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Influence of feed rate and testing variables for low-temperature tri-reforming of methane on the Ni@MWCNT/Ce catalyst

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ABSTRACT

This work proposes the synthesis of the Ni@MWCNT/Ce catalyst and evaluation the influence of feed rate and testing variables on the tri-reforming of methane. Morphology and incorporation of the nanoparticles in carbon nanotubes were investigated by X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM), specific surface area (BET), thermogravimetric analyses (TGA) and Raman spectroscopy. The 5%Ni@MWCNT/5%Ce catalyst was initially tested at 700°C for 44 h and remained stable throughout the test period. The catalyst was evaluated for the tri-reforming of methane, varying temperatures, space velocities, and feed rate concentrations of water and oxygen, using experimental design. The highest CH4 conversions were obtained for similar feed condition (CH4:CO2:H2O:O2:N2) (1:0.34:0.23:0.5:2.1) but for different space velocities and temperatures. Experiment C25 presented 91% conversion of CH4 and 30.8% of CO2 with a H2/CO = 1.88 at 700 °C and space velocity of 2000 ml/g.min. However, the highest conversions (96.8% CH4, 38.7% of CO2 and the ratio H2/CO = 1.88) were obtained for a higher temperature (750°C) and lower space velocity 1250 ml/g.min, which indicates influence of residence time and kinetics. Raman spectra evidenced clearly total absence of coke formation. The CNT support was decomposed or burnt during the reaction resulting in unsupported oxides and nickel metallic particles well dispersed or deposited over residual carbon or growth filaments.

1. Introduction

The synthesis gas is a combination (H2 and CO) of great interest in the production of liquid fuels, methanol or dimethyl ether, through a well-known reaction, such as Fischer-Tropsch synthesis. One of the factors that determine the syngas application is the H2/CO ratio. Budzianowski [1] reported a review based energy consumption, which can be suitable for maximum CO2 removal and low costs.***
The methane tri-reforming reaction used in this work is a synergistic combination of three catalytic processes: methane steam reforming (H₂O + CH₄ → CO + 3H₂ (ΔH° = 206.3 kJ mol⁻¹)), methane partial oxidation (CH₄ + 1/2O₂ → CO + 2H₂ (ΔH° = -35.6 kJ mol⁻¹)) and methane dry reform (CO₂ + CH₄ → 2CO + 2H₂ (ΔH° = 247.3 kJ mol⁻¹)). The combination of dry and steam reforming together with the partial oxidation reaction can greatly reduce the formation of carbon that occurs in large quantities in the dry reforming. The combination of steam and dry reforming together with the partial oxidation reaction can greatly reduce the formation of carbon on the catalyst during the process and increase its activity. In this way, the tri-reforming process solves two important problems, since the addition of O₂ in the reaction generates heat in situ that can be used to increase energy efficiency.

Literature about tri-reforming was first reviewed by Song et al. [2]. Complete reviews for different processes for methane conversion have been published recently by Świrsk et al. [3], Ghoneim et al. [4] and in particular we searched catalysts suitable for the reforming of flue gas rich in CO₂ and related processes. First, we discussed the relevant metal oxides catalysts and the effect of the supports for methane tri-reforming as well as combined or separated reforming processes for syngas production, including thermodynamics of the process, the possible conversions of methane and carbon dioxide for the tri-reforming and the single processes (SMR, DMR and POM). Methane cracking at high temperatures tends to generate carbon. The reduction of CO to carbon and its reverse reaction of coke oxidation by H₂O are temperature dependent, and thermodynamics favors the reverse reaction at lower reaction temperatures. Hernandez B. et al [5] reported the optimization for the production of syngas from biogas by tri-reforming process for the FT reaction and estimated the production costs for a plant of biogas.

Nickel based catalysts are widely used in industrial applications. These catalysts should be resistant to sintering, thermally stable, resistant to coke formation and possess active sites capable of converting CO₂ and CH₄ efficiently in the presence of steam and oxygen. They can be produced at low costs and the ingredients are widely available, making the tri-reforming process feasible and economically viable. The most important research in recent literature concerning Ni based catalysts for tri-reforming (TRM) are reported in a previous publication [6].

In the tri-reforming of methane (TRM), synthesis gas can be produced with desired H₂/CO ratio just varying the feed conditions [7]. Majewski et al. [8] studied specifically the influence of the feedstock composition and temperature for the methane tri-reforming process using nickel-silica core@shell catalyst. For the 11%Ni@SiO₂ catalyst and different feed compositions, the conversions, and in particular the coke deposition varied significantly after 4 h. Pino et al. [9] studied the La- Ce-O-NiO mixed oxide, with different compositions (CeₓLaₓ₃Ni₃Oₓ−₂₈, x = 0.1; 0.2 and 0.25) and the influence of O₂/CH₄, CH₄/CO₂ molar ratios on the reaction at 800 °C and 1 atm. No carbon deposition was detected after 150 h of reaction.

In fact, ceria is a material known for its high oxygen storage/transport capacity (OSC), i.e., its ability to release oxygen in low oxygen environments and rapid re-oxidation in oxygen rich environments. In addition, it is known from various studies that the presence of ceria promotes oxidation reactions, such as CO oxidation, water–gas shift, and steam reforming of methane [10-12]. Garcia-Vargas et al. [13] showed this effect with the β-silicon support and with CeO₂ supports exhibiting high catalytic activity, without significant deactivation rates. Amjad et al. [14] prepared a 1% Pt/CoO₂ catalyst by combustion method and tested the methane steam reforming reaction. The catalyst presented near-equilibrium CH₄ conversion and high H₂ formation (75% dry basis, N₂-free) for a S/C = 2.8 and for GHSV = 24 000 h⁻¹. The catalyst was tested for different cycles of start up and shut down for 150 h with TOS and after reaction analyzed by different techniques. However, coke deposition and sintering continue to be major challenges for methane tri-reforming, indicating the need, as key research priority, to develop new materials that are resistant to carbon formation and sintering.

The carbon nanotubes (CNT) have special properties, structure and topology. Basically the nanotube structure is covalent C–C bonds, formed in layers of graphite. Nanostructured materials, such as, carbon nanotubes, carbon nanofibers and carbon spheres have also been proposed for methane reforming. These carbon nanostructures have high surface area, uniform pore size distribution and resistance to high temperatures [15].

Multi-walled nanotubes (MWCNT) have been studied for greatly minimizing the limitations imposed by mass transfer as observed, for example, in activated carbon. Additionally, control of particle size and possible modification of the electronic properties of the particles inserted inside the tubes also awakened interest. In general, the results obtained with the application of carbon nanotubes as a support, particularly for metal particles, show that to achieve a good dispersion of the particles it is necessary to activate or functionalize the support surface in order to create anchoring sites into the active phase, providing better dispersion of the metal particles [15].

In a recent publication [16], a different model for selective mode of metal addition in and outside the CNT (Fe@MWCNT/Metal, (Metal = Cu and/or Co)) catalysts was studied and tested for methane tri-reforming. After testing the stability, the spent catalyst was investigated for explaining the real state of the catalyst and why it worked so well in this reaction.

The main goal of this work is to investigate a Ni–Ce catalyst on multi-walled carbon nanotubes (MWCNT) for tri-reforming of methane at different temperatures (700–750°C), however, using different feed mixtures (CH₄: CO₂: O₂: He: H₂O) and two weight hourly space velocities (WHSV). Moreover, the selective mode of metal addition in and outside the CNT (Ni@MWCNT/Ce) catalysts is also studied and the real state of the catalyst post-reaction is searched, using different specific techniques. For testing, planning experimental design is used.

2. Materials and methods

2.1. Functionalization of carbon nanotubes

MWCNT, measuring 9.5 nm inside diameter and 1.5 mm length were purchased from Sigma-Aldrich (Number: 412988). The functionalization of carbon nanotubes was performed according to the method outlined by Tessonier et al. [17]. Commercial MWCNT was consequently dispersed in a 65% nitric acid solution. The mixture was then heated from room temperature up to 100°C for 16 h and cooled down. The suspension was subsequently washed extensively with distilled water until achieving the pH of the solution about 6–7 and filtered under vacuum (removing all liquid). The solid layer deposited on the filter was finally kept in the desiccator for the next step of impregnation.

2.1.1. Synthesis of Ni and Ce nanocomposites supported on carbon nanotubes

The catalysts were prepared by impregnation for 5 wt% Ni inside and 5 wt% Ce outside the functionalized MWCNT. First, a nickel nitrate solution was prepared, using small amounts of ethanol and deionized water. The obtained paste was dried overnight (12 h) at 50°C and calcined at 350°C for 2 h under air flow at 100 ml.min⁻¹ and then reduced at 400°C for 2 h under the H₂ flow at 100 ml.min⁻¹. Secondly, 2 ml of ethylene glycol was added to the sample. Then, cerium nitrate solution was prepared, using ethanol and added in small amounts to fill the pores and dispersed in deionized water. The paste obtained was dried overnight (12 h) at 50°C and calcined at 350°C for 2 h under air flow at 100 ml.min⁻¹, and then again reduced at 400°C for 2 h under H₂ flow at 100 ml.min⁻¹. The catalyst was denoted as Ni@MWCNT/Ce.
2.2. Catalyst characterization

The specific surface area of the functionalized carbon nanotubes was determined using nitrogen physisorption at −196°C in the NOVA 1200 equipment (Surface Area & Pore Size Analyzer) of Quantachrome Instruments. Prior to the physisorption analysis the materials were pretreated under vacuum at 200 °C for 17 h. The specific surface area was determined using the BET methodology.

Transmission Electronic Microscopy (TEM) analyzes were performed in a JEOL JEM 2100 Microscope, with maximum acceleration voltage 200 kV, and resolution of 0.23 nm at the point and 0.14 nm on the network, with maximum magnification of 1,500,000 times.

X-ray diffraction (XRD) analyzes were performed in a Rigaku equipment with acquisition in the radiation incidence angle range of 2° < 2θ < 90°. Identification phases in the sample were obtained using the PDF (Powder Diffraction File - PDF2-2003) datasheets as database through the Search-Match program, comparing to their positions in the experimental data.

The Raman spectra were acquired in the range of 100–3500 cm−1 with a Renishaw inVia confocal Raman microscope in backscattering geometry equipped with a CCD detector (−70°C) and HeNe laser supplying the photon at 532 nm. The laser excitation power was kept below 10 mW on the sample surface to minimize the local heating. The total acquisition time was 300 s. All the spectra of the samples after reaction were recorded under identical conditions at room temperature.

Thermal analyses of the samples before and after reaction were performed on a DTG-60H Shimadzu with a TG-DTG simultaneous analyses accessory. The measurements were conducted under flow of nitrogen/oxygen mixture (55 ml/min N2/8 ml/min O2) from 25 to 1000 °C at a heating rate of 10 °C/min.

The samples were also analyzed by scanning electron microscopy (SEM) with field emission. Analyses were performed on a microscope JEOL JSM-7401F, whose maximum operating voltage is 30 kV and nominal resolution of 1.5 nm. The main tension for most analyzes was 20 kV and the images were generated by a detector of secondary electrons and acquired in magnifications ranging from 500 to 800,000 times. The sample in its powder form was placed on a sample holder, using double-sided adhesive tape for fixing carbon.

2.3. Activity tests

The tests were performed in a Microactivity-Effi (PID company) with a Hastelloy X tubular reactor of 9.1 mm diameter and length of 370 mm at atmospheric pressure, varying the temperature range and feed conditions. The feed flows downwards through the catalytic bed and a condenser before running the test. The temperature was measured with a thermocouple and a PID controller. The mass was 100 mg of catalyst in all experiments. Prior, the catalyst was reduced in-situ with pure H2 flow (99.999%, Air Products) for 120 min, at 10°C.min−1 up to 450°C. After purging with N2 flow, the gas was switched to the feed mixture (CH4: CO2: O2: N2 H2O). Water was added in the feed gas nitrogen/oxygen mixture (55 ml/min N2/8 ml/min O2) from 25 to 1000 °C at a heating rate of 10 °C/min.

The micrographs show that the particles were well dispersed, and it was possible to calculate average sizes of the particles positioned inside and outside the carbon nanotubes, using Fig. 2 (c) and the software Image J. It was also possible to calculate average external (18 nm) and internal (11 nm) diameter of the carbon nanotubes, as well as the number of layers, approximately 10 layers.

Table 1 shows the TEM micrographs that also confirm particle sizes, which are comparable to the particle sizes obtained by XRD.

The EDX spectra of individual regions (a) and (b) of the catalyst are shown in Fig. 2f, indicating the presence of cerium, nickel and carbon. Region (b) shows higher concentration of cerium particles dispersed over the carbon nanotubes and region (a) shows higher concentration of nickel particles appearing inside the carbon nanotubes.

3.2. Transmission electron microscopy (TEM)

TEM images show the presence of metals in the oxide form inserted or deposited on the carbon nanotube. Fig. 2 shows pure carbon nanotubes (a and b) and Ni nanoparticles inside the cavity of the MWCNT and decorated with Ce nanoparticles outside (c-f).

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3.3. X-ray analyses (XRD)

Fig. 3 shows the X-ray diffractograms of the functionalized carbon nanotubes and with Ni inside and Ce outside the carbon walls. The diffractograms present diffraction peaks referring to the diffraction pattern of the carbon nanotube. The peak at 26.2° and 44.8° are assigned to CNTs, which correspond to graphite layers of multi-walled carbon nanotubes. This indicates that, after treatment with acid and calcination at high temperature, the graphitic structure is still present, in agreement with Saleh[18]. In addition, the X-ray pattern provided information about the carbon nanotube purity, which allowed inferring the creation of defects caused by the oxidative treatment.

In fact, Peng et al. [19] showed a direct relationship between the ratio of peak intensities (100) and (002), I100/I002, and the increasing defects on carbon nanotubes. In the samples analyzed in Fig. 3, it is observed that the peak (002) is more intense than the peak (100), which illustrates that CNTs produced are made up of graphite and are crystalline. The peak arises due to the inter-layer stacking of graphene sheets [20]. Thus, this crystal in XRD pattern of the samples designates the presence of concentric cylindrical graphene sheets (multi-walled structure) nested together.

In the carbon nanotube impregnated with Ni and Ce nanoparticles, the presence of nickel oxide (NiO) is observed at angles 44.3° and 78.1°, which correspond to the positions (200) and (311) of the nickel crystallographic plane. The diffraction peaks at 28.5°, 33.1° and 47.5° are attributed to the (111), (200) and (220) reflections of face-centered cubic lattice structure of CeO2. Finally, the peak at 56.3° corresponds to the position (311) of the Ce2O3 plane. This behavior was also observed by Ma et al. [15] for Ni loaded inside or outside CNTs, having (111) and (200) crystallographic planes of Ni, respectively.

Crystallite sizes were calculated from the diffractionogram, using Scherrer's equation and the width at half height of the greater intensity peak for each oxide or metal present in the catalyst. Table 2 shows the average crystallite sizes of the oxides or metals present in the catalyst [19]. The results show small crystallite sizes of NiO, CeO2 and Ce2O3 with homogeneous distribution in and out the carbon nanotubes, in agreement with the TEM images.
3.4. Thermogravimetric analyses (TGA)

The thermogravimetric analyses (TGA) and their derivate (DTG) profiles of the bimetallic Ni@MWCNT/Ce catalysts, supported on MWCNTs, are shown in Fig. 4, presenting the weight loss of the pure carbon nanotube (MWCNT) and of the catalyst (Ni@MWCNT/Ce).

The TGA analysis shows three regions: the first one presents a weight loss of approximately 60% at a maximum temperature of 515°C, which is assigned to the decomposition of COOH groups; the second one shows one shoulder and 30% weight loss at 524°C, which suggests defects along the wall of the nanotube and a third one, with lower intensity, indicates 10% weight loss at 584°C (MWCNT) and 590°C (Ni@MWCNT/Ce), indicating decarboxylation. Based on reported results of Saleh et al[18] that studied the effect of HNO3 and other acids on the MWCNT under similar conditions by FTIR, observed the carbonyl and carboxylic groups around. Thus, we can assume that the decarboxylation occurred during the TGA experiments, as indicated in the DTA profile in Fig. 4. The results show that there is loss of mass at 514 and 530°C, which represents the decomposition of these carboxylic groups. These results reveal also almost total mass loss (the formation of carbon exhibits 14 wt% loss and is therefore a pure material). In addition, the temperature of maximum mass loss of the pure carbon nanotube sample was 550°C, in agreement with reported values for multiwalled nanotubes[21].

3.5. Raman

Raman spectroscopy was carried out to analyze the change in electronic structure due to C–C bonds and defects. Fig. 5 shows the Raman spectroscopic results of the carboxylic acid functionalized carbon nanotube and of the catalyst Ni@MWCNT/Ce. Fig. 5 show that the MWCNT doesn’t present the signal relative to the SWNT between 100 and 300 cm$^{-1}$. However, for the catalyst (dark line) Ce appears at 760 cm$^{-1}$ and a little shoulder around 400–500 cm$^{-1}$, confirming the presence of CeO$_2$. However, it is noteworthy that for the catalyst appeared the band in the range of 100–300 cm$^{-1}$, which suggest that after insertion of the metal oxide appeared SWNT.

Noteworthstand are of the two bands at 1310 cm$^{-1}$ and 1630 cm$^{-1}$. The degree of graphitization of the sample was obtained from the ratio between the D and G bands intensities (ID/IG). For “pure” nanotubes this ratio is null, whereas for carbon nanotubes containing defects, such as bifurcations, openings, curvatures and amorphous carbon, while the band located around 1630 cm$^{-1}$ is the G-band, related to the sp$^2$ bonds of the non-defective carbon nanotubes[22].

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The band located around 1310 cm$^{-1}$, is related to the D-band, indicating the degree of disorder of the carbon nanotubes, associated to defects, such as bifurcations, openings, curvatures and amorphous carbon, while the band located around 1630 cm$^{-1}$ is the G-band, related to the sp$^2$ bonds of the non-defective carbon nanotubes[22].

The intensity of the G-band is used for comparison (about
1630 cm$^{-1}$). In fact, when the D band is more intense than the G band, one can understand that this is due to disorder of the sample. This was observed in the Raman spectra of the analyzed samples, showing the effect of functionalization on the disorder (Fig. 5) in which the $I_D/I_G$ value was 1.14, greater than the value 0.87 for the MWCNT and lower than the post reaction sample of the 1.35 (Fig. 11).

This behavior was also observed by Ma et al. [15], in which the $I_D/I_G$ values for samples were 1.06 (acid treated CNTs), 1.36 (Ni outside CNTs) and 1.50 (Ni inside CNTs). It is obvious that the $I_D/I_G$ value increases after acid treatment, indicating that the acid treatment made the CNTs disorderly.

The position of bands D and G did not shift when the metals were inserted, indicating that the carbon structure of the CNT remains unchanged after impregnating the Ce and Ni nanoparticles.

Additionally, Raman spectra of MWCNT and Ni@MWCNT show a
The 2D band is originated from the boundary of Brillion zone phonon. It is observed that the 2D peak is expanded to composite indicating that the nanotube has multiple layers [23,24]. It is observed that the 2D peak of the post reaction catalyst is almost non-existent and therefore the number of layers reduced strongly during the reaction.

### 3.6. Catalytic activity

The performance of the catalyst 5%Ni@MWCNT/5%Ce was investigated for the tri-reforming of methane reaction, varying temperatures, space velocities and feed rate concentrations of water and oxygen, using planning experimental as shown in Table 3. Each experiment was carried out in triplicate with new sample of catalyst.

The 5%Ni@MWCNT/5%Ce catalyst presented high H$_2$O conversion (almost 100%) when compared to CO$_2$ conversion, since steam reforming is less endothermic than CO$_2$ reforming of methane. Noteworthy is that the metallic dispersion and a small size of nickel particles on this support favors the activity of the reforming reaction and inhibits the carbon deposition and deactivation of the catalyst. Moreover, carbon nanotubes as support showed high reactivity for methane reforming reactions, due to their thermal stability and the high oxygen storage capacity of Ceria [25].

In fact, earlier reports showed also that Ceria enhances the performance of the methane tri-reforming and suggested that OSC reduces the ignition temperature, whereas metal dispersion affected the catalytic activity [28,30]. In fact, the 5%Ni–5%Ce supported on carbon nanotubes catalysts showed quite good activity. Cerium oxide serves as an oxygen storage component, which may decrease the carbon formation during the partial oxidation of methane or other reforming reactions. It can act as a powerful promoter that modifies the structural and electronic properties of many catalysts. Cerium oxides obstruct the thermally induced sintering of the support [26-29].

### 3.7. Stability

Fig. 6 shows the catalytic stability of 5%Ni@MWCNT/5%Ce catalyst during the methane tri-reforming at 700°C, for 1250 ml/min.g and running 44 h. The CH$_4$ and CO$_2$ conversions and H$_2$/CO ratio were very stable throughout the test period and did not present any significant initial deactivation. The initial H$_2$/CO ratio was 1.5 and remained for 44 h. Majewski et al. [8] studied the methane tri-reforming process for the nickel-silica core@shell catalyst (11%Ni@SiO$_2$) catalyst and the
catalysts for 700°C and 1250 ml/min.g (condition C11, Table 3).

Water concentration in the feed stream as shown in experiments using ducts of the methane tri-reforming reaction are highly dependent on the addition of H2O in the space velocity (WHSV), varying from 1250 to 2000 ml/min.g and 52% and 78% to 64%, respectively.

Coke deposition varied significantly after 4 h. Danilova et al. [11] studied the combined steam and carbon dioxide reforming of methane to synthesis gas at 750°C with nickel catalysts supported on a porous nickel ribbon with MgO under layer, and showed that this catalyst was stable throughout the test period (18 h).

3.8. Influence of feed composition

The CH4 and CO2 conversions and the selectivity of the main products of the methane tri-reforming reaction are highly dependent on the water concentration in the feed stream as shown in experiments using experimental parameter estimation and presented in Table 3 and Fig. 7. The increasing water concentration favors the steam reforming and the water gas shift reaction (WGSR), reducing the presence of carbon on the structure. The combination of DR and SR can provide an extremely stable throughout the test period (18 h).

3.9. Effect of oxygen

Fig. 8 shows the effect of oxygen concentration on the ratio O2/H2O on the methane tri-reforming reaction for the production of synthesis gas, as function of different variables. Indeed, the addition of oxygen actually helps the thermal balance of the process by compensating the endothermic reactions.

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H^\circ (298 \text{ K}) = 206 \text{ kJ mol}^{-1} \\
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + \text{H}_2 \quad \Delta H^\circ (298 \text{ K}) = 247.3 \text{ kJ mol}^{-1} \\
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H^\circ (298 \text{ K}) = 37.09 \text{ kJ mol}^{-1}
\]

It is important to notice the influence of CO2 content in the reaction mixtures. Following the similar conditions reported in the literature by references [6, 8, 11 and 13], and varying the concentration of CO2 between 0.2 and 0.67 as presented in Table 3, it shows that for similar conditions, the experiments C22 and C23, the results didn’t change significantly the CO2 conversions, 50.1 and 52.5%, however the H2/CO ratio decreased from 2.05 to 1.4.

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H^\circ (298 \text{ K}) = -36 \text{ kJ mol}^{-1} \\
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\[
\text{CH}_4 + (1/2) \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad \Delta H^\circ (298 \text{ K}) = -36 \text{ kJ mol}^{-1} \\
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H^\circ (298 \text{ K}) = -36 \text{ kJ mol}^{-1}
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conversion decreases, which are attributed to the higher concentration of O2 in the feed, inhibiting the dry reforming and increasing the total oxidation of methane.

The influence of temperature is shown in Fig. 8(c) and, as observed, increasing temperature (700 °C to 750 °C) both conversions increased. The conversion of methane was very high, around 80% at 750°C. The conversion of CO2 increased from 50 to 65% at 700 and 750°C, respectively. In fact, the methane oxidation is a highly exothermic reaction and increased oxygen concentration reaches the total oxidation and, consequently, the energy released is high, which favors the water and CO2 reaction with unreacted methane to produce synthesis gas [31].

The higher production of synthesis gas (H2/CO ratio) is attributed to the steam reforming of methane and the WGS (water gas shift) reactions; however, increasing temperature, the (RWGS) reverse shift reaction prevails. Since CO2 is produced during the WGS reaction the conversion of CO2 decreases with the increasing oxygen in the feed and, consequently, reduces the H2/CO ratio.

It is important to stress that the effect of oxygen in the feed for the tri-reforming reaction enhanced the hydrogen production at lower temperatures (700°C) and higher feed rates (2000 ml/min.g) compared to the steam and dry reforming of methane.

In fact, in the second case, the residence time is lower and the activity increases with temperature. Increasing reaction temperature favored endothermic reactions such as steam (1) and dry reforming of methane (2). This is particularly the case for dry reforming, as the highly endothermic reaction became more intensive at elevated temperature.

As a result, increasing reaction temperature methane increases conversion and decreases CO2 due to higher CO production. Moreover, the reverse water–gas shift reaction was thermodynamically favored at high reaction temperature. The reverse water–gas shift reaction consumed part of the hydrogen produced by methane reforming and produced more CO.

It is noteworthy to observe in Table 4 that the highest CH4 conversions were obtained for similar feed condition (CH4:CO2:H2O:O2:N2) (1:0.34:0.23:0.5:2.1) but for different space velocities and temperatures. Experiment C25 presented 91% conversion of CH4 and 30.8% of CO2 with a H2/CO = 1.88 at 700°C and space velocity 2000 ml/g.min. However, the highest conversion was 96.8% CH4, 38.7% of CO2 and H2/CO 1.88 for a higher temperature (750°C) and lower space velocity 1250 ml/g.min, which indicate the influence of residence times and kinetics.

For comparison to literature, almost similar conditions of experiments C44 and those of Majewski et al. [8] are considered, as shown in Table 4. The methane and CO2 conversions reported in the literature were little lower than those obtained in the experiments, however, the H2/CO ratio was 2.6, significantly higher than 1.4 in the experiments, which indicates higher CO formation, favoring the steam reaction. These authors obtained also the highest CH4 conversion, however, for higher oxygen content in the feed and smaller space velocity (GHSV). In fact, increasing the residence time or the weight of the catalyst improves the activity.
3.10. Post reaction analyses

The key question is to understand what occurred during the reaction, which was performed at higher temperature than the calcined and reduced catalyst before the reaction. In fact, Fig. 6 shows that the it is stable during the 48 h reaction and during the first 10 h there is an increasing methane conversion that stabilized. TGA experiments, show that the material decomposed above 500°C (Fig. 4) and comparing the Raman spectra (Fig. 10, before and after reaction, respectively evidencing that band D and G, and band 2700 cm\(^{-1}\) disappeared, which indicate destruction of the CNT, but shows markedly the presence of Ce bands around 500 cm\(^{-1}\), and not bands corresponding to the Ni. In fact, the catalyst as prepared was transformed due to the presence of oxygen in the feed. In fact, in our previous report and reported results by Ma et al.\([15]\) for the dry reforming only the CNT were preserved, in opposite was is observed here in the presence of oxygen, and moreover, depending on the oxygen concentration in the feed.

The Ni@MWCNT/Ce catalyst was investigated after 44 h methane tri-reforming reaction, using specific techniques that allow evaluating the structure and morphology of the catalyst after chemical reaction. From the TEM and XRD results before the reaction (Figs. 2 and 3), NiO particles inside and CeO\(_2\) particles outside the carbon nanotubes and well-structured carbon nanotube were observed.

Fig. 9 show the TEM analyze for the 5%Ni@MWCNT/5%Ce catalyst after reaction. Images show different morphology of agglomerated large particles on the surface of the carbon nanotubes, almost like a “cloud”. The growth of the Ni particles was from 2.8 nm to 6.6 nm after 44 h.

The EDS analysis of different observed particles in Fig. 9 and marked as (a-d) showed dark regions, indicating predominately the nickel structure, while the light regions suggest cerium oxide structure in it images.

### Table 4
Comparison of reaction conditions and results of the methane tri-reforming.

<table>
<thead>
<tr>
<th>Group</th>
<th>T (°C)</th>
<th>GHSV (mL/min.g)</th>
<th>((\text{CH}_4\text{CO}_2\text{H}_2\text{O}:\text{O}_2\text{N}_2)) (mL/min)</th>
<th>(X_{\text{CH}_4}) (%)</th>
<th>(X_{\text{CO}_2}) (%)</th>
<th>(\text{H}_2/\text{CO})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C25*</td>
<td>700</td>
<td>2000</td>
<td>(1.34:0.23:0.5:2.1)</td>
<td>91.0</td>
<td>30.8</td>
<td>1.8</td>
</tr>
<tr>
<td>C35*</td>
<td>750</td>
<td>1250</td>
<td>(1.34:0.23:0.5:2.12)</td>
<td>96.8</td>
<td>38.7</td>
<td>1.9</td>
</tr>
<tr>
<td>C44*</td>
<td>750</td>
<td>2000</td>
<td>(1.34:0.37:1.7:1.97)</td>
<td>79.2</td>
<td>61.7</td>
<td>1.4</td>
</tr>
<tr>
<td>Majewski et al. [8]**</td>
<td>750</td>
<td>312.5</td>
<td>(1.5:0.5:0.1:0.4)</td>
<td>73.0</td>
<td>55.6</td>
<td>2.6</td>
</tr>
</tbody>
</table>

* 0.1 g of the 5%Ni@MWCNT/5%Ce catalyst.
** 0.2 g of the 11%Ni@SiO\(_2\) catalyst.
all carbon nanotubes were burnt during the reaction. Ce oxide phase at 443 and 573 cm$^{-1}$ was also observed, which suggest that after reaction the oxide phases exist as separate scattered particles. Nickel was not detected in this spectrum (red), which also suggests that there are highly dispersed NiO particles. In fact, these are the principal sites for the reaction at high temperature, as unsupported oxides. It is important to stress that most catalysts for the tri-reforming reaction are supported oxides [25]. However, these results suggest that during the reaction at high 750°C the metal oxides remain stable as randomly dispersed non supported particles, as shown in the images after reaction in Fig. 9, where Ni species are the principal dispersed sites for the reaction and exhibit high stability for more than 48 h, as shown in Fig. 6.

The Raman spectra after reaction show yet bands assigned to carbon on the surface as noted in Fig. 10, which probably may be formed during the reaction at high temperature. However, the bands of the CeO$_x$ are more pronounced after reaction.

In fact, the thermal analysis (TGA) of the sample Ni@MWCNT/Ce after the reaction (Fig. 11) shows mass growth of approximately 7% in relation to the initial mass up to 750°C and stabilized after this temperature. However, the profile (dark line) shows gain of mass until 350°C, which is attributed to carbon formation, and above this temperature lost mass until 700 °C, while the gain of mass (red line) increases continuously up to 700°C. It evidences an oxidation step of the metallic particles starting at 450 °C up to 700°C. According to these results, the mass gain is suggested to be attributed to the carbon formation, and principally to the oxidation of Ni and Ce species [11].
Majewski et al. [8] observed after reaction under \((\text{CH}_4: \text{CO}_2: \text{H}_2: \text{O}_2: \text{He}) \times 1:0.5:0.5:1:0.4\) during 4 h, mass loss around 5%, which is close to value obtained in this work for similar condition but for 44 h. However, from TGA results coke formation was not observed and the profile shows only the formation of carbon, which is attributed to the carbon filaments formed during the reaction. Raman spectra evidenced clearly total absence of coke formation. In fact, silica support is an acidic material, which promotes the formation of carbon on the surface. In opposite, the carbon support was decomposed or burnt during the reaction resulting unsupported oxides or nickel metallic particles well dispersed or deposited on carbon filaments, evidenced by Raman and TGA results after reaction, in comparison to the analyzed catalysts before reaction.

In fact, the catalyst as prepared was not the same after reaction and evidence though long test that it works and is attributed to the dispersion of metallic oxide of Ni and Ce surface in and outside the CNT formed during the reaction on these metal oxides, as shown in the TEM images after reaction.

4. Conclusions

In this work a selective mode of addition of metal inside and outside the functionalized carbon nanotube as bimetallic catalyst was synthesized. The activity and stability of 5%Ni@MWCNT/5%Ce catalyst for methane tri-reforming reaction were studied considering different feed conditions. In the tested catalyst, high dispersion of Ni particles, strong interaction metal-support and high activity (52–95% CH\(_4\) conversion and 17–87% CO\(_2\) conversion) were observed. In general, the experimental study of the catalyst enabled the knowledge of characteristics of carbon nanotubes with Ni as active metal and Ce as promoter for complex reactions such as methane tri-reforming for the CO\(_2\) utilization. The 5%Ni@MWCNT/5%Ce catalyst was tested at 700°C for 44 h and remained stable throughout the test period. TGA results shows only the formation of carbon, which is attributed to the carbon filaments formed during the reaction. Raman spectra evidenced clearly total absence of coke formation. The carbon CNT support was decomposed or burnt during the reaction resulting in unsupported oxides and nickel metallic particles well dispersed or deposited on residual carbon or growth filaments, evidenced by Raman and TGA results after reaction, in comparison to the analyzed catalysts before the reaction.

CRediT authorship contribution statement

Camila Emilia Kozonoe: Investigation, Methodology, Supervision, Validation, Writing - original draft, Writing - review & editing. Rita M. Brito Alves: Project administration, Visualization. Martin Schmal: Conceptualization, Methodology, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2020.118749.

References


Fig. 10. Raman spectra take from Ni@MWCNT/Ce catalyst post reaction at \(\lambda = 532\) nm.

Fig. 11. TGA and DTA curve of the post reaction Ni@MWCNT/Ce catalyst.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2020.118749.