to the growth and agglomeration of the Ni particle during the test, resulting the mentioned decline for catalytic activity. It is worthy to mention that small amount of zirconia highly dispersed on Al_2O_3 could act as a structural promoter to avoid the aggregation of nickel species [26, 27]

Table 2. CO_2 conversion to methane in presence of regenerated catalysts

Catalyst/ regeneration procedure	Fresh catalyst	Used catalyst/ regenerate 200˚C		Used catalyst/ regenerate 250˚C		Used catalyst/ regenerate 350˚C		Used catalyst/ regenerate 400˚C	
		2 h	4 h	2 h	4 h	2 h	4 h	2 h	4 h
Conversion (%)	99.8	28.3	42.2	69.3	83.8	88.6	92.4	87.2	88.4

4 Conclusion

In actual study we were interested by carrying out the methanation reaction over Ni base catalyst at atmospheric pressure. Ni/Al_2O_3-SiO_2 with Ni loadings ranging from 12 to 22%wt. were prepared, and characterized. The catalytic activity of these samples was evaluated for the first time in CO_2 hydrogenation. Several optimization parameters including the reaction temperature, H_2/CO_2 molar ratio, GHSV, reproducibility and, finally, regeneration tests, were conducted on Ni/Al_2O_3-SiO_2 as a potential catalyst for CO_2 conversion,.

The remarkable values for selectivity (more than 99.8%) were obtained at an unprecedented almost total conversion under moderate hydrogenation conditions from the perspective of methane synthesis, offering without doubt competitive costs for CH_4 obtaining as fuel. The reaction is straight-forward and mild reaction conditions permit the reuse of CO_2.

The experimental results justify the opportunity and possibility of using Ni/Al_2O_3-SiO_2 catalyst for CH_4 obtaining, due to a high conversion easily obtained in a process appearing as a useful procedure for CO_2 turning to account. For this reason, the tested catalysts could have potential applications in CO_2 conversion.

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