Biogas dry reforming over Ni-Ce catalyst supported on nanofibered alumina

*J.J. González, J.F. Da Costa-Serra, A. Chica**

Instituto de Tecnología Química (Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas), Avd. de los Naranjos s/n, 46022 Valencia (Spain).

*Corresponding author. Tel.: +34 963 87 70 00-78508; fax: +34 963 87 78 09.

E-mail address: achica@itq.upv.es

Abstract

Four catalysts based on Ni and Ni-Ce supported on two γ -aluminas with different morphology (nanofibers and nanograins) have been prepared and studied in the dry reforming of simulated biogas. Catalysts were characterized by N_2 physisorption, X-ray diffraction (XRD), temperature-programmed reduction (TPR), transmission electron microscopy (TEM), scanning electron microscopy (SEM), inductively coupled plasma with optical emission spectrometer (ICP-OES), chemisorption of H_2 and elemental analysis (EA) to determine their most relevant physicochemical properties. Characterization results show that metallic Ni particles supported on nanofibered alumina (NFA) presents a higher dispersion and smaller size than that supported on the nanograined alumina (NGA) probably due to the higher mesoporosity presented by the NFA support. On the other hand, the incorporation of Ce has a similar effect than the fibrous morphology, decreasing also the size of the Ni metallic particles and increasing their dispersion. In the dry reforming of synthetic biogas ($CH_4/CO_2 = 1.5$) the nanofibered alumina containing 5 wt.% Ni and 1.5 wt.% Ce (NiCe/NFA) showed the highest catalytic activity at 750 °C (98% CO_2 conversion) and stability (7.7% nickel sinterization level and 2.9 wt.% carbon deposition). The stability of this catalyst was also demonstrated at 750 °C during 55 h of reaction time with a loss of activity at the steady state under 2%. In addition, the catalyst was regenerated at 600 °C in oxygen flow, recovering completely its initial catalytic performance. The excellent catalytic behavior of NiCe/NFA material has been related to the fibrous morphology of the alumina support, which promotes a better dispersion of the supported Ni metal particles, decreasing their size and increasing the number of active sites where dry reforming reaction can take place. In addition, the incorporation of Ce seems to have also an important role by increasing the Ni-support interactions, decreasing sinterization of the metallic Ni particles and coke deposition. The contribution of both effects (morphology and Ce), separately and in combination, have been proved to enhance significantly the catalytic activity and stability of the synthesized catalysts in the dry reforming of simulated biogas.

Keywords: Dry reforming, nanofibered alumina, nickel and cerium catalysts, H_2 production, syngas, biogas.

1. Introduction.

The interest to develop renewable fuels to alleviate important problems of our current energetic system, such as the scarcity of fossil fuels and the emission of pollutants, is in continuous growing. Renewable energy target in the European Union for 2020 is expected to achieve from bioenergy, among which at least 25% will be biogas [1]. Thus, biogas, among other renewable biofuels, represents an attractive renewable carbon source and its exploitation would be advantageous from both financial and environmental points of view. Biogas can be produced by fermentation processes or anaerobic digestion of organic waste coming from different sources such as sewage, sludge, landfill or industry [2]. It is mainly composed of CH_4 , CO_2 and minor species such as sulphur, nitrogen or water, varying the composition according to the starting substrate [2-4]. Thus, dry reforming of biogas (Eq. (1)) would be interesting processes to produce synthesis gas [5]. The high levels of CO_2 (45-75%) and CH_4 (55-75%) enable the conversion of biogas to synthesis

gas (CO and H₂, syngas) by dry reforming, avoiding the high cost of the purification process to separate CO₂ from CH₄. Thus, biogas dry reforming has recently emerged as an attractive technological solution that would eradicate the need for CO₂ removal from biogas and its release to the atmosphere. On the other hand, produced syngas is a crucial intermediate to produce hydrogen, ammonia, methanol, and synthetic hydrocarbon fuels. Thus, liquid biofuels can be produced by biogas dry reforming to produce syngas, and the subsequent Fischer-Tropsch process to produce biofuels in the selected range (gasoline, diesel or jet) [6].

Methane dry reforming is a highly endothermic reaction, which takes place at high reaction temperatures (800-1000 °C). Carbon deposition can easily occur at that high temperatures according to the Eqs. (2), (3) and (4), covering the catalyst active sites and reduces the activity of catalyst significantly [7].

An important problem related to the dry reforming reaction of methane is the coke generation, one of the main reason why this reaction has not yet been commercialized [8-11]. Catalyst nature clearly affects the coke formation rate, so current research efforts have focused on developing highly stable catalysts with low carbon production [12-16]. Among them, nickel based catalysts have attracted interest due to their lower cost and higher availability compared with noble metal catalysts, and also by its significant intrinsic activity, especially when the Ni is highly dispersed on the support [17-34]. However, as already mentioned, they suffer deactivation due to carbon formation and sinterization of metallic particles, due to a lack of adequate thermal stability [35, 36]. In addition, catalyst support has also an important role since it can help to stabilize the metallic particles through efficient interactions support-metallic particles, decreasing the coke formation and the sinterization of the metallic particles [37-39]. Together with the nature of the support, its morphology has been also reported that can modify the size and dispersion of the supported metallic particles, improving their catalytic performance via low coke formation and metal sinterization [39, 40]. On the other hand, the incorporation of metals as Ce in Ni-based catalysts has been also reported that can increase the stability during the dry reforming reaction [41-46]. Specifically, it has been reported that formation of cerium aluminate phase (CeAlO₃) enhances significantly the catalyst resistance to carbon deposition, while dry reforming activity is retained. Cerium aluminate shows ability for decomposing CO₂ to form active surface oxygen, minimizing deactivation by carbon deposition [47]. Also the presence of Ce helps to increase the metallic nickel dispersion with strong metal-support interactions, retaining the small Ni particles size and improving the stability of these particles against sintering at the same time that the growing of carbon whiskers is inhibited [48].

In this paper is showed by the first time the individual and combined effect of the morphology of the support and Ce presence in the development of Ni-based catalysts with high activity and stability in the dry reforming of methane. Ni supported on un-promoted and promoted with CeO₂ alumina catalysts have been prepared using two alumina supports with different morphology (nanograins and nanofibers). The catalysts were characterized by different techniques to know their most relevant physicochemical properties and tested at different temperatures in the dry reforming of a simulated biogas. To assess our catalyst in more realistic biogas applications, a typical range of CH₄/CO₂ of 1.5 was applied. The experimental results demonstrated that support morphology, together Ce presence, have a positive effect in the preparation of high active and stable catalysts in the dry reforming of methane by decreasing coke deposition and sinterization of supported metallic nickel significantly.

2. Experimental.

2.1. Preparation of catalyst.

Nanofibered alumina (NFA) was prepared by sol-gel method. Aluminium isopropoxide (98%, Strem Chemicals), acetic acid (99%, Sigma-Aldrich) and 2-propanol (99.5%, Fisher) were used as starting

materials for the synthesis of nanofibered alumina. Aluminium isopropoxide was dissolved in 2-propanol and Milli-Q water with continuous stirring at 80 °C for few minutes. Then, the other solution containing acetic acid and Milli-Q water was slowly added and the obtained gel was stirred at 80 °C for 20 hours under reflux. The final precipitate was filtered, washed with 2-propanol and dried at 80 °C for 12 hours. The obtained solid was calcined at 750 °C for 4 hours, to obtain the nanofibered alumina (NFA).

Nanograined alumina (NGA) was a commercial γ -Alumina provided by Strem Chemicals (γ -Alumina, 97%).

Nickel and cerium were incorporated in the nanofibered and nanograined alumina by incipient wetness impregnation method with an aqueous solution containing the required amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (supplied by Sigma Aldrich, 98.5% and 99% respectively) to obtain a nickel and cerium content of 5 wt.% and 1.5 wt.%, respectively. After impregnation, the samples were dried overnight at 100 °C and then they were calcined in a muffle furnace for 3 hours at 400 °C (Ni/NGA, NiCe/NGA, Ni/NFA and NiCe/NFA).

2.2. Characterization techniques.

The catalysts used in this study have been subjected to inductively coupled plasma with optical emission spectrometer (ICP-OES) in a Varian 700-ES Series to determine the amount of Ni and Ce incorporated.

Textural properties (BET area and pore volume) were measured using an ASAP 2420 apparatus (Micromeritics) at 77 K. Before the analysis, 200 mg of each pelletized sample (0.25-0.40 mm) were degassed at 673 K with high vacuum ($\sim 5 \times 10^{-6}$ bar) overnight. The BET surface area was calculated by using the Brunauer–Emmett–Teller equation, micropore volume was calculated by the t-plot method.

X-ray diffraction (XRD) has been carried out to identify the crystalline phases present in each catalyst. Measurements were carried out at room temperature in a Panalytical CubiX diffractometer using $\text{CuK}\alpha$ radiation. The identification of the crystalline phases has been carried out using the X'Pert HighScore Plus software.

Temperature programmed reduction (TPR) were carried out to study the reduction properties of supported nickel. Measurements were carried out in a Micromeritics Autochem 2910 equipment. Between 30 and 100 mg of sample, in the granulometry 0.25-0.40 mm were loaded in a quartz U-tube, a fixed bed between quartz wool. Samples were treated in Ar flow at room temperature for 30 minutes and then the circulating gas was replaced with 10% H_2 (vol)/Ar (50 mL/min) and the temperature was increased from room temperature to 1173 K at a rate of 10 K/min. Downstream of the reactor, a 2-propanol/ N_2 (l) trap was placed to retain the water formed in the reductions, and H_2 consumption was recorded on a thermal conductivity detector (TCD), previously calibrated using the reduction of CuO as a reference.

The amount of carbon deposited in the catalysts after reaction was determined by elemental analysis using a Carlo Erba 1106 analyzer.

The morphology of alumina support and the size of the nickel metallic particles were studied by transmission electron microscopy (TEM) using a JEOL-JEM2100F microscope.

The morphology of catalysts was also studied by scanning electron microscopy (SEM) using a JEOL-JSM6300 microscope.

The active metallic surface area (AMSA) was estimated from H_2 adsorption using the double isotherm method on a Quantachrome Autosorb-1 equipment. Prior to adsorption, the samples (ca. 0.3 g) were pre-treated in flowing He at 393 K for 1 h and then reduced in situ by flowing pure H_2 at 973 K for 3 h. After reduction, the samples were degassed and cooled to 373 K to register the adsorption isotherm.

2.3. Catalytic study.

Dry reforming of simulated biogas ($\text{CH}_4/\text{CO}_2 = 1.5$ mol/mol) was performed in a continuous fixed bed reactor at atmospheric pressure, GHSV of 1000 h^{-1} and a range of temperatures between 600 and 900 °C. Before setting up the reaction, the catalysts were reduced “in situ” in H_2 flow at 700 °C during 2 h. Afterwards, simulated biogas was fed into the reactor. The gas products were analyzed using an online gas

chromatograph Bruker 450-GC equipped with two detectors (TCD and FID) and three columns (Carbosieve S-II, Hayesep Q and Hayesep T).

CO₂ and CH₄ conversion and H₂/CO ratio were determined according to the Eqs. (5), (6) and (7), where $F_{CH_4,in}$ and $F_{CO_2,in}$ are the molar flow rate of CH₄ and CO₂ at the reactor inlet and $F_{CH_4,out}$ and $F_{CO_2,out}$ are the molar flow rate of CH₄ and CO₂ at the reactor outlet.

$$X_{CH_4} (\%, mol) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100 \quad (5)$$

$$X_{CO_2} (\%, mol) = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100 \quad (6)$$

$$\frac{H_2}{CO} \text{ ratio} = \frac{\text{moles of } H_2 \text{ produced}}{\text{moles of } CO \text{ produced}} \quad (7)$$

3. Results and discussion.

3.1. Supports and catalysts characterization.

Characterization by X-ray diffraction (XRD) has been carried out to identify the crystalline phases present in the studied catalysts. X-ray diffraction patterns of catalysts and their corresponding alumina supports are shown in Figure 1a and 1b. As it can be seen diffraction peaks corresponding to Ni or Ce phases are not detected in any of the two series of catalysts. The observed diffraction peaks can be attributed to the alumina support and they are related to the aluminum oxide [JCPDS 00-001-1303] and aluminum oxide hydrate (Bayerite o Gibbsite) [JCPDS 00-001-0287] [49, 50]. This circumstance could be explained considering that: i) diffraction peaks of Ni and Ce oxides could be hid by the wide diffraction peaks of the alumina support [51, 52], ii) a high dispersion of Ni and Ce oxides is occurring, iii) percentage of Ni and Ce is very low to detect their corresponding phases, iv) the formation of other compounds such as NiAl₂O₄ and CeAlO₃ could be occurring, however these compounds present diffraction peaks at similar angles to those presented by alumina support, being very difficult to detect them when they are present in a low concentrations [53].

Figure 1. XRD of the different catalysts studied in this work. a) XRD of calcined Ni/NGA and NiCe/NGA catalysts and their corresponding NGA support. b) XRD of calcined Ni/NFA and NiCe/NFA catalysts and their corresponding NFA support.

The morphology of the alumina supports and their corresponding catalysts with Ni and NiCe has been also investigated by SEM (Figure 2) and TEM (Figure 3). As it can be seen in Figure 2 the NFA support has a

more frayed appearance compared to NGA, due to its nanofibrated morphology. In general, the addition of Ni and NiCe to the supports and the subsequent calcination do not produce drastic changes in the appearance of the final catalysts, keeping the nanograined and nanofibered morphologies similar to the original aluminas.

Figure 2. SEM images of calcined catalysts and their corresponding supports.

TEM images of calcined catalysts and their corresponding supports are showed in Figure 3. Now, the morphology differences between nanograined and nanofibered alumina result more evident. Specifically, the NFA support is formed clearly by nanofibers while the NGA present “nanograins”. It can be seen also that the incorporation of Ni and Ce does not vary in excess the TEM images for any of the catalysts as it was already found in the studies by SEM.

Figure 3. TEM images of calcined catalysts and their corresponding supports.

BET surface area, pore volume and metal content (Ce and Ni) for the studied catalysts are showed in Table 1. As it can be seen levels of Ni between 5 and 6 wt.% has been determined for all the catalysts and 1.5 wt.% of Ce for the samples containing this metal. In relation to the textural properties, a decreasing of BET surface area and pore volume can be observed when Ni and Ce are incorporated in the alumina supports.

This fact could be explained considering a partial blockage of the alumina micropores by the nanoparticles of NiO and CeO₂ formed during the calcination step [54-62]. In general, not significantly differences in the BET surface area is found for the four catalysts here studied.

Table 1. Ni and Ce content, BET surface area and pore volume for the catalysts studied in this work.

Sample	BET surface area (m ² /g)	Pore vol. (m ³ /g)	Ni, wt. %	Ce, wt. %
NGA	278	0.477	-	-
NFA	248	0.501	-	-
Ni/NGA	254	0.381	5.9	-
NiCe/NGA	242	0.373	5.8	1.4
Ni/NFA	234	0.488	5.2	-
NiCe/NFA	226	0.483	5.0	1.5

Figure 4 shows adsorption/desorption isotherms and pore diameter distributions of the alumina supports studied in this work. NFA support shows an adsorption/desorption isotherm typical of a mesoporous material and also a higher average pore diameter compared to NGA support.

Figure 4. a) Adsorption/Desorption isotherms and b) pore diameters of the NGA and NFA supports.

Characterization of the reduced catalysts was also carried out. The XRD of the reduced catalysts is showed in Figure 5. Previously, XRD of the calcined catalysts showed only diffraction peaks corresponding to the alumina support, Figure 1. Now, together with the aluminum oxide phase [JCPDS 00-001-1303], corresponding to the alumina support, diffraction peaks corresponding to metallic nickel [JCPDS 03-065-0380] can also be found.

Figure 5. XRD of the different catalysts studied in this work. a) XRD of reduced Ni/NGA and NiCe/NGA catalysts and their corresponding NGA support. b) XRD of reduced Ni/NFA and NiCe/NFA catalysts and their corresponding NFA support.

The crystalline size of metallic nickel (Ni^0) has been determined from the XRD of the reduced catalysts, using the Scherrer equation [63]. As it can be seen in Table 2, when samples containing only Ni are compared (Ni/NGA and Ni/NFA), the metallic nickel supported on NFA (Ni/NFA) presents a smaller crystallite size than that supported on NGA (Ni/NGA) (5.4 and 7.7 nm, respectively). This result seems to indicate that the nanofibered morphology would having a positive effect promoting the formation of Ni^0 with smaller size. In the case of the Ce, if the samples with and without Ce for the same alumina support are compared (Ni/NGA-NiCe/NGA and Ni/NFA-NiCe/NFA), it can be seen a similar effect than those found for the morphology, that is, the smallest size of Ni^0 is found for the samples containing Ce. Finally, it can be seen that the smallest crystallite sizes correspond to the sample containing Ni and Ce supported on nanofibered alumina (NiCe/NFA, 3.9 nm), where the effects of the morphology and Ce concurrent simultaneously.

Crystallite size of metallic nickel has been also determined by TEM. Figure 6 shows the TEM images of the reduced catalysts. Distribution frequencies of sizes have been also determined for each catalyst. As it can be seen, the same trend than those determined by XRD was found. Again, the smallest sizes were found for the sample containing Ni and Ce supported on nanofibered alumina.

Figure 6. TEM images of reduced catalysts and their corresponding particle size distribution of metallic Ni.

Active metal surface area (AMSA) and dispersion of the metallic Ni particles have been also determined by H_2 -Chemisorption, Table 2. Comparing the catalysts containing only Ni (Ni/NGA and Ni/NFA), it can be seen that catalyst prepared with NFA presents a larger active metal surface area, suggesting again that the nanofibered morphology could be promoting an improvement of the metallic nickel distribution and its accessibility. It is possible that the mesoporosity presented by the NFA support favor the diffusion of the metallic precursors during the impregnation step, improving the dispersion of the Ni and Ce in the final catalyst and explaining the lower size of the metallic particles detected in this support. On the other hand, the incorporation of Ce leads to an additional increasing in the active metal surface area, confirming the observation already reported in literature [48].

Table 2. Size of the metallic nickel particles determined by XRD and TEM, active metal surface area (AMSA) and metal dispersion determined by H₂-Chemisorption and reducibility determined by TPR.

Sample	Ni ⁰ , XRD (nm)	Ni ⁰ , TEM (nm)	AMSA (m ² /g)	Dispersion %	Reducibility %, (700°C)
Ni/NGA	7.7	7.9	1.64	4.9	84
NiCe/NGA	7.3	6.5	1.79	5.4	81
Ni/NFA	5.4	4.3	2.50	7.5	73
NiCe/NFA	3.9	3.2	2.70	8.1	58

The reducibility of the catalysts has been also studied by temperature programmed reduction (TPR). TPR profile for each catalyst is shown in Figure 7. In general, three large reduction peaks can be delimited in the reduction profiles for all catalysts. The first reduction peak appears at low reduction temperatures (100-400 °C). This peak would correspond to the reduction of nickel with slight interaction with the support (bulk NiO without interaction with the alumina support or with a weak interaction) [64-68]. The second reduction peak appears at intermediates reduction temperatures (400-700 °C) and would correspond to the reduction of nickel with a higher interaction with the alumina support. It would be related with mixtures of Ni and Al oxides with high content in nickel [64-68]. Finally, the third peak appears at the higher reduction temperatures (700-900 °C). This peak would correspond with the reduction of nickel with high interaction with the alumina support and would be related with the reduction of nickel aluminate species, NiAl₂O₄ [64-68]. As it can be seen, the sample NiCe/NFA present a TPR profile shifted a high reduction temperatures, suggesting a larger interaction of Ni with the nanofibered alumina support and justifying the lower size of the metallic nickel particles determined by XRD and TEM for this sample.

Table 2 also shows the percentages of reduced nickel present in the catalysts at 700 °C. This data has been obtained from the TPR profiles. The selection of this temperature to calculate the reducibility is because this is the temperature at which the reduction pretreatment is carried out before the catalytic tests. As it was to be expected, from the high interaction Ni-support, the NiCe/NFA sample presented the lowest percentage of reduced nickel.

Figure 7. TPR of calcined catalysts studied in this work.

3.2. Catalytic activity.

Catalytic tests have been carried out using a synthetic biogas containing a CH_4/CO_2 ratio of 1.5. Figure 8 shows the CO_2 and CH_4 conversion values obtained for the four synthesized catalysts in the dry reforming of biogas. Thermodynamic data for CO_2 and CH_4 conversion is also shown in this figure with black dashed lines [69]. When the samples containing only Ni are compared (Ni/NGA and Ni/NFA) it can be seen that the catalyst based on nanofibered alumina (Ni/NFA) exhibits a better catalytic activity with higher conversion values for CO_2 and CH_4 , especially at low reaction temperatures (600-700 °C). These results are in concordance with lower size of the metallic nickel particles present in this sample and with its higher active metal surface area determined by H_2 -Chemisorption. The nanofibered morphology of the alumina support could be considered the final responsible of the higher catalytic activity exhibited by this sample Ni/NFA because its particular morphology would be promoting the formation of metallic nickel particles of lower size and larger active metal surface area. When the samples with and without Ce are compared (Ni/NGA-NiCe/NGA and Ni/NFA-NiCe/NFA) an improvement in the catalytic activity is observed for the samples containing Ce. The Ce presence seems to have a similar effect than that observed for the nanofibered morphology, favoring the dispersion of metallic Ni and allowing the formation of smaller metallic particles, what would justify the observed improvement in the catalytic performance [42]. Finally, it is important to note that the sample containing Ni-Ce supported on nanofibered alumina (NiCe/NFA) presents the highest catalytic activity, which can be explained by the combination of the positive effects of nanofibered morphology and presence of Ce. Thus, combined effect dues to morphology and Ce presence seem to be critical in the preparation of dry reforming catalysts with improved catalytic activity and this effect seem to be higher than the effect that the morphology and Ce show separately.

Figure 8. Variation of the CO_2 (a) and CH_4 (b) conversions with reaction temperature for the catalysts studied in this work. Reaction conditions: $\text{CH}_4/\text{CO}_2 = 1.5$, GHSV = 1000 h^{-1} and atmospheric pressure. Black dashed lines correspond to the thermodynamic equilibrium [69].

H_2 and CO were the only obtained products in the dry reforming reaction. The H_2/CO molar ratio versus temperature reaction is shown in Figure 9. This ratio increases with the reaction temperature, achieving values of 1 at high reaction temperatures, when the CO_2 conversion is completed. Similar H_2/CO molar ratios were found for all the catalysts, indicating that the nanofibered morphology or the presence of Ce have not a relevant effect on the catalytic selectivity, at least at the reactions conditions here studied.

Figure 9. Variation of the H_2/CO ratio with the reaction temperature for the catalysts studied in this work. Reaction conditions: $CH_4/CO_2 = 1.5$, GHSV = 1000 h^{-1} and atmospheric pressure.

3.3. Catalytic deactivation.

As it was mentioned in the introduction part deactivation is one of the most important problem of the dry reforming catalysts. In order to know the modification of the catalysts here studied during the dry reforming reaction they were characterized after reaction by XRD and elemental analysis. X-ray diffraction pattern of used catalysts is shown in Figure 10. As it can be seen the spent catalysts present the same phases than those observed before reaction: aluminum oxide [JCPDS 00-001-1303] and metallic nickel [JCPDS 03-065-0380]. Nevertheless, one more phase at $2\theta = 26.347^\circ$ is observed, which corresponds to deposited carbon [JCPDS 00-001-0640]. This fact indicates that during the reaction coke is being deposited in the catalysts, which would indicate that deactivation is occurring. The amount of coke in used catalysts has been determined by elemental analysis (Table 3). As it can be seen a decreasing of the deposited coke were observed when nanofibered alumina is used as support or when Ce is present. Again, the morphology of the support and the presence of Ce seems to have separately a positive influence. However, the combination of both effects seem to entail the largest difference, being the lowest amounts of coke produced by the catalyst with Ni and Ce supported on nanofibered alumina.

Figure 10. XRD of the used catalyst studied in the dry reforming of simulated biogas. a) XRD of used Ni/NGA, NiCe/NGA and their corresponding NGA support. b) XRD of used Ni/NFA, NiCe/NFA and their NFA support

Together with deposition of coke the sinterization of metallic particles is another important parameter affecting the deactivation of dry reforming catalysts. Table 3 shows the size of the metallic nickel particles before and after reaction determined by XRD and the level of sinterization. As it can be seen all the catalysts suffer sinterization during reaction. However, sinterization occurs in a shorter extension in the samples containing Ce. As it has been already reported in literature the incorporation of Ce favors the dispersion of Ni catalysts with strong metal-support interactions and allows the retention of small Ni particle size, improving the stability of the metallic particles against sintering and inhibits the carbon formation [42]. Similar effect is detected for the nanofibered morphology since a decreasing in the sinterization level is also observed.

Table 3. Crystallite size of metallic nickel particles determined by XRD in the fresh and spent catalysts, percentage of sinterization and C deposition after reaction for the catalysts studied in this work.

Sample	Ni ⁰ , XRD _{AR} (nm)	Ni ⁰ , XRD _{BR} (nm)	Sintering % ⁽¹⁾	C deposition, wt. %
Ni/NGA	10.4	7.7	35.0	10.1
NiCe/NGA	9.1	7.3	24.6	8.7
Ni/NFA	6.2	5.5	12.7	7.2
NiCe/NFA	4.3	3.9	10.2	2.9

⁽¹⁾ Sinterization level was calculated as follows: $\{[\text{size after reaction (XRD}_{AR}) - \text{size before reaction (XRD}_{BR})] / \text{size before reaction (XRD}_{BR})\} * 100$

The contribution of the morphology and Ce addition to sintering and coke deposition has been studied in deeper. Table 4 shows the contribution of each effect expressed as percentages. In one intent to quantify contribution of the morphology, catalysts containing the same metals have been compared. Thus, catalysts containing only Ni have been compared by one hand (Ni/NGA and Ni/NFA) and by the other the catalysts containing Ni-Ce (NiCe/NGA and NiCe/NFA). To determine the Ce contribution the catalysts prepared with NGA support was compared by one hand (Ni/NGA and NiCe/NGA) and by other the catalysts prepared with NFA (Ni/NFA and NiCe/NFA). Comparing these pairs of catalysts, the morphology and Ce contributions can be determined separately. Finally, the combined contribution of both, morphology and Ce, has been determined comparing the samples Ni/NGA and NiCe/NFA.

As it can be seen in Table 3 the major contributor to avoid the sinterization of the metallic nickel particles and coke deposition is clearly the morphology. Nevertheless, for carbon deposition the differences between morphology and Ce are lower, specifically for the catalyst prepared with NFA, where the Ce contribution is close to the morphology contribution (59.7 % and 66.7 %, respectively). Thus, it is clear that nanofibered morphology is a strong contributor in the preparation of alumina-based catalysts with improved stability against sinterization and carbon deposition. On the other hand, the major contribution of the Ce seems to be more related to the coke deposition, which was clearly lower when Ce is supported on nanofibered alumina. Finally, when the combined contribution is considered it can be seen it is very similar for both, morphology and Ce presence. However, the obtained values cannot be explained by the single addition of the individual contribution, suggesting that the combination of both effects would need a more detailed study.

Table 4. Morphology and Ce contributions for sintering and carbon deposition. Percentage of individual and combined contributions.

Sample	Sintering, % ^(a)			C deposition, wt.% ^(b)		
	Support effect	Ce effect	Combined effect	Support effect	Ce effect	Combined effect
Ni/NGA	-	-	-	-	-	-
NiCe/NGA	-	29.7	-	-	13.9	-
Ni/NFA	-	-	-	-	-	-
NiCe/NFA	-	19.7	-	-	59.7	-
Ni/NGA	-	-	-	-	-	-
Ni/NFA	63.7	-	-	28.7	-	-
NiCe/NGA	-	-	-	-	-	-
NiCe/NFA	58.5	-	-	66.7	-	-
Ni/NGA	-	-	-	-	-	-
NiCe/NFA	-	-	70.9	-	-	71.3

The values of these table have been calculated from data of Table 3 as follow:

^(a) Sintering: {[Sintering % of first catalyst–sintering % of second catalyst] /sintering % of first catalyst} * 100

^(b) C deposition: {[C deposition on first catalyst– C deposition on second catalyst] / C deposition on first catalyst} * 100

3.4. Catalytic stability test.

From the before studies, it has been found that NiCe/NFA catalyst exhibits the highest catalytic activity with the lowest metal sintering and carbon deposition. It has been seen that this sample combines the positive effects of the nanofibered morphology of alumina support and the presence of Ce. Thus, it is an excellent candidate for long-term stability tests as previous step for its scaled up and industrial application. Stability test has been carried out at 750 °C, CH₄:CO₂ = 55:45 and GHSV = 1000 h⁻¹. Figure 11 shows the CO₂ and CH₄ conversion and H₂ and CO selectivity values with reaction time for the dry reforming of simulated biogas. As it can be seen the conversion values fall down very fast in the first 20 hours (from 95% to 87% for CO₂). Later a very low deactivation is detected with a loss of activity under 2% during the following 35 hours.

Regeneration of the catalyst was also carried out after 55 hours of reaction time in air at 600 °C for 2 h. As it can be seen in Figure 11 the initial catalytic activity is completely recovered, detecting now a lower initial rate of deactivation and, in general, a lower deactivation rate during the following 45 hours. The results obtained in the catalytic stability test, together with the regeneration test, suggest that this catalytic material, based on nanofibered alumina promoted with Ni and Ce (NiCe/NFA), presents an excellent stability with reaction time and after regeneration step, offering a high potential to be scaled up and applied at industrial level.

Figure 11. CO₂ and CH₄ conversion and H₂ and CO selectivity values with the reaction time for the dry reforming of simulated biogas using the NiCe/NFA catalyst. Reaction conditions: 750 °C, CH₄:CO₂ = 55:45 (mol/mol) and GHSV = 1000 h⁻¹.

According to the results presented in this study the excellent catalytic performance exhibited by the NiCe/NFA sample seem to be related to combined effect of the nanofibered morphology of the alumina support and the presence of Ce, which allow the preparation of a nickel-based catalyst with smaller metallic Ni particles and with higher resistance against sinterization and coke deposition.

4. Conclusions.

Catalysts based on nanograined (NGA) and nanofibered γ -alumina (NFA) support promoted with Ni and Ni-Ce has been prepared with high catalytic activity and stability in the dry reforming of synthetic biogas. For the first time, the separated and combined effects of the support morphology and Ce presence in Ni-based alumina catalysts have been studied in the dry reforming of methane. It has been shown that the alumina morphology has an important influence in the preparation of alumina-based catalysts with high catalytic activity. The morphology effect seem to be related to the mesoporosity and higher pore diameter presented by the nanofibered alumina, which would be improving the diffusion of the nickel and cerium precursors during the impregnation step, favoring the dispersion of the metallic particles and the formation of particles of smaller size. On the other hand, the presence of Ce has been proved that has similar effects. However, when morphology and Ce effects are studied separately in the sinterization of the Ni metallic particles and coke deposition, it has been seen that morphology has a larger influence than Ce, decreasing in a higher extension sinterization and carbon formation. The presence of Ce only has a similar effect than morphology in the coke deposition, when Ce is supported on nanofibered alumina. When morphology and Ce effects are combined an additive effect is not clearly found. Thus, more detailed studies are needed for a better understanding and explanation of this behavior. The best catalytic results were obtained with the NiCe/NFA catalyst. Thus, a stability study with reaction time was carried out, finding a low rate of deactivation during the steady state after 55 hours of reaction time (< 2%). It was also found that the initial catalytic activity can be completely recovered after a regeneration in air at 600 °C. The results here shown suggest that the catalytic material based on nanofibered alumina promoted with Ni and Ce (NiCe/NFA) presents an excellent potential to be scaled up and applied at industrial level.

Acknowledgements

Thank you to the Spanish Government (Project RTI2018-102161-I00) and Generalitat Valenciana (PROMETEO/2018/006 grant) for the financial support. The support of the microscopy service at Universitat Politècnica de València (UPV) for the SEM and TEM analysis is also recognized.

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