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Methane transformation in presence of carbon dioxide on activated carbon supported nickel–calcium catalysts

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The objective of the present work was to study the catalytic reformation of methane in presence of carbon dioxide on activated carbon-supported nickel and calcium catalysts. Results are very promising ones because they suggests that it is possible to transform methane on these catalysts by using mild reaction conditions.

KEY WORDS: methane reformation; activated carbon; nickel–calcium catalysts.

1. Introduction

The upgrading of natural gas, which consists mostly of methane, to higher value products, by means of dry reformation with carbon dioxide has received great variety of studies [1–3]. This process yields synthesis gas (syngas) by means of reaction (1):

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad H_2/CO = 1. \qquad (1)$$

In addition, this type of gaseous mixture commonly has been employed in several important industrial processes [4–8], such as methanol or Fischer–Tropsch synthesis [4–8].

On the other hand, although upgrading of natural gas is of great value, it is difficult to achieve by means of reformation. Several catalysts have been studied [9–11], among them, noble metals as Rh, Pt, Ru and Ir yield high activities and selectivity, but due to the low availability and high price of such metals, nickel has been explored as a possible substitute of noble metals [1,11,12]. However, several studies have shown that Ni has higher tendency to be deactivated than noble metals, principally by the deposition of carbon [1,9,10]. Also, studies concerning the dry reformation of methane on supported nickel catalysts [12–15] have shown that support can play an important role on the activity and deactivation by coking, and the nature of such carbonaceous deposits is intimately related with catalyst structure. It has been suggested that carbon deposition can be attenuated or even suppressed when the metal is supported on a metal oxide with a strong Lewis basicity [13,16,17]. Therefore, the alkaline earth metal oxides, such as MgO, CaO, SrO or BaO, should be good choices as supports [17] or structural promoters [18].

Carbon as catalytic support shows several desirable properties [19,20], e.g., low cost, high surface area, possibility to modify the pore size distribution and surface functionalities, reductive properties, as well as facile recovery of the active metals from the spent catalysts by burning off the support [21]. In hydrotreatment reactions, particularly in hydrodesulfuration (HDS) [22] and alkenes hydrogenation (HYD) [19,20], activated carbon (AC) has received some attention as it was earlier believed to render higher activities in HDS of thiophene and ethylene hydrogenation than conventional formulations supported on alumina or other catalytic supports. In line with this, the main objective of the present work was to study the catalytic transformation of methane in presence of carbon dioxide on activated carbon-supported nickel and calcium catalysts employing soft reaction conditions, particularly low temperature (550 °C) and atmospheric pressure, and without submitting catalysts to reductive pre-treatments with hydrogen.

In addition to the very well-known fact that active carbon supported Ni catalysts was seldom reported for the methane reforming reaction, the reason to employ a low temperature is due principally to avoid gasification of the carbon support by reverse Boudouard reaction:

$$C + CO_2 \rightarrow 2CO. \qquad (2)$$

In the present case this reaction can be negligible because it occurs spontaneously at temperature higher than 700 °C.

Therefore, this study would permit to verify the potential application of AC in the dry reformation reaction of methane not only as an alternative catalytic

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support, but also, taking in account its high micropore volume, activated carbon would be able to storage the hydrogen produced by this reaction to be then employed in fuel cells.

2. Experimental

2.1. Catalyst preparation

The catalysts were synthesized by incipient wetness impregnation of an AC of commercial origin [(Merck, Darmstandt, Germany) with BET surface area 893 $m^2 g^{-1}$ with around 90% of micropore surface, maximum pore volume 0.57 $cm^3 g^{-1}$,median pore diameter 7.9 Å, ash content < 1wt%] with nickel and calcium nitrate solutions, heating on a stirring plate at 80 °C to apparent dryness and drying at 120 °C in static air oven for 3 h. For the bi-metallic catalyst, the order of impregnations was varied to verify its influence on catalytic activity. The catalysts were not calcined, but for convenience in the comparison with conventional alumina-supported catalysts the composition is reported as the calculated content of NiO (0.25 and 5%) and CaO (1%) and they were labeled as Ni/AC and Ca/AC for single catalysts. For bi-metallic catalysts Ni–Ca/AC or Ca–Ni/AC, the order of impregnation is given by the sequence of elements, i.e., Ni followed of Ca for Ni–Ca/AC. In the first column of table 1 it can be noted, between brackets, the corresponding nominal concentrations of catalysts prepared.

2.2. Catalyst characterization

Homogeneity in the preparation of catalysts was inferred from gravimetric analysis of ashes obtained after submitting the catalysts to the pyrolysis of carbonaceous material at 550 °C for 16 h in a ceramic oven (muffle) from Heraeus following a standard test [23]. Compositions of catalysts were checked from these ashes by Inductively Coupled Plasma-Atomic Emission (ICP) in a Perkin Elmer Optima 3000 apparatus. Analytical results are compiled in table 1.

X-ray Photoelectron Spectroscopy (XPS) was employed to determine the nature of the chemical species on the surface of some of catalysts studied. This was carried out by means of an ESCALAB 220i-XL spectrometer (VG scientific) equipped with a hemispherical electron analyzer and a double anode Mg–Al non-monochromatic X-ray source. The pressure in the analysis chamber was kept below 10^9 Torr. Pre-treated samples were protected from exposition to the atmosphere by immersion into a hydrocarbon solvent (purified heptanes) while transferring from the reactor to the preparation chamber of the spectrometer.

Textural characterization of catalysts was performed by means of N_2 adsorption at 77 K in order to obtain the B.E.T. surface areas. The full isotherms in the range of 0.03 up to 630 Torr were measured employing a Micromeritics ASAP-2010 apparatus. Other experimental conditions related to the textural characterization have been already reported [19,20,24].

2.3. Catalyst pre-treatment

Samples were submitted to *in situ* pre-treatment before activity test under Helium flow (50 ml min^{-1},14.5 psi pressure) starting at room temperature up to 550 °C, using a heating rate of about 10 °C min^{-1}, and the time of pre-treatment (60 min) was counted from the moment the final temperature was reached.

2.4. Catalytic test

Activity in the reaction of methane reformation under carbon dioxide flow was followed by means of a continuous flow system (quartz reactor) flowing both reactants (CH_4 and CO_2) at nearly atmospheric pressure (14.5 psi). Methane was purchased from Matheson (UHP) and CO_2 from BOC (purity higher than 99.9%).

Analysis of methane was carried out with an on-line gas chromatograph (Varian 3700 GC apparatus) with TCD detection, employing a Porapak R packed column at 50 °C. In the present conditions of equipment only methane could be detected in the gaseous stream off the

Table 1
Gravimetric and chemical analysis of catalysts

Catalyst[a]	Ash (wt%)[b]	NiO (wt%)[c]	CaO (wt%)[c]	Total (wt%)[d]
Ca (1%)/AC	1.72 ± 0.09	–	0.92	0.92
Ni (0.25%)/AC	0.27 ± 0.01	0.25	–	0.25
Ni (5%)/AC	4.69 ± 0.01	4.61	–	4.61
Ca (1%)–Ni (0.25)/AC	2.02 ± 0.11	0.26	0.93	1.19
Ca (1%)–Ni (5%)/AC	5.67 ± 0.21	4.60	1.69	6.29
Ni (0.25%)–Ca (1%)/AC	2.21 ± 0.03	0.26	0.94	1.20
Ni (5%)–Ca (1%)/AC	6.44 ± 0.23	4.60	0.95	5.55

[a] The numbers between brackets indicate nominal composition of impregnated metallic oxides.
[b] Obtained by gravimetrical analysis after subtract the inorganic ash content of the activated carbon (0.48 ± 0.01)%.
[c] Nickel and Calcium (as oxides, NiO and CaO) by ICP.
[d] Total amount of Nickel plus Calcium oxides.

reactor, and for that reason the catalytic activity is reported as percent methane conversion as a function of reaction time.

The reaction conditions employed were: 100 g of catalyst sample; 80 ml min^{-1} flow of both methane and carbon dioxide (50 vol% each reactant); reaction temperature was 550 °C (similar than that of pre-treatment). Some activity tests were done by duplicate or triplicate, the reproducibility of results being better than 5%.

3. Results and discussion

3.1. Characterization of catalysts

Table 1 lists the gravimetric and chemical analysis of catalysts performed by ICP. The corresponding ash values obtained from the pyrolysis of several carbon-supported samples indicate a good homogeneity of catalysts prepared. This can be inferred from the small standard deviations shown in the second column of table 1. On the other hand, the values obtained from ICP of nickel and calcium (reported as oxides: NiO and CaO) suggest that catalysts prepared have a similar composition than nominal values, indicated between brackets in the first column.

Table 2 contains the results of B.E.T. surface areas obtained from adsorption isotherm of N_2 at 77 K of catalysts after submitting to pre-treatment under helium flow. In general, it can be noted that catalysts have lower surface areas in comparison to the AC support (893 m^2 g^{-1}). This, in part, can be attributed to a dilution effect of the support as consequence of metal species impregnated. However, monometallic Ca(1%)/AC and Ni(0.25%)/AC catalysts show the opposite effect. In other words, these two catalysts have higher surface areas than that of AC alone. In the case of Ca(1%)/AC it can be suggested that after the thermal decomposition of calcium nitrate a very well dispersed oxide calcium phase was formed contributing with a lightly increase in the total surface area respecting to AC alone. For Ni(0.25%)/AC sample, we suggest that this increase in surface are can be the consequence of a clean up of the AC porous structure during the thermal pre-treatment. This clean up effect would involve the reaction between the steam evolved during the thermal degradation of the hydrated nitrate nickel salts with AC support ($C + H_2O \rightarrow CO + H_2$). This reaction occurs spontaneously at temperature higher than 650 °C but it might be induced at lower temperatures by the well know coal gasification behavior of alkali carbonates and/or metal transition nitrates that can play as catalysts in this reaction [25]. This would be particularly true for very low nickel quantities in order to avoid the dilution effect of the support discussed above.

Table 2
B.E.T. surface areas (S_{BET}) of catalysts studied

Solids	S_{BET} (m^2 /g)
Ca (1%)/AC	910.8 ± 25.15
Ni (0.25%)/AC	952.8 ± 27.61
Ni (5%)/AC	811.9 ± 24.87
Ca (1%)–Ni (0.25)/AC	855.1 ± 29.20
Ca (1%)–Ni (5%)/AC	863.8 ± 24.61
Ni (0.25%)–Ca (1%)/AC	884.6 ± 28.74
Ni (5%)–Ca (1%)/AC	844.5 ± 30.27

Figures 1 and 2 show the XPS spectra in the Ni 2p region for Ni(0.25%)/AC and Ni(5%)/AC catalysts, respectively. It can be noted in both figures that the corresponding peaks of nickel ($2p_{1/2}$ and $2p_{3/2}$) show a clear attenuation in intensity, more pronounced in the Ni $2p_{3/2}$ signal after catalysts were submitted to the pre-treatment indicated above. We attribute this result to a migration of nickel species, principally NiO, into the pore system of the activated carbon in line with the fact that Ni content as atomic obtained from the XPS report corresponding to the Ni $2p_{3/2}$ peak decrease about 20% (1.855% against 2.338%). Also, peak positions corresponding to Ni^{+2}, even after pretreatments, did not show a representative reduction in the oxidation state of nickel, and only was detected a small decrease in the binding energy, i.e., 854.20 against 855.92 eV for the case Ni $2p_{3/2}$ peak and 872.00 in stead of 873.41 eV after submitting Ni(5%)/AC to the pretreatment under helium flow. This fact might be associated with a higher electronic density around Ni^{+2} inside the porous structure of AC inducing XPS signals with lower binding energies or also can be associated to the formation of nickel carbide during catalysts pretreatment [26].

3.2. Catalytic activity

Plots of the catalytic activity in terms of methane conversion as a function of time can be seen in figures 3 and 4 for mono- and bi-metallic catalysts, respectively. Table 3 shows methane conversions (%) at selected times of reaction. It can be noted from figure 3 that the Ni(5%)/AC catalyst show the highest initial methane conversion (14%) of monometallic catalysts. However, it is deactivated easily, showing about 6% of methane conversion after 60 min of reaction.

As a general trend, single metal catalysts show very similar methane conversion (2–6%) after this period of time. Also, is important to note from figure 3 the catalytic activity profile developed by Ca(1%)/AC and Ni(0.25%)/AC. Both catalysts show an increase of methane conversion up to maximum values around 30 and 45 min, respectively, to then suffer a clear deactivation until negligible conversion values. This catalytic behavior might be associated with an induction period of reaction in that nickel or calcium oxides could be suffering a total or partial reduction to elemental oxidation state as some of us have already report [19].

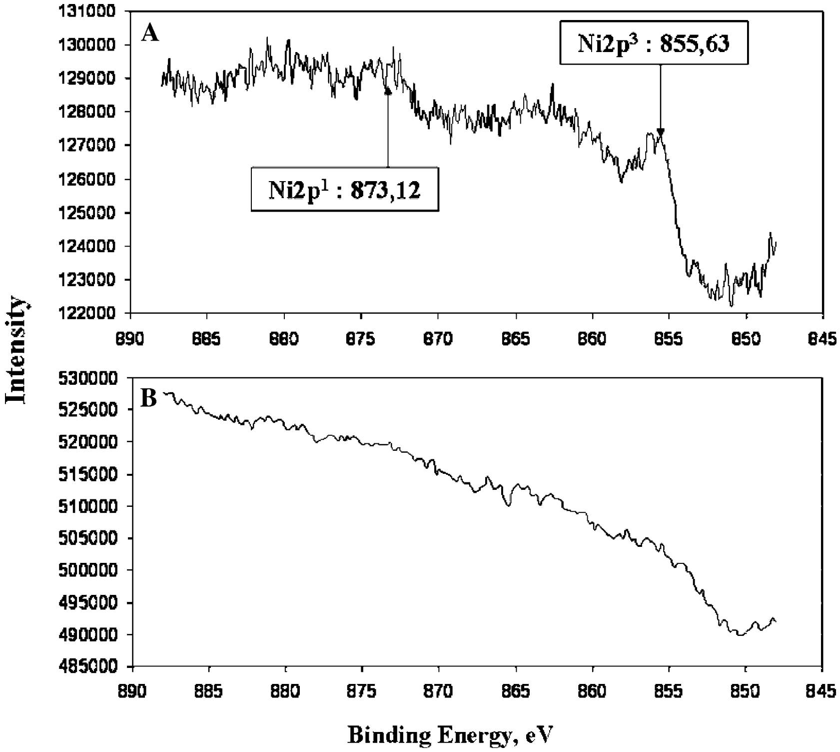

Figure 1. XPS spectra in the Ni 2p region for Ni(0.25%)/AC_M catalyst. (A) Without pre-treatment; (B) Pre-treated.

However, as a consequence of a very poor metal dispersion, and co-sintering of metal phases, single metal catalyst can suffer deactivation easily [1,9,10,20] as seems to indicate figure 3. On the other hand, as the catalysts was not reduced before reforming experiments, the consumed methane shown in single nickel catalysts (figure 3) might be due to the reaction between NiO and methane [27,28], in which the NiO reduced, and then the

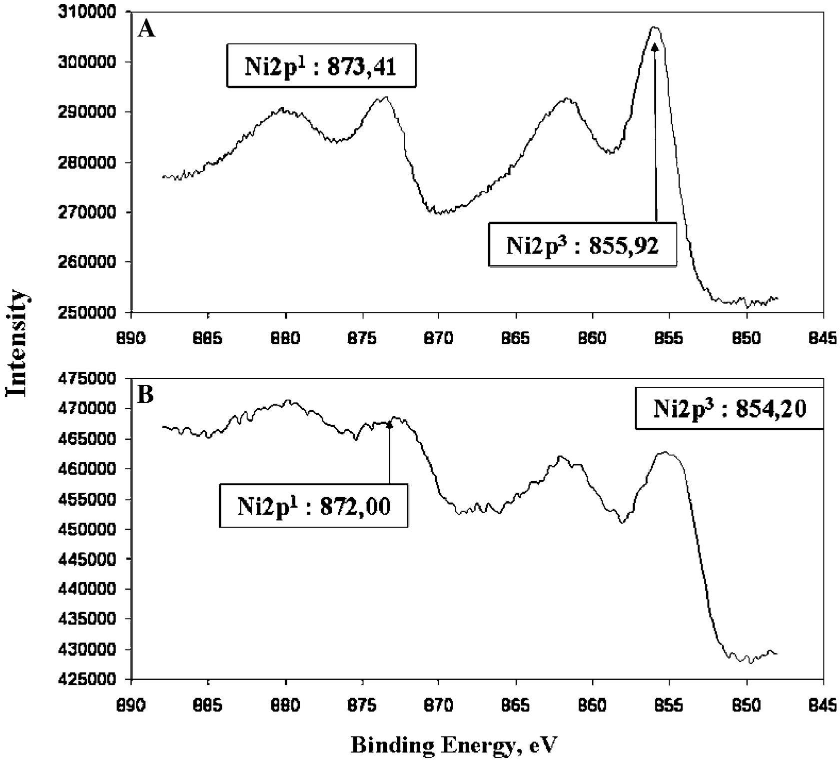

Figure 2. XPS spectra in the Ni 2p region for Ni(5%)/AC_M catalyst. (A) Without pre-treatment; (B) Pre-treated.

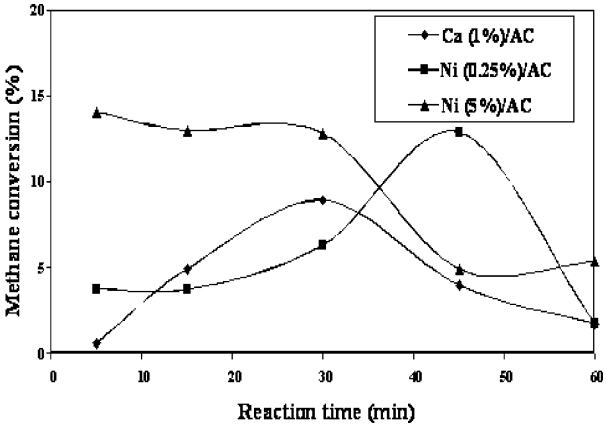

Figure 3. Catalytic activity of monometallic catalysts.

Table 3
Methane conversion (%) at selected reaction times (t_r)

Catalysts	t_r = 5 min	t_r = 60 min	t_r = 120 min
AC_M	5.2	2.2	2.5
Ca (1%)/AC	0.6	1.7	1.1
Ni (0.25%)/AC	3.7	1.7	4.4
Ni (5%)/AC	14.1	5.3	5.1
Ca (1%)–Ni (0.25)/AC	4.2	2.9	0.5
Ca (1%)–Ni (5%)/AC	12.5	9.2	7.3
Ni (0.25)–Ca (1%)/AC	3.3	5.4	1.8
Ni (5%)–Ca (1%)/AC	19.4	11.7	11.1

detected methane conversion decreases as the amount of NiO got reduced. As indicated above, in our XPS spectra analysis no reduction of nickel to metallic phase was detected. Therefore, the present activity of catalyst could be attributed to the formation of another phase, as for example nickel carbide as was observed by means of X-ray diffraction (not shown). However, it must to be appointed that both Ni_3C and NiC and a metallic Ni phase shown similar XRD patterns. In other words, with the present results is practically impossible to conclude which phase is formed during pretreatment under He flow. However, previous results [27] show that nickel carbide can be formed under inert atmosphere at temperature as low as about 500 °C and therefore we suggest that at the present conditions a mixture of nickel carbides and elemental nickel phases would being forming induced by the presence of a very-well known reductive solid as activated carbon [29]. Moreover, it is clear that temperature programmed reduction would allow to elucidate the type of nickel phase formed after pre-treatment. Some of us, in a previous work [19] have already studied the TPR profiles of carbon-supported Ni catalyst and we found that after pre-treatment of catalysts under He flow at 300 °C, the nickel precursor showed a TPR peak at temperature as low as 384 °C. We attribute such TPR peak to a very well dispersed nickel phase on activated carbon, probably nickel carbide, as present results suggest.

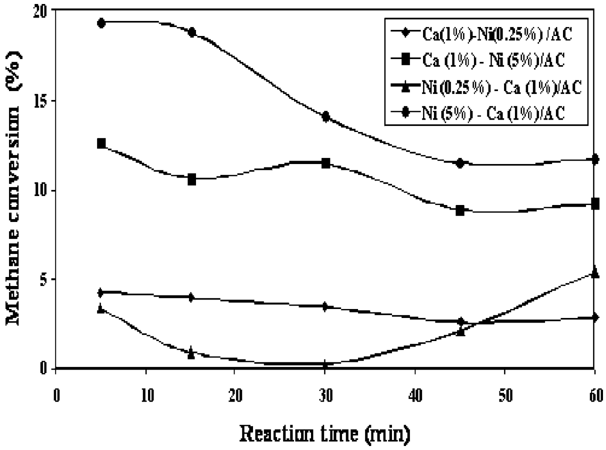

Figure 4. Catalytic activity of bi-metallic catalysts.

Figure 4 shows the catalytic activity of bi-metallic catalysts. Only the Ni–Ca catalysts containing 5% NiO show methane conversions higher than 10%, both at the initial time and also after 60 min of reaction. This behavior is in agreement with the case before where single catalysts with 5% of nickel show the highest methane conversion (figure 3). Also, it is important to be noted from figure 4 that though the catalytic activity trend of Ca(1%)–Ni(5%)/AC and Ni(5%)–Ca(1%)/AC catalysts were very similar, in the case where nickel was first impregnated first [Ni(5%)–Ca(1%)/AC], the catalyst show higher methane conversions along all the reaction time studied. It must be noted that it is very important to establish well the role of calcium in the present catalytic system. Días and Assaf found [18] that when calcium is added to the alumina before nickel, the formation of nickel species with low interaction with support is favored. Activated carbon, as a less interacting support, could enhance this situation: nickel phase must be remaining on the support as an oxide agglomerate, should be more reducible at low temperature by means of a solid–solid interaction with carbon. Also, in the present experimental conditions it is possible the formation of a stable calcium carbide phase that could be responsible for the stabilization and proper regeneration of the catalyst. For example, the catalytic behaviors and stability of the Ni(5%)–Ca(1%)/AC catalyst was verified performing experiences (not shown here) at longer reaction times (around 5 h) and from such studies we conclude that calcium plays an important role in the inhibition of deactivation of catalyst. However, it is important to perform a fully study of catalyst regeneration employing similar experimental conditions in order to verify the real potential of the present catalytic system.

It can be proposed that the presence of CaO stabilizes NiO, which means, decreasing its natural trend to suffer deactivation by carbon deposition, in a similar manner that has been reported for the case of MgO–NiO [13,16,17]. Moreover, the present results are in agreement with those obtained by Dias and Assaf [18] for the case of NiO–CaO/γ-Al_2O_3 catalytic system, where they reported that the catalytic activity of such system increases in presence of very low quantities of calcium as consequence of the interaction between mixed oxide phases of nickel and calcium.

Though the different trends of the variation of methane conversion corresponding to different catalysts, to compare the catalytic behavior of mono- and bi-metallic catalysts discussed above in figures 3 and 4, in table 3 are compiled values obtained of methane conversion at some selected reaction times. It can be noted that methane conversion shown by Ni(5%)–Ca(1%)/AC is higher in 5, 60 and 120 min than those show by single metal catalysts Ni(5%)/AC or Ca(1%)/AC. The addition of methane conversions shown by both monometallic catalysts is lower than that obtained on the bi-metallic catalysts. It can be suggested that such system presents a kind of promoter effect, attributed to CaO which is able to decrease the Lewis acidity of the catalytic system [13, 16–18]. As can be deduced from the values in table 3, the impregnation of Ca before Ni practically does not play such an important role on the catalytic activity of single samples. On the contrary, the addition of Ca after nickel impregnation, contributes not only to a better stability of the bi-metallic system, but also seems to inhibit the deactivation of catalysts in agreement with previous reported studies for different [13,16,17] or similar [18] catalytic systems. In addition to this, in spite of the influence of the carbon support is not explored in the present study, the AC employed in this study has a basic chemical nature with a surface pH of about 8 [19]. Therefore, although steady state condition in the reactor has not reached, as can be inferred from the unstable catalytic trends (figures 3 and 4), it must to be appointed that this H-type [29] AC has shown a great capacity to stabilize catalysts at longer period of time as have been observed by some of us in previous works for ethylene hydrogenation [19,20,24] and more recently for Methane reformation [26]. On the other hand, as we expected from experiments performed up to 650 °C (not shown) heating of AC monoliths under CO_2 flow, it must to be remarked that AC did not suffer gasification by means of the reverse Boudouard reaction ($C + CO_2 \rightarrow 2CO$) and therefore, any influence of carbon dioxide upon AC can be negligible at the present experimental conditions of low temperature.

4. Conclusions and future studies

In spite of methane conversions being lower than 20%, the results obtained in present study are promising ones because they suggest that it is possible to transform methane on activated carbon-supported Ni–Ca catalysts in presence of carbon dioxide and using mild reaction conditions. We think that this is a very important result because it opens a door in the research of novel catalysts employing carbon composites as catalytic supports, particularly in line with the research for novel systems for the catalytic conversion of natural gas aimed at obtaining hydrogen, then to storage it for finally to be employed in fuel cells.

Finally, as in methane reformation with CO_2, the most important things are the coke deposition and sintering of the Ni particles which would deactivate the catalysts, at present a study of these parameters is being develop by us, as well as others concerning the influence of pre-reduction of catalysts with hydrogen, longer reaction time, temperature and the influence of physicochemical properties of the support upon the activity and stability of the catalysts.

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