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Relationship between carbon morphology and catalyst deactivation in the catalytic decomposition of biogas using Ni, Co and Fe based catalysts.

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Abstract

A novel approach to the decomposition of biogas consisting in the simultaneous production of syngas (H₂ and CO mixture) and bio-nanostructured filamentous carbon (BNFC) is proposed. Catalysts with different active phases such as Ni, Co or Fe on Al₂O₃ are studied in the temperature range between 600 and 900 °C. Their behaviour was analysed considering CH₄ and CO₂ conversions, reaction rates, catalyst stability and carbon production. Additionally, the BNFC produced were characterised by transmission electron microscopy. Depending on the active phase and the reaction temperature, different carbon types were identified: fishbone, parallel and chain-like BNFC and encapsulating carbon. Large amounts of BNFC and good catalyst stability were achieved with the Ni/Al₂O₃ catalyst at 600 °C, pointing out that carbon accumulation is not directly responsible of catalyst deactivation and that the key factor is the nature of carbon formed during the reaction.

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1. INTRODUCTION

Biogas, mainly composed by CH₄ and CO₂, is obtained by anaerobic digestion of biodegradable wastes. Its composition makes biogas an interesting feedstock for the dry reforming of methane (DRM) process ($\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{H}_2 + 2\text{CO}$, $\Delta H^\circ = 247 \text{ kJ}\cdot\text{mol}^{-1}$). DRM has been extensively studied over different catalysts [1] and research efforts are aimed to synthesize an active and H₂ selective catalyst that minimizes surface carbon accumulation in order to avoid catalyst deactivation [2]. It is well known that noble metal catalysts meet those requirements [3, 4]. However, the high cost of these materials prompted the research on less expensive catalysts like Ni [5-10], Co [11-14] or Fe [15], even though they are prone to carbon generation via CH₄ decomposition ($\text{CH}_4 \leftrightarrow 2\text{H}_2 + \text{C}$, $\Delta H^\circ = 75 \text{ kJ}\cdot\text{mol}^{-1}$) or Boudouard reaction ($2\text{CO} \leftrightarrow \text{C} + \text{CO}_2$, $\Delta H^\circ = -171 \text{ kJ}\cdot\text{mol}^{-1}$) [16].

Different strategies are proposed in the literature to prevent catalyst deactivation by carbon accumulation. Operating conditions as temperature or feedstock composition (CH₄:CO₂ ratio) are key factors [17, 18]. Thermodynamic analysis revealed that high temperatures and/or CH₄:CO₂ ratios below the unity are necessary to avoid carbon formation [19], even though from an industrial point of view the opposite conditions are more convenient. Ni crystal size also plays an important role and a good dispersion of the active phase prevented carbon formation [20-22]. Support selection and the addition of different dopants can also help decreasing carbon accumulation. Guo et al. [23] studied a Ni/MgAl₂O₄ catalyst and suggested that catalyst low acidity and sintering resistance allowed an effective way for CO₂ activation through formation of

carbonate/bicarbonate species which contribute to carbon elimination. Increasing surface basicity by adding basic metal oxides such as Na, K, Mg or Ca, increased CO₂ concentration at the surface resulting in a decrease of Ni ability for CH₄ decomposition [24-26]. Ceria was also studied as dopant and its participation in redox reactions removed carbon depositions from the surface of the catalyst [27].

However, a different approach to overcome deactivation problems by carbon accumulation can be envisaged attending to nanostructured filamentous carbon (NFC) formation mechanism [28, 29]: i) decomposition of CH₄ and carbon formation at the surface of the catalyst, ii) diffusion of dissolved carbon through the catalyst particle and iii) precipitation of dissolved carbon at the metal-nanofilament interface. In DRM, surface carbon gasification by CO₂, iv), should also be taken into account in the previous mechanism, resulting in a lower surface carbon formation rate. Depending on the previous relative rates, catalyst deactivation could be prevented if steps ii) and iii) are faster than iv) [30]. Under these conditions, the front face of catalyst particles remain free of carbon, leaving accessible active sites to CH₄ and CO₂ and allowing the formation of NFC without catalyst deactivation [12, 17, 31]. With this background in mind, we recently addressed a novel approach to the decomposition of CH₄/CO₂ mixtures (the so-called catalytic decomposition of biogas (CDB)) which consisted in the simultaneous production of syngas (H₂ and CO mixture) and bio-nanostructured filamentous carbon (BNFC) [32].

NFC are high valuable materials [33] that depending on their structure and surface properties can be employed in different applications such as catalyst support [34, 35], anode in Li-ion batteries [36, 37] or additive in polymer composites [38, 39]. NFC formation during DRM has been extensively reported [6, 22, 40, 41], although scarce information about the NFC characteristics is available in the literature. Serrano et al.

[42] observed the formation of hollow core fishbone-like carbon nanofibers (CNF) over a La-NiMgAlO catalyst. Corthals et al. [43] reported the formation of multiwall carbon nanotubes (MWCNT) over a NiMgTiO₃ catalyst and fishbone-like CNF over a NiMgAl₂O₄ catalyst. Our previous studies with a Ni/Al₂O₃ catalyst [17, 32, 44] revealed the formation of fishbone-like CNF at 600 °C and a mixture of fishbone and parallel-like CNF at 700 °C. In the previous studies, NFC were produced employing different metal-based catalysts. As a result, metal particles are located at the tip or the base of the NFC. Depending on the future application of the NFC, metals need to be removed. For that purpose, metal elimination can be performed by reflux in concentrated HNO₃ or HNO₃:H₂SO₄ mixtures [35, 45].

In an effort to expand our previous work on the CDB, different active phases such as Ni, Co or Fe on Al₂O₃ are studied in the temperature range between 600 and 900 °C. Their behaviour on the CDB process was analysed considering CH₄ and CO₂ conversions, reaction rates, catalyst stability and carbon production. Additionally, the BNFC produced were characterised by transmission electron microscopy (TEM) in order to address the effect of the different active phases on the carbon morphology.

2. EXPERIMENTAL

2.1 Catalysts synthesis

Ni, Co and Fe based catalysts using Al₂O₃ as textural promoter with an X:Al molar ratio of 67:33 (X: Ni, Co or Fe) and denoted as Ni/Al₂O₃, Co/Al₂O₃ and Fe/Al₂O₃, were prepared by the fusion method previously described in [46]: briefly, nitric salts of the metal and aluminium were crushed, followed by calcination of the resulting mixture at 450 °C for 8h. The powder samples were grounded and sieved to particle size in the 100-200 µm range to avoid external and internal mass transfer limitations [30]. Before

each test, catalysts were in-situ reduced with an H_2 flow of $100 \text{ mL}_N \cdot \text{min}^{-1}$ for 1h. Different reduction temperatures were chosen for each catalyst according to TPR analysis (**Fig. S1**): 550°C for $\text{Ni}/\text{Al}_2\text{O}_3$, 650°C for $\text{Co}/\text{Al}_2\text{O}_3$ and 750°C for $\text{Fe}/\text{Al}_2\text{O}_3$. X-ray analyses of the fresh and reduced catalysts confirmed the complete reduction of the active phases from NiO , Co_3O_4 and Fe_2O_3 to Ni , Co and Fe respectively (**Fig. S2 to S4**).

2.2 Experimental procedure

To carry out the experiments, a synthetic $\text{CH}_4:\text{CO}_2$ mixture with a volume ratio of 60:40 (v:v) was selected in order to mimic biogas composition. Catalytic experiments were carried out in a fixed-bed quartz reactor, 15 mm i.d, 750 mm height, fed by the top and heated by an electric furnace. A Peltier cooler was placed after the reactor to condense steam formed during the reaction. A synthetic biogas flow rate of $50 \text{ mL}_N \cdot \text{min}^{-1}$ was chosen. In each test, 0.1 g of catalyst was placed in the reactor to obtain a WHSV (Weight Hourly Space Velocity, defined here as the total flow rate at STP conditions per gram of catalyst initially loaded) of $30 \text{ L}_N \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$. Four different temperatures, 600, 700, 800 and 900°C , were studied. In order to discard the contribution of thermal decomposition, a blank experiment was carried out in the absence of catalyst at 900°C . $X_{\text{CH}_4,5\text{min}}$ was negligible ($<1\%$) and therefore, results here presented can only be attributed to a catalytic effect. A deviation less of the 5% for C, O and H was obtained in the mass balances.

CH_4 and CO_2 conversions, $X_{i,t}$ (**Eq. 1**), reaction rates, $-r_{i,t}$ (**Eq. 2**), sustainability factors, $S.F._i$ (**Eq. 3**) and carbon accumulation rate, $r_{\text{carbon},t}$ (**Eq. 4**) were calculated as follows:

$$X_{i,t} = \frac{(F_{in,i,t} - F_{out,i,t})}{F_{in,i,t}} * 100 \quad (\text{Eq. 1})$$

$$-r_{i,t} = \frac{X_{i,t}}{W/F_{in,i,t}} \quad (\text{Eq. 2})$$

$$S.F._i = \frac{(-r_{i,180 \text{ min}})}{(-r_{i,5 \text{ min}})} \quad (\text{Eq. 3})$$

$$r_{\text{carbon},t} = \frac{(F_{CH_4,t} + F_{CO_2,t})_{in} - (F_{CH_4,t} + F_{CO_2,t} + F_{CO,t})_{out}}{W} \quad (\text{Eq. 4})$$

In **Eq.1**, $F_{in,i,t}$ and $F_{out,i,t}$ represent CH₄ or CO₂ molar flow rates entering (*in*) or leaving (*out*) the reactor at a certain time (*t*). In **Eq. 2** and **Eq. 4**, W represents the grams of catalyst initially loaded in the reactor. In **Eq. 3**, $-r_{i,180 \text{ min}}$ and $-r_{i,5 \text{ min}}$ represent CH₄ and CO₂ reaction rates after 180 and 5 minutes time on stream (TOS), respectively, being “*i*” CH₄ or CO₂ in all cases. Finally, CH₄, CO₂ and CO molar flow rates entering or leaving the reactor at a certain time are included in **Eq. 4** to calculate the net carbon formation rate.

The sustainability factor (S.F._{*i*}) has been used to compare the stability of the different catalysts over time. The S.F._{*i*} compares CH₄ or CO₂ reaction rates at the beginning and at the end of the experiment (5 and 180 minutes TOS, respectively). If catalyst activity is maintained, the value of the S.F._{*i*} will be one. On the other hand, if the catalyst is completely deactivated after 180 min TOS, this value will be zero.

2.3 Characterization techniques

In order to determine the outlet gases composition (syngases composition), bag samples were taken and analysed by means of gas chromatography in a micro GC Varian CP4900 equipped with two packed columns (Molecular Sieve and Porapack) and a TCD detector to quantify H₂, CO, CH₄ and CO₂ concentrations.

The carbon yield (Y_c), expressed as grams of carbon generated per gram of catalyst ($\text{g}_{\text{carbon}} \cdot \text{g}_{\text{cat}}^{-1}$), was determined by temperature programmed oxidation (TPO) in a

Setaram Thermogravimetric Analyzer. Samples obtained after reaction were heated under air flow at a rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ from room temperature to $1000\text{ }^{\circ}\text{C}$. Ni, Co and Fe oxidations were taken into account to make calculations.

The morphology of the BNFC was studied by transmission electron microscopy (TEM). With that purpose Ni/Al₂O₃ spent catalysts were analysed in a JEOL-2000 FXII microscope operating at 200 keV, while Co/Al₂O₃ and Fe/Al₂O₃ spent catalysts were analysed in a Tecnai F30 equipped with a cannon of 300 keV.

3. RESULTS AND DISCUSSION

3.1 Initial conversions and reaction rates

Initial CH₄ conversions ($X_{\text{CH}_4,5\text{min}}$) obtained with the catalysts under study are shown in **Fig. 1a**. Regardless the catalyst employed, $X_{\text{CH}_4,5\text{min}}$ increased with temperature. This behavior was expected due to the endothermic nature of the main reactions involved in the process [32]. At low temperatures (600 and 700 °C), the highest $X_{\text{CH}_4,5\text{min}}$ was obtained with the Ni/Al₂O₃ catalyst followed by the Co/Al₂O₃ one. The $X_{\text{CH}_4,5\text{min}}$ obtained with the Fe/Al₂O₃ catalyst at 700 °C was zero, pointing out that the activation temperature for this catalyst in the CDB is over 700 °C. Similar findings were reported by Li et al. [47] and Abbas et al. [48] when studying Fe-based catalyst in the CH₄ decomposition reaction. At higher temperatures (800 and 900 °C), differences in $X_{\text{CH}_4,5\text{min}}$ between Ni and Co-based catalysts were almost negligible while $X_{\text{CH}_4,5\text{min}}$ obtained with the Fe/Al₂O₃ catalyst were lower as compared to Ni and Co-based catalysts, especially at 800 °C. Initial CH₄ reaction rates ($-r_{\text{CH}_4,5\text{min}}$) are reported in **Fig. 1b**. The same trend as that observed for $X_{\text{CH}_4,5\text{min}}$ was observed. Maximum values (ca. $12\text{ mmol}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{min}^{-1}$) were obtained at 900 °C.

Initial CO₂ conversions (**Fig. S5a**) were consistently higher than initial CH₄ conversions, except at 900 °C when both were very close (ca. 97%), probably due to CO₂ participation in the reverse water gas shift reaction. However, as shown in **Fig. S5b**, the opposite behavior was observed when comparing initial reaction rates ($-r_{\text{CO}_2,5\text{min}} < -r_{\text{CH}_4,5\text{min}}$). This can be due to the lower content of CO₂ in the feedstock (CH₄:CO₂ ratio= 60:40).

3.2 Catalysts stability over time

To compare the catalyst performance in the CDB, catalyst stability should be taken into account along with catalytic activity. In **Table 1**, S.F._{CH₄} values are shown. S.F._{CH₄} for Ni/Al₂O₃ catalyst decreased gradually from 0.90 to 0.60 in the temperature range between 600 and 800 °C, while from 800 to 900 °C it remained constant. This is reflected on the evolution of the $-r_{\text{CH}_4}$ over time (**Fig. 2a**). At 600 °C, Ni catalyst presented a very stable behavior, even though a slight decrease of $-r_{\text{CH}_4}$ over time was observed. However, at 800 and 900 °C, an important reduction of the $-r_{\text{CH}_4}$ took place in the first 60-90 minutes TOS, sharper as reaction temperature increased, and after that, $-r_{\text{CH}_4}$ stabilized. At 700 °C, $-r_{\text{CH}_4}$ evolution over time presented an intermediate behavior. In the case of the Co/Al₂O₃ catalyst, an improvement of the S.F._{CH₄} (**Table 1**) was observed when reaction temperature was increased from 600 to 700 °C (from 0.44 to 0.68). Increasing temperature up to 800 °C did not affect S.F._{CH₄} but further rising up to 900 °C slightly decreased it down to 0.63. $-r_{\text{CH}_4}$ evolution over time for Co/Al₂O₃ experiments is plotted in **Fig. 2b**. In the whole temperature range studied, $-r_{\text{CH}_4}$ suffered a decrease in the first 60 minutes TOS and the drop was more accentuated as the reaction temperature increased. After a certain time, $-r_{\text{CH}_4}$ reached a steady state, as it was observed in the experiments carried out with the Ni/Al₂O₃ catalyst at 800 and 900 °C.

Finally, results obtained with the Fe/Al₂O₃ catalyst are discussed. At 800 °C, the S.F._{CH₄} was 0.57 and at 900 °C it increased till 0.69, a higher value than those obtained with the Ni/Al₂O₃ or the Co/Al₂O₃ catalysts at the same temperature (0.60 and 0.63, respectively). In **Fig. 2c**, -r_{CH₄} evolution over time was plotted and presented similar trend as the one observed with the Ni/Al₂O₃ catalyst at 800 and 900 °C. However in this case, the -r_{CH₄} decay was extended to 120 minutes TOS instead of 60 minutes. (Fe/Al₂O₃ catalyst was inactive at 700 °C, hence S.F._{CH₄} and -r_{CH₄} data at this temperature were not calculated).

In an effort to explain the aforementioned behaviors, carbon accumulation rates (r_{carbon,t}) over time are plotted in **Fig. 3**. r_{carbon,t} represents the net carbon formation rate and was calculated from mass balances (**Eq. 4**). As it occurred with the -r_{CH₄} evolution over time, two different behaviors according to r_{carbon,t} were observed. In experiments, in which catalysts presented a good stability (S.F._{CH₄}>0.75), r_{carbon,t} was higher than zero throughout the 180 minutes experiment and presented a trend over time similar to that presented by -r_{CH₄}. In contrast, in experiments in which catalysts deactivation was more pronounced (S.F._{CH₄}<0.69) in the first 60-90 minutes, r_{carbon,t} decreased in the same way until reaching zero or even negative values, implying that either carbon is not generated or even consumed during the runs. Therefore, and considering that the purpose of the CDB is the simultaneous production of syngas and BNFC, catalyst stability is of major importance, even though a high S.F._{CH₄} implies obtaining lower reaction rates at the beginning of the experiment as it occurred with the Ni/Al₂O₃ catalyst at 600 °C. Besides, these results pointed out that carbon accumulation is not directly responsible of catalyst deactivation and probably the key factor is the nature of carbon formed during the reaction. In the next section, the relationship between carbon morphology and catalyst deactivation is discussed.

3.3 BNFC morphology and production

Catalyst particles encapsulation by carbon is considered one of the main causes of deactivation in process in which hydrocarbons are decomposed [2, 49]. In steam and dry reforming of methane, it is generally accepted that different kinds of carbon are formed during reaction [49-52], so it is likely that the same structures are formed in the CDB: high reactive carbon (C_α or atomic carbon), amorphous carbon (C_β), and graphitic carbon (C_γ). C_α corresponds to highly reactive carbon species produced from the decomposition of a hydrocarbon (methane in this case). In the CDB, C_α may be further gasified by CO_2 or be converted to less active carbon (C_β). In turn, C_β may also be gasified, evolved to produce encapsulating carbon (C_γ) or dissolved in the catalyst bulk. Dissolved carbon is the responsible of the subsequent nanostructured filamentous carbon (NFC) formation. Accumulation of adsorbed carbon in the front face of the catalyst particles, which eventually leads to catalyst particle encapsulation, takes place due to an imbalance between carbon formation rate and carbon removal rate. In the CDB, the former includes C_α production from CH_4 decomposition while the latter includes C_α and C_β gasification to produce CO and C_β diffusion through the bulk to generate BNFC. It is important to note that the formation of BNFC does not imply the deactivation of the catalyst [52]. Carbon diffusion through the catalyst bulk is the rate determining step in the NFC formation and the driving force is generally associated to a carbon concentration gradient [53-56].

In **Fig. 4**, TEM micrographs of the Ni/ Al_2O_3 spent catalysts are showed. In the whole range of temperatures studied, the formation of carbon was observed. This observation agrees with the presence of a peak around 26° , which corresponds with graphitic carbon, in the XRD pattern of the Ni/ Al_2O_3 spent catalysts (**Fig. S2**). At 600 °C a great amount of BNFC with a diameter in the 30-50 nm range was observed (**Fig. 4a**). Due to the well

defined arrow-head shape of the catalyst particle, fishbone-like BNFC without hollow core were formed (**Fig. 4a**). The absence of encapsulating carbon at the leading face of the catalyst can be the reason of the stable behavior of the Ni/Al₂O₃ catalyst at 600 °C (S.F._{CH4}=0.90). At 700 °C, a considerable amount of BNFC was also formed (**Fig. 4b**). However, at this temperature, poor defined pearshaped Ni particles were observed. As a consequence, hollow BNFC of parallel and fishbone-like types with diameters from 15 to 30 nm were formed. Beside this, small amounts of encapsulating carbon covered the leading face of the catalyst particles (**Fig. 4b**). This can be the cause of the slight drop of the catalyst stability registered at 700 °C (S.F._{CH4}=0.75). When increasing temperature up to 800 °C (**Fig. 4c**), the amount of BNFC diminished. Parallel like BNFC, with diameters from 15 to 50 nm, were observed. At this temperature, large particles covered by encapsulating carbon and Ni particles isolated in the inner part of the BNFC were also observed. Finally at 900 °C, the amount of BNFC was even lower than at 800 °C and the presence of coarse particles encapsulated by graphitic carbon along with isolated Ni particles in the BNFC inner part was more evident (**Fig. 4d**). BNFC observed at 900 °C adopted a parallel like type with diameters from 20 to 100 nm. At both 800 and 900 °C, -r_{CH4} suffered a quick deactivation in the first 60 minutes (**Fig. 2a**), concurring with the sharp drop of carbon accumulation rate observed in **Fig. 3a**, and after that time -r_{CH4} presented a stable behavior (**Fig. 2a**). Two different reasons can account for this situation. First, during the formation of a new BNFC carbon layer, the Ni particle suffered a stress towards the BNFC growing direction and as a result a part of it can be stripped and isolated in the inner part of the BNFC. The progressive formation of these isolated Ni particles contributed to the decrease of the catalytic activity. Once the accumulation of carbon finished (**Fig. 3a**) and hence the BNFC growing process, no more segregation of Ni particles is expected and catalyst

deactivation provoked by this phenomenon is stopped. Second, the high $-r_{\text{CH}_4}$ obtained at the beginning of these experiments (**Fig. 1b**) might provoke an imbalance between carbon formation rate and carbon removal rate at the surface of the catalyst. As a result, some active catalyst particles, where CH_4 is adsorbed and decomposed, may be encapsulated by carbon resulting in a progressive decrease of the $-r_{\text{CH}_4}$ over time (behavior observed in the first 60 minutes TOS). Once carbon formation rate is equaled to carbon removal rate, a stable activity is reached.

With the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst, parallel like BNFC with hollow core were obtained after tests performed at all reaction temperatures studied (**Fig. 5**). As it happened with the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst, the amount of BNFC observed by TEM decreased at high temperatures while the amount of large particles, inactive towards BNFC production, increased. The diameter of the BNFC became larger as reaction temperature increased and was ranged between 10-35 nm at 600 and 700 °C (**Fig. 5a and Fig. 5b**) and between 20-70 nm at 800 and 900 °C (**Fig. 5c and Fig. 5d**). As commented before, a strong catalyst deactivation was observed with the $\text{Co}/\text{Al}_2\text{O}_3$ catalyst at 600 °C ($\text{S.F.}_{\text{CH}_4}=0.44$). Nevertheless, a great amount of BNFC was formed (**Fig. 5a**). Probably, the presence of large particles (ca. 65 nm) coated by graphitic layers along with isolated Co particles in the inner part of the BNFC can explain this behavior. However, at 600°C the amount of both kinds of particles was lower than at 700, 800 and specially 900 °C and its presence was probably not the only reason of the strong deactivation observed. Taking into account that bulk hcp-Co is stable below 420-450 °C [57], the appearance of two small peaks related to hcp-Co, along with a prominent one related to fcc-Co, in the XRD pattern of the $\text{Co}/\text{Al}_2\text{O}_3$ spent catalyst after reaction at 600 °C (**Fig. S3**) is particularly striking. This hcp-Co phase was generated during reaction at 600 °C since in the XRD pattern of the reduced $\text{Co}/\text{Al}_2\text{O}_3$ catalyst only the fcc-Co phase was detected

(**Fig. S3**). After reaction at 700 °C, a small peak related to hcp-Co was still observed while at 800 and 900 °C only fcc-Co peaks were detected (**Fig. S3**). De la Peña O'Shea et al. [58] also observed hcp-Co nanoparticles at temperatures above 420-450 °C. According to their results, the responsible of the stabilization of hcp-Co at 700 °C was a graphitic layer encapsulating catalyst particles. Thus, the presence of this hcp structure can be related to the strong catalyst deactivation observed at 600 °C. As reaction temperature increased, the peak related to the hcp-Co disappeared and the deactivation observed was probably due to the same reasons explained before for the Ni/Al₂O₃ catalyst.

Finally, in **Fig. 6**, TEM micrographs of the Fe/Al₂O₃ spent catalyst after reaction at 900 °C revealed the presence of large spherical particles aggregates along with BNFC. Most of the BNFC showed diameter between 30 and 45 nm, however BNFC with a diameter up to 200 nm were also observed. Two different kinds of BNFC were formed regardless the reaction temperature. The previously observed parallel type (**Fig. 6a**) and a new one called chain like BNFC (**Fig. 6b**). Fe/Al₂O₃ spent catalyst after reaction at 700 and 800 °C were not analyzed by TEM since according to TPO (**Table 2**) and XRD patterns (**Fig. S4**) no carbon was obtained after 180 minutes reaction in those experiments. Only the presence of non active Fe₃O₄ and small peaks related to FeAl₂O₄ phase were detected at 700 °C, suggesting a re-oxidation of the Fe/Al₂O₃ catalyst. In contrast, at 800 °C an important peak related to α -Fe was observed along with small peaks of FeAl₂O₄. Finally at 900 °C, the characteristic peaks of graphitic carbon, α -Fe and Fe₃C along with two new peaks at 43.8 and 51.1° (**Fig. S4**) were detected. The position of these two peaks did not correspond with the γ -Fe peaks position (45.8 and 53.4°). However it has been reported [59] that carbon atoms can dissolve on γ -Fe structure, expanding the lattice and shifting the diffraction lines to lower angles. Both, high reaction

temperatures (900 °C) and carbon production can lead to the formation of this γ -Fe phase with carbon atoms dissolved in the Fe FCC structure.

In order to calculate accurately carbon production (Y_c), TPO analyses were carried out. Ni/Al₂O₃ catalyst presented the greatest ability to generate carbon. As observed in **Table 2**, the highest carbon production ($8.79 \text{ g}_{\text{carbon}} \cdot \text{g}_{\text{cat}}^{-1}$) was obtained with the Ni/Al₂O₃ catalyst at 600 °C, being this value 2.1 and 2.7 times higher than the highest production obtained with the Co/Al₂O₃ ($4.24 \text{ g}_{\text{carbon}} \cdot \text{g}_{\text{cat}}^{-1}$ at 800 °C) and Fe/Al₂O₃ ($3.24 \text{ g}_{\text{carbon}} \cdot \text{g}_{\text{cat}}^{-1}$ at 900 °C) catalysts. However, the highest carbon productions obtained with those catalysts did not present such high BNFC concentration as the one observed by TEM with the Ni/Al₂O₃ catalyst at 600 °C. Moreover, in the case of the Co/Al₂O₃ catalyst, the maximum carbon production was obtained at 800 °C while according to the TEM study the maximum concentration of BNFC was observed at 600 °C. These results point out that not only the production of carbon is important but the morphology must be taken into account since it is related to catalyst stability and the deactivation phenomenon.

4. CONCLUSIONS

On the basis of the results described above we concluded as follows:

- At low temperatures (600-700 °C), Ni/Al₂O₃ catalyst presented both higher initial activity ($-r_{\text{CH}_4,5\text{min}}$) and higher stability ($S.F._{\text{CH}_4}$) than Co and Fe-based catalysts. It was noteworthy that at 700 °C the Fe/Al₂O₃ catalyst was not active ($X_{\text{CH}_4,5\text{min}}=0\%$), pointing out that its activation temperature is over 700 °C. At high temperatures (800-900 °C), Ni/Al₂O₃ and Co/Al₂O₃ presented a similar performance. Regarding, the Fe/Al₂O₃ catalyst only results obtained at 900 °C were comparable to those obtained with the other catalysts at the same temperature.

- The highest carbon production ($8.79 \text{ g}_{\text{carbon}} \cdot \text{g}_{\text{cat}}^{-1}$) was obtained in the experiment carried out with the Ni/Al₂O₃ catalyst at 600 °C. This experiment showed the greatest catalyst stability (S.F._{CH₄}=0.90), pointing out that carbon accumulation is not directly responsible of catalyst deactivation and that the key factor is the nature of carbon formed during the reaction.
- Maximum carbon production obtained with the Co ($4.24 \text{ g}_{\text{carbon}} \cdot \text{g}_{\text{cat}}^{-1}$) and Fe-based ($3.24 \text{ g}_{\text{carbon}} \cdot \text{g}_{\text{cat}}^{-1}$) catalysts were obtained at 800 and 900 °C, respectively. However, at these temperatures the amount of BNFC observed by TEM was much lower than the amount observed with the Ni/Al₂O₃ catalyst at 600 °C.
- Different carbon types were identified along this paper: BNFC and encapsulating carbon. Among the BNFC, three different structures were observed: fishbone, parallel and chain-like BNFC. Fishbone-like BNFC were only formed with the Ni/Al₂O₃ catalyst at low temperatures (600 and 700 °C). Chain-like BNFC were obtained with the Fe/Al₂O₃ catalyst at 900 °C. And finally, the formation of parallel-like BNFC was observed with all the catalysts studied. Regarding encapsulating carbon, its presence was more evident at higher temperatures.
- Results presented point out that the CDB process, producing simultaneously syngas and high valuable BNFC, can be an alternative to direct biogas combustion.

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- [1] M.C.J. Bradford, M.A. Vannice, CO₂ reforming of CH₄, *Catal Rev - Sci Eng*, 41 (1999) 1-42.
- [2] C.-J. Liu, J. Ye, J. Jiang, Y. Pan, Progresses in the Preparation of Coke Resistant Ni-based Catalyst for Steam and CO₂ Reforming of Methane, *ChemCatChem*, 3 (2011) 529-541.
- [3] J.R. Rostrupnielsen, J.H.B. Hansen, CO₂-Reforming of Methane over Transition Metals, *J Catal*, 144 (1993) 38-49.
- [4] J. Wei, E. Iglesia, Isotopic and kinetic assessment of the mechanism of reactions of CH₄ with CO₂ or H₂O to form synthesis gas and carbon on nickel catalysts, *J Catal*, 224 (2004) 370-383.
- [5] A.M. Gadalla, B. Bower, The role of catalyst support on the activity of nickel for reforming methane with CO₂, *Chem Eng Sci*, 43 (1988) 3049-3062.
- [6] M.C.J. Bradford, M.A. Vannice, Catalytic reforming of methane with carbon dioxide over nickel catalysts I. Catalyst characterization and activity, *Appl Catal A*, 142 (1996) 73-96.
- [7] M.C.J. Bradford, M.A. Vannice, Catalytic reforming of methane with carbon dioxide over nickel catalysts II. Reaction kinetics, *Appl Catal A*, 142 (1996) 97-122.
- [8] K. Asai, K. Takane, Y. Nagayasu, S. Iwamoto, E. Yagasaki, M. Inoue, Decomposition of methane in the presence of carbon dioxide over Ni catalysts, *Chem Eng Sci*, 63 (2008) 5083-5088.
- [9] S. Corthals, J. Van Nederkassel, H. De Winne, J. Geboers, P. Jacobs, B. Sels, Design of active and stable NiCeO₂ZrO₂MgAl₂O₄ dry reforming catalysts, *Appl Catal B*, 105 (2011) 263-275.
- [10] B. Fidalgo, L. Zubizarreta, J.M. Bermúdez, A. Arenillas, J.A. Menéndez, Synthesis of carbon-supported nickel catalysts for the dry reforming of CH₄, *Fuel Process Technol*, 91 (2010) 765-769.
- [11] E. Ruckenstein, H.Y. Wang, Carbon dioxide reforming of methane to synthesis gas over supported cobalt catalysts, *Appl Catal A*, 204 (2000) 257-263.
- [12] D. San-José-Alonso, J. Juan-Juan, M.J. Illán-Gómez, M.C. Román-Martínez, Ni, Co and bimetallic Ni-Co catalysts for the dry reforming of methane, *Appl Catal A*, 371 (2009) 54-59.
- [13] V.M. Gonzalez-delaCruz, R. Pereñíguez, F. Ternero, J.P. Holgado, A. Caballero, In Situ XAS Study of Synergic Effects on Ni-Co/ZrO₂ Methane Reforming Catalysts, *J Phys Chem C*, 116 (2011) 2919-2926.
- [14] I. Luisetto, S. Tuti, E. Di Bartolomeo, Co and Ni supported on CeO₂ as selective bimetallic catalyst for dry reforming of methane, *Int J Hydrog Energy*, 37 (2012) 15992-15999.
- [15] K. Murata, M. Inaba, M. Saito, I. Takahara, N. Mimura, Methane Decomposition over Iron-based Catalysts in the Presence of O₂ and CO₂, *J Jpn Pet Inst*, 46 (2003) 196-202.
- [16] S. Corthals, J. Van Nederkassel, J. Geboers, H. De Winne, J. Van Noyen, B. Moens, B. Sels, P. Jacobs, Influence of composition of MgAl₂O₄ supported NiCeO₂ZrO₂ catalysts on coke formation and catalyst stability for dry reforming of methane, *Catal Today*, 138 (2008) 28-32.
- [17] S. de Llobet, J.L. Pinilla, M.J. Lázaro, R. Moliner, I. Suelves, Catalytic decomposition of biogas to produce H₂-rich fuel gas and carbon nanofibers. Parametric study and characterization, *Int J Hydrog Energy*, 37 (2012) 7067-7076.
- [18] A. Serrano-Lotina, L. Daza, Influence of the operating parameters over dry reforming of methane to syngas, *Int J Hydrog Energy*, 39 (2013) 4089-4094.

- [19] D. Fraenkel, R. Levitan, M. Levy, A solar thermochemical pipe based on the CO₂:CH₄ (1:1) system, *Int J Hydrog Energy*, 11 (1986) 267-277.
- [20] S. Tang, L. Ji, J. Lin, H.C. Zeng, K.L. Tan, K. Li, CO₂ Reforming of Methane to Synthesis Gas over Sol–Gel-made Ni/ γ -Al₂O₃ Catalysts from Organometallic Precursors, *J Catal*, 194 (2000) 424-430.
- [21] H.S. Bengaard, J.K. Nørskov, J. Sehested, B.S. Clausen, L.P. Nielsen, A.M. Molenbroek, J.R. Rostrup-Nielsen, Steam Reforming and Graphite Formation on Ni Catalysts, *J Catal*, 209 (2002) 365-384.
- [22] J. Zhang, H. Wang, A.K. Dalai, Development of stable bimetallic catalysts for carbon dioxide reforming of methane, *J Catal*, 249 (2007) 300-310.
- [23] J. Guo, H. Lou, L. Mo, X. Zheng, The reactivity of surface active carbonaceous species with CO₂ and its role on hydrocarbon conversion reactions, *J Mol Catal A: Chem*, 316 (2010) 1-7.
- [24] Z.L. Zhang, X.E. Verykios, Carbon dioxide reforming of methane to synthesis gas over supported Ni catalysts, *Catal Today*, 21 (1994) 589-595.
- [25] T. Horiuchi, K. Sakuma, T. Fukui, Y. Kubo, T. Osaki, T. Mori, Suppression of carbon deposition in the CO₂-reforming of CH₄ by adding basic metal oxides to a Ni/Al₂O₃ catalyst, *Appl Catal A*, 144 (1996) 111-120.
- [26] K. Tomishige, Y.-g. Chen, K. Fujimoto, Studies on Carbon Deposition in CO₂ Reforming of CH₄ over Nickel–Magnesia Solid Solution Catalysts, *J Catal*, 181 (1999) 91-103.
- [27] S.Y. Foo, C.K. Cheng, T.-H. Nguyen, A.A. Adesina, Kinetic study of methane CO₂ reforming on Co–Ni/Al₂O₃ and Ce–Co–Ni/Al₂O₃ catalysts, *Catal Today*, 164 (2011) 221-226.
- [28] R.T.K. Baker, M.A. Barber, P.S. Harris, F.S. Feates, R.J. Waite, Nucleation and growth of carbon deposits from the nickel catalyzed decomposition of acetylene, *J Catal*, 26 (1972) 51-62.
- [29] I. Alstrup, M.T. Tavares, C.A. Bernardo, O. Sørensen, J.R. Rostrup-Nielsen, Carbon formation on nickel and nickel-copper alloy catalysts, *Mater Corros*, 49 (1998) 367-372.
- [30] S. de Llobet, J.L. Pinilla, M.J. Lazaro, R. Moliner, I. Suelves, CH₄ and CO₂ partial pressures influence and deactivation study on the Catalytic Decomposition of Biogas over a Ni catalyst, *Fuel*, 111 (2013) 778-783.
- [31] H.S.A. de Sousa, A.N. da Silva, A.J.R. Castro, A. Campos, J.M. Filho, A.C. Oliveira, Mesoporous catalysts for dry reforming of methane: Correlation between structure and deactivation behaviour of Ni-containing catalysts, *Int J Hydrog Energy*, 37 (2012) 12281-12291.
- [32] J.L. Pinilla, S. de Llobet, I. Suelves, R. Utrilla, M.J. Lázaro, R. Moliner, Catalytic decomposition of methane and methane/CO₂ mixtures to produce synthesis gas and nanostructured carbonaceous material, *Fuel*, 90 (2011) 2245-2253.
- [33] N.M. Rodriguez, A review of catalytically grown carbon nanofibers, *J Mater Res*, 8 (1993) 3233-3250.
- [34] A. Chambers, T. Nemes, N.M. Rodriguez, R.T.K. Baker, Catalytic behavior of graphite nanofiber supported nickel particles. 1. Comparison with other support media, *J Phys Chem B*, 102 (1998) 2251-2258.
- [35] J.L. Pinilla, H. Purón, D. Torres, S. de Llobet, R. Moliner, I. Suelves, M. Millan, Carbon nanofibres coated with Ni decorated MoS₂ nanosheets as catalyst for vacuum residue hydroprocessing, *Appl Catal B*, 148–149 (2014) 357-365.

- [36] S.H. Yoon, C.W. Park, H. Yang, Y. Korai, I. Mochida, R.T.K. Baker, N.M. Rodriguez, Novel carbon nanofibers of high graphitization as anodic materials for lithium ion secondary batteries, *Carbon*, 42 (2004) 21-32.
- [37] I. Cameán, A.B. García, I. Suelves, J.L. Pinilla, M.J. Lázaro, R. Moliner, Graphitized carbon nanofibers for use as anodes in lithium-ion batteries: Importance of textural and structural properties, *J Power Sources*, 198 (2012) 303-307.
- [38] E. Hammel, X. Tang, M. Trampert, T. Schmitt, K. Mauthner, A. Eder, P. Pötschke, Carbon nanofibers for composite applications, *Carbon*, 42 (2004) 1153-1158.
- [39] I. Suelves, R. Utrilla, D. Torres, S. de Llobet, J.L. Pinilla, M.J. Lázaro, R. Moliner, Preparation of polymer composites using nanostructured carbon produced at large scale by catalytic decomposition of methane, *Mater Chem Phys*, 137 (2013) 859-865.
- [40] V.C.H. Kroll, H.M. Swaan, C. Mirodatos, Methane Reforming Reaction with Carbon Dioxide Over Ni/SiO₂ Catalyst: I. Deactivation Studies, *J Catal*, 161 (1996) 409-422.
- [41] A.E. Castro Luna, M.E. Iriarte, Carbon dioxide reforming of methane over a metal modified Ni-Al₂O₃ catalyst, *Appl Catal A*, 343 (2008) 10-15.
- [42] A. Serrano-Lotina, L. Daza, Long-term stability test of Ni-based catalyst in carbon dioxide reforming of methane, *Appl Catal A*, In press (2013).
- [43] S. Corthals, J. Van Noyen, J. Geboers, T. Vosch, D. Liang, X. Ke, J. Hofkens, G. Van Tendeloo, P. Jacobs, B. Sels, The beneficial effect of CO₂ in the low temperature synthesis of high quality carbon nanofibers and thin multiwalled carbon nanotubes from CH₄ over Ni catalysts, *Carbon*, 50 (2012) 372-384.
- [44] S. de Llobet, J.L. Pinilla, R. Moliner, I. Suelves, J. Arroyo, F. Moreno, M. Muñoz, C. Monné, I. Cameán, A. Ramos, N. Cuesta, A.B. Garcia, Catalytic decomposition of biogas to produce hydrogen rich fuels for SI engines and valuable nanocarbons, *Int J Hydrog Energy*, 38 (2013) 15084-15091.
- [45] D. Sebastián, I. Suelves, R. Moliner, M.J. Lázaro, The effect of the functionalization of carbon nanofibers on their electronic conductivity, *Carbon*, 48 (2010) 4421-4431.
- [46] I. Suelves, M.J. Lázaro, R. Moliner, Y. Echegoyen, J.M. Palacios, Characterization of NiAl and NiCuAl catalysts prepared by different methods for hydrogen production by thermo catalytic decomposition of methane, *Catal Today*, 116 (2006) 271-280.
- [47] Y. Li, D. Li, G. Wang, Methane decomposition to CO_x-free hydrogen and nano-carbon material on group 8–10 base metal catalysts: A review, *Catal Today*, 162 (2011) 1-48.
- [48] H.F. Abbas, W.M.A. Wan Daud, Hydrogen production by methane decomposition: A review, *Int J Hydrog Energy*, 35 (2010) 1160-1190.
- [49] C.H. Bartholomew, Carbon deposition in steam reforming and methanation, *Catalysis reviews*, 24 (1982) 67-112.
- [50] T.M. Duncan, P. Winslow, A.T. Bell, The characterization of carbonaceous species on ruthenium catalysts with ¹³C nuclear magnetic resonance spectroscopy, *J Catal*, 93 (1985) 1-22.
- [51] D.L. Trimm, Coke formation and minimisation during steam reforming reactions, *Catal Today*, 37 (1997) 233-238.
- [52] C. Wang, N. Sun, N. Zhao, W. Wei, J. Zhang, T. Zhao, Y. Sun, C. Sun, H. Liu, C.E. Snape, The Properties of Individual Carbon Residuals and Their Influence on The Deactivation of Ni–CaO–ZrO₂ Catalysts in CH₄ Dry Reforming, *ChemCatChem*, 6 (2014) 640-648.
- [53] J. Rostrup-Nielsen, D.L. Trimm, Mechanisms of carbon formation on nickel-containing catalysts, *J Catal*, 48 (1977) 155-165.

- [54] I. Alstrup, A new model explaining carbon filament growth on nickel, iron, and Ni□Cu alloy catalysts, *J Catal*, 109 (1988) 241-251.
- [55] J.W. Snoeck, G.F. Froment, M. Fowles, Filamentous Carbon Formation and Gasification: Thermodynamics, Driving Force, Nucleation, and Steady-State Growth, *J Catal*, 169 (1997) 240-249.
- [56] K.P. De Jong, J.W. Geus, Carbon Nanofibers: Catalytic Synthesis and Applications, *Catalysis Reviews*, 42 (2000) 481-510.
- [57] S.P. Gubin, Y.A. Koksharov, Preparation, Structure, and Properties of Magnetic Materials Based on Co-Containing Nanoparticles, *Inorganic Materials*, 38 (2002) 1085-1099.
- [58] V.A. De La Peña O'Shea, P.R. De la Piscina, N. Homs, G. Aromí, J.L.G. Fierro, Development of hexagonal closed-packed cobalt nanoparticles stable at high temperature, *Chem Mater*, 21 (2009) 5637-5643.
- [59] S. Takenaka, M. Serizawa, K. Otsuka, Formation of filamentous carbons over supported Fe catalysts through methane decomposition, *J Catal*, 222 (2004) 520-531.

Table 1- CH₄ sustainability factors (S.F._{CH4}) obtained in the different experiments.

	S.F._{CH4}		
	Ni/Al ₂ O ₃	Co/Al ₂ O ₃	Fe/Al ₂ O ₃
600 °C	0.90	0.44	-
700 °C	0.75	0.68	-
800 °C	0.60	0.68	0.57
900 °C	0.60	0.63	0.69

Table 2- Carbon production per gram of catalyst initially loaded (Y_c) obtained in the different experiments.

	Y_c (g_{carbon}·g_{cat}⁻¹)		
	Ni/Al ₂ O ₃	Co/Al ₂ O ₃	Fe/Al ₂ O ₃
600 °C	8.79	1.08	-
700 °C	6.84	3.66	0.00
800 °C	3.02	4.24	0.00
900 °C	2.32	2.10	3.24

Figure 1- CH₄ conversions ($X_{CH_4,5min}$) (a) and CH₄ reaction rates ($-r_{CH_4,5min}$) (b) calculated after 5 minutes TOS for the different catalysts at different reaction temperatures. $WHSV=30 L_N \cdot g_{cat}^{-1} \cdot h^{-1}$.

Figure 2- CH₄ reaction rate ($-r_{CH_4,t}$) as a function of the reaction temperature and the TOS for the a) Ni/Al₂O₃, b) Co/Al₂O₃ and c) Fe/Al₂O₃ catalysts.

Figure 3- Carbon accumulation rate ($r_{carbon,t}$) as a function of the reaction temperature and the TOS for the a) Ni/Al₂O₃, b) Co/Al₂O₃ and c) Fe/Al₂O₃ catalysts (calculated from mass balances).

Figure 4- TEM micrographs of the Ni/Al₂O₃ spent catalysts after 180 minutes TOS at 600 (a), 700 (b), 800 (c) and 900 °C (d). $WHSV=30 L_N \cdot g_{cat}^{-1} \cdot h^{-1}$.

Figure 5- TEM micrographs of the Co/Al₂O₃ spent catalysts after 180 minutes TOS at 600 (a), 700 (b), 800 (c) and 900 °C (d). $WHSV=30 L_N \cdot g_{cat}^{-1} \cdot h^{-1}$.

Figure 6- TEM micrographs of the Fe/Al₂O₃ spent catalyst after 180 minutes TOS at 900 °C. $WHSV=30 L_N \cdot g_{cat}^{-1} \cdot h^{-1}$.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6