Selective Synthesis of Carbon Nanotubes by Catalytic Decomposition of Methane using Co-Cu/Cellulose Derived Carbon Catalysts: A Comprehensive Kinetic Study

W. Henao[1], F. Cazaña[1], P. Tarifa[1], E. Romeo[1], N. Latorre[1], V. Sebastian[1], J.J. Delgado[2], A. Monzón[1,*]

[1] *Institute of Nanoscience of Aragon (INA), University of Zaragoza, E-50.018, Spain.*

[2] *Department of Materials Science, Metallurgical Engineering and Inorganic Chemistry, University of Cádiz, E-11510 Puerto Real, Spain.*

*Corresponding author: amonzon@unizar.es

ABSTRACT

Determination of the optimal operating conditions for large-scale production of carbonaceous nanomaterials (CNTs), mainly carbon nanotubes (CNTs) but also graphene-related materials (GRMs), remains as a major industrial and scientific challenge. For this purpose, our group is conducting an extensive study to evaluate the effect of the reaction conditions and catalyst compositions on the productivity and selectivity to different carbonaceous nanomaterials. In the case of Co-based catalysts, we have found that the promotion with Cu or Mn has a dramatic effect on the type of carbon nanomaterials synthesized. Thus, the presence of Cu promotes the growth of CNTs, while Mn favors the formation of two-dimensional GRMs. In this context, we present here a comprehensive study of the CNTs growth via catalytic decomposition of methane using a Co-Cu/cellulose derived carbon catalyst. The influence of the reaction temperature (650-950 °C) and feed composition (7.1% to 42.9% of CH_4 and H_2) on the yield and CNTs quality was evaluated. A transition in the characteristics of the carbonaceous nanomaterial growth was observed at about 800 ºC. Below this temperature, the reaction was selective towards the formation of CNTs, while above 800 ºC, the obtained nanomaterial exhibited a graphite-like morphology. In addition, the catalyst deactivation was quite low in the CNTs growth regime, attaining high productivity under 11 hours of operation. The model used to study the kinetics of carbon formation allowed understanding the most influential variables in the growth process, revealing the existence of a transition temperature at which there is a change in the preferential path for the formation of CNTs or GRMs. After exploring a large set of reaction conditions, the best operating parameters for growing CNTs with high productivity (0.29 gC/gcat·h) and quality ($I_D/I_G=1.10$, $I_{2D}/I_G=0.13$) were found at 750 °C under 28.6% CH_4:14.3% H_2:57.1% N_2.

Keywords: Carbonaceous Nanomaterials, Catalytic Decomposition of Methane, Co-Cu, Cellulose Derived Carbon, Growth kinetics, Catalyst deactivation.

1. INTRODUCTION

During the last decades, production of carbon nanotubes (CNTs) with different wall structures (single-walled (SWCNTs) [1], multiwalled (MWCNTs) [2]) and tubular morphologies (straight [3], bamboo-like [4], cup-stacked [5], helical [6]) has received a great industrial and scientific interest due to their extraordinary physical and chemical properties. Their high aspect-ratio, thermal conductivity, tensile strength, chemical surface and electronic properties give rise to new opportunities in a large variety of disciplines, including catalysis [7,8], sensors [9,10], energy storage [11,12], environmental remediation [13] and biomedicine [14,15]. Despite extensive progress in CNTs synthesis, obtaining CNTs with a well-defined structure at the industrial level is still a difficult process to achieve by a cost-effective technique. Therefore, enormous efforts have been devoted worldwide to find the most appropriate operating conditions and catalyst compositions that provide both high carbon yield, quality and selectivity towards the desired carbon structure [16–18]. Among the currently available CNTs production technologies, catalytic chemical vapor deposition (CCVD) stands for the most attractive method to meet this demand, due to its low-cost and easy scalability for mass production in large-scale manufacturing scenarios [19,20].

In this technique, transition metal nanoparticles are exposed to a gaseous carbon source, commonly a light hydrocarbon (e.g., CH_4, C_2H_2, C_2H_4), which is decomposed into carbon atoms, molecular hydrogen and, in some cases, cracking by-products at high reaction temperatures (600–1200º C). When CH_4 is used as a carbon feedstock, the co-production of COx-free hydrogen and the absence of cracking by-products constitute an additional advantage [21]. CNTs growth starts with the hydrocarbon dissociation by the metal nanoparticles into carbon atoms that diffuse either through the bulk metal or along its surface. After the metal reaches its carbon solubility limit, the diffusing carbon atoms precipitate on the opposite side, forming the carbonaceous nanomaterial. Depending on the metal nanoparticle−catalyst support interaction, the CNTs can grow via a tip-growth or a base-growth mechanism, whether the metal is lifted up or remains attached to the substrate, respectively [16]. Carbon growth continues as long as the metal nanoparticles have active sites available for the carbon source dissociation, and there is a favorable carbon concentration gradient between the surface of the nanoparticles exposed to the gas and the exit points where the precipitation of carbon atoms occurs [22].

Thus far, the most commonly used transition metals are Fe, Co, Ni because of their high carbon solubility and diffusion rate at elevated temperatures [16]. Furthermore, the high melting point and the low equilibrium vapor pressure of these metals offer a wide range of operating conditions in the CVD process. Other non-iron group metals such as Cu [23], Mn [24], Cr [25], Mo [26], Pt [27], Pd [28], and

Au [29] have been incorporated as promoters since they allow modulating the carbon diffusion and the final structure of the carbonaceous nanomaterial obtained. In this regard, our group is investigating the effect of the reaction operating conditions and catalyst compositions on the yield and morphology of the carbon nanomaterial grown [30-38]. In the case of Co-based catalysts, we have recently found that the promotion with Cu or Mn has a strong effect on the type of carbon nanomaterials synthesized [39]. Thus, the addition of Cu promotes the formation of CNTs, while Mn intensifies the selectivity towards graphene-related materials (GRMs).

Cu-based catalysts have usually been quoted as not efficient for CVD-grown CNTs [40]. This fact has been explained considering the filled electronic d-shell of Cu which causes a barrier for the dissociative adsorption of hydrocarbons and does not form stable carbides [41]. However, its electron density can be enhanced by doping with alkaline elements [42] or by accepting the electron density of Lewis-base supports [43], attaining a stable [Ar] $4s^2\,3d^{10}$ configuration. More recent reports have shown notable improvements in the catalytic activity of Cu for growing both random networks and aligned arrays of CNTs [44-46]. Besides, Cu has some attractive properties that make the understanding of its behavior interesting for co-catalyzed CVD processes. Compared with Co, Ni or Fe, carbon atoms could precipitate on the outer surface of Cu more easily because its carbon solubility is much lower. Additionally, Cu presents a lower hydrocarbon dissociation rate, which slows down the carbon amount released into the reactive gas atmosphere. This could be an advantage to reduce the formation of amorphous carbon deposits. On the other hand, although the low melting point of Cu promotes the sintering of the metal nanoparticles, CNTs growth could proceed at lower temperatures. In that view, these features encourage the exploration of CVD operating conditions such as reaction temperature, carbon feedstock and flow rates over new catalyst compositions for CNTs growth.

Accordingly, the design of new formulations of both metal nanoparticles and supports is being increasingly investigated [17,47,48]. It is well known that the catalyst support plays an important role in the dispersion and catalytic activity of metals, which affects some properties of the CNTs grown such as diameter distribution and growth arrangement [49,50]. Renewable lignocellulosic raw materials for catalyst supports emerge as an attractive alternative to the commonly expensive and laborious-synthesized metal oxides, due to their high availability, low-cost and unique textural properties [51]. Natural lignocellulosic materials present a rich hierarchical structure that serves as a high surface area template to provide a fine dispersion of metal nanoparticles [52]. An additional advantage is that the catalysts can be prepared in a single step by a biomorphic mineralization technique, which involves the reductive thermal decomposition of the lignocellulosic material previously impregnated with the metallic precursors [53].

The use of cellulose and vine shoots wastes as raw catalyst supports has been previously studied in our group for growing several carbonaceous nanomaterials (carbon nanotubes, carbon nanofibers, few-layer graphene) via Ni [30] or Ni-Cu [31] catalyzed CVD reactions. The developed catalysts exhibited high catalytic activity and good dispersion of metal nanoparticles, which resulted in a high number of nucleation sites for carbon precipitation and a high performance in the growth of carbonaceous nanomaterials.

Owing to the crucial role of the catalyst efficiency in the mass production of CNTs with a well-defined structure, the investigation of its activation, deactivation and growth mechanism is certainly essential. Unfortunately, there are still several unanswered questions today about what are the critical steps that allow better structural control in large-scale CNTs manufacturing processes. Hence, this work aims at contributing to the CNTs research field through a fundamental understanding of the influence of the operating conditions —reaction temperature and feed gas composition— on the quality and yield of CVD-grown CNTs. For this purpose, we have developed a kinetic model involving the main stages of the CNTs growth mechanism, which has been continuously adapted to different synthesis conditions and catalyst compositions [30-42], this time a novel Co-Cu/cellulose derived carbon (CDC) catalyst.

2. EXPERIMENTAL

2.1. Catalysts preparation

Co-Cu/CDC catalyst was prepared by thermal decomposition of a commercial cellulose (Sigma Aldrich, ref: C6288) under reductive atmosphere, as described elsewhere [53]. First, the dried cellulose was impregnated by incipient wetness with the appropriate amount of an aqueous solution containing the precursor salts ($Co(NO_3)_2{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$, Sigma-Aldrich), in order to obtain a nominal weight composition of 5%Co−1.35%Cu (atomic ratio Co/Cu=4) regarding the initial amount of cellulose. After impregnation, the solid was dried at 80 °C overnight and then thermally decomposed under reductive atmosphere (15% H_2/85% N_2) at 850 °C during 75 min with a heating rate of 50 °C/min. Finally, the catalyst was milled and sieved obtaining a particle size distribution ranging from 10 μm to 200 μm.

2.2. Catalytic decomposition of methane

CNTs were obtained by catalytic decomposition of methane (CDM) under atmospheric pressure in a quartz thermobalance (CI Electronics Ltd., UK, model MK2) operated as a continuous fixed-bed differential reactor. Carbon mass evolution and temperature were continuously recorded during the CNTs growth along 120 min of reaction. The temperature range evaluated was 650–950 °C while the feed gas composition was modulated from 7.1% to 42.9% of CH_4 and H_2, using N_2 as balance gas (total flow rate 700 mL/min). In a typical experiment, 25 mg Co-Cu/CDC catalyst was placed into a copper mesh sample holder and then, after performing a weight calibration procedure, the sample was heated at 10 ºC/min under N_2 flow (700 mL/min) until reaching the desired reaction temperature. Once the selected reaction temperature was achieved, the reactive gas mixture $CH_4/H_2/N_2$ (700 mL/min) was introduced into the reactor keeping constant the temperature for 120 min. Finally, the sample was cooled down to room temperature under N_2 atmosphere.

2.3. Catalyst and carbonaceous nanomaterial characterization

The metal content of the Co-Cu/CDC catalyst was determined by thermogravimetric analysis under oxidative atmosphere (air, 50 mL/min) in a Mettler Toledo TGA/SDTA 851 equipment. A precisely weighed quantity of catalyst (10 mg) was heated from room temperature to 1000 ºC with a heating rate of 10 ºC/min. The final percentage of Co and Cu was calculated considering the nominal metal amount incorporated and the resulting mixture of metal oxides obtained upon combustion of the CDC support during the TGA-air experiment.

Specific surface area and porosity were obtained from N_2 adsorption-desorption isotherms measured at -196 °C using a TriStar 3000 instrument. Prior to the analysis, the samples were degassed at 200 °C for 8 h. BET specific surface area was calculated in the relative pressure range of P/P_0=0.01–0.10. Total pore volume was obtained at the maximum relative pressure reached by the adsorption branch (P/P_0> 0.989), whereas micropore volume was estimated by the t-plot method.

Crystalline phase identification of the fresh Co-Cu/CDC catalyst was performed by X-ray diffraction (XRD) in a Rigaku D/Max 2500 apparatus from 5° to 90° 2θ degrees using Cu Kα radiation (λ = 1.5406 Å). Surface chemical composition was characterized by X-ray photoelectron spectroscopy (XPS) in a Kratos Axis ULTRA spectrometer using non-monochromatic Al Kα radiation (hυ= 1486.7 eV). All spectra were analyzed in the CASA® XPS software by applying a Shirley-type background.

Morphological information on the carbonaceous nanomaterials formed during CDM reaction was obtained by electron microscopy. Transmission electron microscopy (TEM) images were taken using a FEI Tecnai T-20 microscope operated at 200 kV. Scanning electron microscopy (SEM) and energy dispersive X-Rays spectroscopy (EDS) analysis were carried out in a FEI Inspect F50 microscope.

In-depth chemical analysis of the samples before and after reaction was performed using a double Cs aberration-corrected FEI Titan3 Themis 60–300 microscope operated at 200 kV. The microscope is equipped with an X-FEG gun, a monochromator, and a high efficiency XEDS ChemiSTEM. The latter device consists of a 4-windowless SDD detectors and, in combination with the scanning transmission electron microscope mode, allow to perform XEDS mappings. These experiments were carried out using a beam current of 200 pA and a dwelling time per pixel of 128 μs. To improve the visual quality of the elemental maps, these were filtered using a Gaussian blur of 0.8 using Velox software. HR-STEM imaging was performed using a high-angle annular dark-field (HAADF) detector with a camera length of 11.5 cm. The HAADF-STEM technique is sensitive to the atomic number of the elements and it makes possible to distinguish the small nanoparticles dispersed on the light CDC support.

The carbonaceous structure of the Co-Cu/CDC catalyst support and the quality of the CNTs grown were characterized by Raman spectroscopy using a WiTec Alpha300 confocal Raman microscope with a 488 nm laser excitation beam. The intensity ratios I_D/I_G, I_{2D}/I_G of the characteristic bands D (~1350 cm^{-1}), G (~1580 cm^{-1}), and 2D (~2690 cm^{-1}) from different sample spots (5 spectra) were used to evaluate the defects in the carbon structure of the CNTs obtained. The quantification of the C sp^2 disorder was addressed by considering intensity ratios I_D/I_G, I_{2D}/I_G instead of area ratios A_D/A_G, A_{2D}/A_G, due to the noise contribution from the amorphous CDC support to the Raman signal of the carbonaceous nanomaterials grown [54].

2.4. Kinetic model of carbon nanotubes growth

The effect of the operating conditions on the CNTs growth kinetics was further analyzed by a phenomenological model developed in previous works [30-32]. This kinetic model considers the fundamental steps of the reaction growth mechanism summarized in **Scheme 1**, consisting of i) adsorption and catalytic decomposition of CH_4 molecules on the metal nanoparticles surface; ii) formation of a metastable metallic carbide which decomposes into carbon atoms at the carbide−metal nanoparticle interface; iii) diffusion of the carbon atoms through the metal nanoparticle, or along its surface, and subsequent carbon precipitation at the metal−catalyst support interface; iv) formation and growth of the carbonaceous nanomaterial whose nature (nanotubes, nanofibers, graphite) depends on the operating conditions and the catalyst composition; v) carbon growth termination either due to catalyst deactivation or steric hindrance of the nanomaterial grown.

This model is based on the most accepted growth mechanism of CNTs on supported metal nanoparticles, which involves the continuous formation and decomposition of a metastable surface carbide [55-58]. After decomposition, the carbon atoms are delivered inside the metal nanoparticles migrating by diffusion to the opposite (rear) surface. Then, the precipitation and formation of the carbon nanotubes are produced draining the carbon inside the nanoparticles. This dynamic transformation has been demonstrated by in-situ time-resolved X-ray photoelectron spectroscopy [59,60].

Scheme 1. Formation of CNTs over metal nanoparticles by catalytic decomposition of methane.

The main kinetic parameters involved in the CNTs growth process were determined by non-linear regression of the carbon mass evolution curves of each experiment using the kinetic model expressed in **Equation 1:**

$$m_C = j_{C_0} \cdot \left(a_S \cdot t^n + \frac{(1-a_S)}{\psi_G} \cdot \left(1 - \exp(-\psi_G \cdot t^n)\right) \right) \tag{1}$$

In this equation, j_{C_0} stands for the intrinsic carbon growth rate of the catalyst (gC/gcat·min) under a given operating condition; ψ_G represents the sum of the kinetic parameters of deactivation and regeneration, $\psi_G = \psi_d + \psi_r$, respectively, having units of min^{-1}. The term a_S, corresponds to the residual activity of the catalyst, defined as: $a_S = \psi_r / (\psi_d + \psi_r)$; and n is a power parameter that allows modulating the effect of the carbon diffusivity in the evaluated temperature range [30,31].

These kinetic parameters vary with both the reaction temperature and the feed gas composition used in each experiment, and their dependence with the CH_4 and H_2 concentrations is expressed as power−law functions:

$$j_{C_0} = k_C \cdot p_{CH_4}^{c_1} \cdot p_{H_2}^{c_2} \quad , \quad \psi_d = k_d \cdot p_{CH_4}^{d_1} \cdot p_{H_2}^{d_2} \quad , \quad \psi_r = k_r \cdot p_{CH_4}^{r_1} \cdot p_{H_2}^{r_2} \tag{2}$$

Where k_C, k_d, and k_r are the intrinsic kinetic constants that follow an Arrhenius-type dependence with the reaction temperature, and *c*, *d*, and *r* are the corresponding kinetic orders with respect to CH_4 and H_2. These parameters were estimated by non-linear least-squares multivariable regression of the carbon mass evolution curves using a Model Selection Criterion (*MSC*) as maximized objective function [61], defined in the Supporting Information file.

3. RESULTS AND DISCUSSION

3.1. Fresh catalyst characterization

Morphology and particle size distribution of the bulk Co-Cu/CDC catalyst and the impregnated metal nanoparticles were addressed by electron microscopy images shown in **Figure 1**. SEM-EDS elemental mapping depicted in **Figures 1(A−C)** indicates that Co and Cu transition metals were well distributed on the CDC support owing to its characteristic biomorphic surface texture. TEM images were used to estimate the particle size of the incorporated metals by measuring at least 500 particles from different sample areas. **Figure 1(D) s**hows a multimodal metal particle size distribution with a large number of spherical nanoparticles about 3 nm and a low number of nanoparticles about 11 nm and 21 nm. This broad metal size distribution is a consequence of the high temperature and heating rate used during the catalyst synthesis. High-resolution STEM-EDS of the fresh Co-Cu/CDC catalyst reveals that there is an intimate interaction between both metals, in which Cu atoms are mainly dispersed on the surface of Co core nanoparticles, **Figures 1(E, F)**.

Figure 1. Electron microscopy study of the fresh Co-Cu/CDC catalyst: (A) general view conducted by SEM, (B, C) SEM-EDS elemental mapping, (D) TEM image of metal particle size distribution, (E) STEM-HAADF image for morphology and (F) sub-nanometric chemical analysis performed by STEM-EDS.

Even though Co-Cu/CDC was prepared with a nominal weight composition of 5%Co−1.35%Cu with respect to the initial amount of cellulose, the metal content of the resulting catalyst measured by TGA-air was substantially higher (23.9 wt.% Co and 6.4 wt.% Cu), see **Figure S.I.-1** in the Supplementary information file. This increase in the metal content is due to the weight loss of carbonaceous support during the thermal decomposition of cellulose, a crucial step to control both the final content and the dispersion of the metal nanoparticles in the obtained catalyst [31]. Nonetheless, the atomic ratio Co/Cu=4 was preserved after catalyst preparation, which was corroborated by SEM-EDS spectroscopy. Regarding the textural properties, Co-Cu/CDC catalyst exhibited a BET surface area of 438 m^2/g, a pore volume of 0.206 cm^3/g and 78% microporosity.

Information about the crystalline phase and surface composition of the impregnated metals before reaction was addressed by XRD pattern and XPS spectra collected on Supporting Information file, **Figures S.I.-2 and S.I.-3**. XRD pattern depicted in **Figure S.I.-2** reveals that both Co and Cu were present in metallic state (Co^0 (15-0806 JCPDS), Cu^0 (04-0806 JCPDS). The broad diffraction peak at about 24° 2θ degrees, ascribed to the (002) plane of the hexagonal graphite structure (75-2078 JCPDS), denotes the amorphous nature of the carbonaceous CDC support. Further analysis by XPS indicates that the surface of the Co and Cu nanoparticles was oxidized to CoO (83.6 at.%) and CuO (54.6 at.%), respectively (**Figure S.I.-3**). These results indicate the presence of metallic Co and Cu, and oxide species formed after exposition of the catalyst to the air environment. During the reaction, the highly reductive atmosphere (CH_4/H_2 mixture) avoids the formation of any oxide phase, and all the active components (Co and Cu) are expected to be in either metallic or carbide state, therefore the catalytic activity during CDM reaction is not compromised.

The carbonaceous structure of the fresh Co-Cu/CDC catalyst was characterized by Raman spectroscopy shown in **Figure S.I.-4.** The typical G band attributed to the in-plane vibration of the C sp^2-hybridized bonds was observed at 1584 cm^{-1}, while the D band assigned to defects within the C sp^2 network of the carbonaceous support was detected at 1348 cm^{-1} [62]. The broad and weak peak at about 2800 cm^{-1}, known as the overtone of the D band, reflects the amorphous nature of the catalyst support, which is in accordance with the XRD pattern shown in **Figure S.I.-2**. The Lorentzian peak deconvolution of the D and G bands presented in **Figure S.I.-4** inset shows five peaks related to several C sp^2 structural domains with different graphitic order degrees [63]. These peaks were respectively associated to the C=C chain stretching and the C−H wagging contributions (peak 1 at ~1250 cm^{-1}) [64], to the in-plane vibrations of the C sp^2 within defective graphitic domains (peak 2 (D) at ~1350 cm^{-1}) [65,66], to the amorphous C sp^2 -bonded phase (peak 3 at ~1490 cm^{-1}) [66], to the in-plane vibrations of the crystalline C sp^2-bonded phase (peak 4 (G) at ~1584 cm^{-1}) [67] and to disorders resulting from the finite size effect or distortion of the graphite crystallite (peak 5 at ~1616 cm^{-1}) [67,68].

3.2. Catalytic decomposition of methane to carbon nanotubes

3.2.1. Influence of the reaction temperature

The effect of the reaction temperature on the yield and morphology of the CNTs grown was evaluated from 650 ºC to 950 ºC using a feed gas composition of 28.6% CH_4:14.3% H_2:57.1% N_2. **Figure 2** shows the carbon growth evolution over time at different reaction temperatures and the respective fitted curves obtained by applying the kinetic growth model (**Equation 1**). A gradual increase in both the productivity and the initial carbon growth rate was observed from 650 ºC to 800ºC, reaching a maximum carbon productivity of 0.33 gC/gcat·h at 800 ºC. This improvement in the carbon growth rate with the temperature can be explained by the fact that high reaction temperatures promote a rapid diffusion of the carbon atoms through the metal nanoparticles (**Scheme 1; stage iii**), which increases the carbon precipitation rate at the metal-catalyst support interface and thereby favoring carbonaceous nanomaterials growth (**Scheme 1; stage iv**) [69]. Moreover, from 650 ºC to 750 ºC the carbon mass evolution curves followed a linear growth and no catalyst deactivation was observed along 2 hours of reaction. On the contrary, as the temperature was increased above 800 ºC, the carbon mass evolution reached a plateau after 40 min of reaction and the carbon productivity was monotonically reduced.

Figure 2. Influence of the reaction temperature on the evolution of carbon concentration along time. Feed gas composition of 28.6% CH_4:14.3% H_2:57.1% N_2.

Accordingly, transmission electron microscopy characterization shown in **Figure 3** reveals a transition in the growth of the carbonaceous nanomaterials at about 800 ºC. Below this temperature, the catalytic methane decomposition reaction was selective towards the formation of bamboo-like carbon nanotubes grown in a random direction. The formation of long CNTs was favored by increasing the reaction temperature from 650 ºC to 800 ºC, most likely due to the promotion of the methane decomposition and the diffusion of the carbon atoms through the metal nanoparticles. Interestingly, some metal nanoparticles were lifted up from the CDC support and embedded in the tip of the CNTs grown, revealing a tip-growth mechanism due to the weak interaction of the metal nanoparticles and the catalyst support [22]. On the contrary, when the temperature was increased above 800 ºC, the obtained carbonaceous nanomaterial exhibited a graphite-like morphology surrounding the metal nanoparticles. These encapsulating graphite-like nanolayers prevent the decomposition of new CH_4 molecules on the catalyst surface, triggering the early catalytic activity decay and the detriment of the carbon productivity observed in the carbon evolution curves of **Figure 2**. The severe sintering and reconstruction of the metal nanoparticles observed above 800 ºC also promote the drop of the catalyst activity due to the loss of active sites on the surface, decreasing its selectivity towards CNTs [70, 71].

Figure 3. SEM and TEM images of the carbonaceous nanomaterials grown at different reaction temperatures, using a feed gas composition of 28.6% CH_4:14.3% H_2:57.1% N_2.

Table 1 summarizes the textural properties of the Co-Cu/CDC catalyst before and after CDM reaction at different reaction temperatures. Upon catalytic decomposition of methane, both the surface area and the porosity of the Co-Cu/CDC catalyst decreased with the increase of the reaction temperature, probably due to the blocking of pores by the carbonaceous nanomaterials grown. This blockage caused a linear relationship (R^2=0.974) between the percentage volume of micropores and the BET surface area of the samples. Thus, the strongest reduction of the micropore volume and BET surface area was observed operating the catalyst at 800 ºC, which is coincident with the high carbon productivity achieved at this reaction temperature (0.33 gC/gcat·h). In line with the carbon evolution curves and the SEM images shown in **Figure 2** and **Figure 3**, respectively, these results confirm that raising the reaction temperature in the CNTs production regime (650−800 ºC) promotes the carbon yield and the coverage of the catalyst surface by the CNTs grown.

Table 1. Textural properties of the Co-Cu/CDC catalyst before and after CDM reaction at different temperatures using a feed gas composition of 28.6% CH_4:14.3% H_2:57.1% N_2.

XRD and XPS measurements of the spent catalyst are presented in **Figure S.I.-2** and **Figure S.I.-3**, respectively. XRD analysis showed the presence of the (111), (200) and (220) planes from CoO, suggesting that not only the surface of Co was oxidized to Co(2+) but also the bulk of some metal nanoparticles as a result of the air exposition after reaction. Accordingly, XPS surface composition shows that the Co/CoO and Cu/CuO ratios strongly decreased after reaction, indicating a noticeable oxidation of the metal nanoparticles. In particular, Co was more prone to oxidation than Cu because of its negative standard reduction potential ($E^0_{Cu^{2+}/Cu^0} = +0.34\ V;\ E^0_{Co^{2+}/Co^0} = -0.28\ V$).

In addition to the electron microscopy studies, Raman spectroscopy was used to further investigate the quality of the CNTs grown. The I_D/I_G and I_{2D}/I_G intensity ratios from the D (~1350 cm^{-1}), G (~1580 cm^{-1}), and 2D (~2690 cm^{-1}) bands were used as a rough measure of the relative number of defects in the CNTs obtained. An increase in I_D/I_G ratio denotes a loss of the C sp^2 aromaticity in the graphitic C−C rings due to defects induced by C sp^3 hybridization [66], which in turn decreases the in-plane crystallite size (La) of the carbonaceous nanomaterials obtained [72]. On the other hand, the I_{2D}/I_G ratio is related to the number of graphene layers stacked within the graphitic domains of the CNTs and their order along the crystallographic c-axis [73]. The values of the I_D/I_G and I_{2D}/I_G ratios and those of the crystallite size (La) collected from the Raman spectra are summarized in **Table S.I.-1**.

Figure 4. Raman spectra of the carbonaceous nanomaterials grown at different reaction temperatures using a feed gas composition of 28.6% CH_4:14.3% H_2:57.1% N_2.

Figure 4 shows the Raman spectra of the carbonaceous nanomaterials grown at different reaction temperatures. A drop in the D band intensity was observed with increasing temperature, which indicates a decrease in the number of defects of the obtained nanomaterials and suggests that the graphitic domains formed were more crystalline when grown at high temperatures. Besides, as the growth temperature increases, the separation between the D and G bands became larger, and the intermediate shoulder between both bands almost disappeared. This result is indicative of the coverage level of the catalyst surface by the carbonaceous nanomaterials grown [31], which was evidently higher as the carbon productivity increased with the reaction temperature (**Figure 2**). Interestingly, the 2D band intensity became higher above 800 ºC, revealing the transition in the nature of the CNTs grown towards the formation of a two-dimensional graphitic carbon structure, as noticed in the electron microscopy study shown in **Figure 3**. The intensity ratio $I_{2D}/I_G<0.50$ suggests that such graphitic carbon structures comprised more than five stacked layers of graphene [73]. Indeed, the in-plane crystallite size (La) was significantly increased from 13 nm to 30 nm when the carbonaceous nanomaterials were grown above 850 ºC.

1.1.1. Influence of methane and hydrogen partial pressure

The effect of the feed gas composition on the yield and morphology of the grown CNTs was further evaluated by varying the methane and hydrogen concentration from 7.1% to 42.9% with N_2 as balance gas (total flow rate 700 mL/min). All the experiments were conducted at 750 ºC due to the high activity and selectivity towards CNTs exhibited by the Co-Cu/CDC catalyst at this reaction temperature. **Figure 5A** shows the carbon growth evolution over time at different methane partial pressures and the respective fitted curves obtained by applying the kinetic growth model (**Equation 1**). Remarkably, all the experiments followed a linear carbon growth and no catalyst deactivation was observed along the reaction time evaluated. The increase in the methane partial pressure enhanced both the productivity and the CNTs growth rate. This is because during CDM reaction, the increase of methane concentration promotes the metal nanoparticles carburization, increasing the number of carbon atoms dissolved in them and thus favoring the carbon precipitation at the metal-catalyst support interface (**Scheme 1; stages ii–iv**) [31]. In this case, a maximum productivity of 0.38 gC/gcat·h was achieved using a feed composition of 42.9% CH_4:14.3% H_2:42.9% N_2.

Figure 5. Evolution of carbon concentration along time: (A) Influence of the methane partial pressure; (B) Influence of the hydrogen partial pressure. Reaction temperature: 750 °C; N_2 as balance.

Electron microscopy images displayed in **Figure 6** confirm the improvement of CNTs production as the methane concentration increases in the feed gas mixture. Additionally, it can be noted that high methane concentrations shortened the synthesized CNTs, revealing a drop in the activity of the metal nanoparticles probably due to amorphous carbon accumulation on their surface. This coke fouling hinders the formation of the metallic carbide on the metal surface during the induction period of the CNTs growth, which triggers a premature growth termination (**Scheme 1; stage v**) [30]. This idea will be discussed in detail in section 3.3 where the causes of catalyst deactivation are analyzed.

Figure 6. SEM and TEM images of the carbon nanotubes grown at different partial pressures of methane. The reactions were carried out at 750 °C using N_2 as balance gas (total flow= 700 mL/min).

The influence of the hydrogen partial pressure on the CNTs growth was also investigated (**Figure 5B**). Conversely to the observed by increasing the methane concentration in the feed, the raise of the hydrogen partial pressure led to low carbon productivities and slow CNTs growth rates. These results can be explained due to the competitive adsorption between CH_4 and H_2 molecules on the metal nanoparticles surface during the early beginning of the reaction mechanism. Under certain operating conditions the CH_4 adsorption sites can be occupied by H_2 molecules in excess, which hinders the catalytic decomposition of new CH_4 molecules and slows down the initial stage of the carburization process (**Scheme 1; stages i, ii**). This fact was evident when an extreme concentration of methane or hydrogen was used in the feed gas mixture (**Figure S.I.-5**). A methane excess of 42.9% CH_4:7.1% H_2 resulted in a fast carbon growth rate and enhanced carbon productivity, attaining 0.30 gC/gcat·h upon 2 hours of reaction. Nevertheless, a slight decrease in the catalyst activity was observed during the last minutes of reaction. On the other hand, when using a hydrogen excess of 7.1 %CH_4:42.9 %H_2, the attained carbon productivity was one order of magnitude lower (0.03 gC/gcat·h) and the carbon growth rate was extremely slow, which demonstrates the blocking of the CH_4 adsorption sites by the H_2 molecules in excess.

Electron microscopy images displayed in **Figure 7** corroborate the detriment of CNTs production as the hydrogen partial pressure in the feed increases. Under low hydrogen concentrations, i.e. high methane percentages in the reactive atmosphere (42.9% CH_4:7.1% H_2), the Co-Cu/CDC catalyst surface was entirely covered by the CNTs grown. However, as the hydrogen content was increased to 7.1% CH_4:42.9% H_2, the catalyst surface exhibited some bare areas as a consequence of the low carbon mass productivity. Particularly, it was noted that high hydrogen concentrations induced the formation of short CNTs with a poorly defined structure, maybe due to a non-homogeneous carbon precipitation along the metal nanoparticles surface of the catalyst.

Figure 7. SEM and TEM images of the carbon nanotubes grown at different partial pressures of hydrogen. The reactions were carried out at 750 °C using N_2 as balance gas (total flow= 700 mL/min).

Additionally, the variation in the feed gas composition also affected the quality of the CNTs grown (**Figure 8**). For instance, the raise of the methane concentration caused an increase in the intensity of the D band, revealing the formation of more defective CNTs (**Figure 8A**). As mentioned before, a high methane concentration in the reactive atmosphere shortens the CNTs grown and promotes the formation of amorphous carbon that accumulates on both the top and the bottom of the nanotube (**Figure 6**). Therefore, as the nanotubes become smaller, the density of defects is greater [74]. The separation between the D and G bands was more evident as the methane concentration increased, indicating greater coverage of the catalyst surface by the CNTs grown due to the improvement of the carbon yield under these reaction conditions. On the other hand, the 2D band was almost negligible in most of the spectra evaluated and only appeared under extremely high methane concentrations. This indicates that the CNTs obtained under low methane concentrations present in general a low graphitization degree.

Similarly, excessive hydrogen concentrations led to an increase in the I_D/I_G ratio revealing the detriment in the CNTs quality (**Figure 8B**). Although the quality of the carbonaceous nanomaterials was expected to improve due to the ability of hydrogen to gasify the amorphous carbon formed [75,76], the electron microscopy images of **Figure 7** show that short CNTs with a poorly defined structure are grown under high hydrogen partial pressures, as a result of the competitive surface adsorption between CH_4 and H_2 molecules during CDM reaction. From the Raman spectra evaluated, it is observed that the maximum quality (I_D/I_G=0.93) was reached by using moderated concentrations of methane and hydrogen in the feed (14.3% CH_4:14.3% H_2:71.4% N_2).

Figure 8. Raman spectra of the carbonaceous nanomaterials grown at different feed gas compositions: (A) effect methane partial pressure and (B) effect of hydrogen partial pressure.

Physical characterization conducted herein demonstrates the great influence of the temperature and CH_4/H_2 partial pressure on both the quality and productivity of the carbonaceous nanomaterials grown. CNTs productivity and quality seem to be inversely correlated factors, in which high productivity involves an increase in the defects of the nanomaterials obtained, either due to amorphous carbon accumulation or CH_4/H_2 excess limiting the catalyst surface accessibility. Hence, the relevance of finding the optimal operating conditions that allow the best balance between quality and carbon productivity in the CNTs growth process.

3.3. Stability of the catalyst at the CNT growth regime (T < 800 ºC)

Deactivation of metal catalyst particles during CVD growth remains a barrier to attain CNTs mass production at high growth rates. From **Figures 2** and **5**, it can be seen that the Co-Cu/CDC catalyst is stable during 2 hours of reaction at temperatures below 800 ºC. In order to elucidate the intrinsic stability of the catalyst at this low operating temperature regime, we have carried out long-term experiments using a feed gas composition of 28.6% CH_4:14.3% H_2:57.1% N_2. **Figure 9** shows the evolution of the carbon concentration along 11 hours of reaction at 700, 725 and 750 ºC. In agreement with the results presented in **Figures 2** and **5**, during the first 2 hours of reaction the formation of CNTs followed a linear growth and no apparent activity loss was recorded in this period. However, as the reaction time increased up to 8 or 11 hours, a decrease in the carbon growth rate was observed, which was more evident at 750 ºC (**Figure 8B**). Otherwise, the deactivation rate was lower operating at 700 ºC during 11 hours of reaction and the initial carbon growth rate was not greatly affected, which significantly enlarges the operation time of the catalyst maintaining both the productivity and selectivity towards CNTs. In any case, the observed decay in the carbon growth rate is usually related to metal nanoparticles deactivation and saturation of the carbon grown, which determines the final evolution of the catalyst activity [32].

Figure 9. (A) Long term evolution of carbon concentration; and (B) Carbon growth rate vs. time curves at 700, 725 and 750 ºC. Feed gas composition of 28.6% CH_4:14.3% H_2:57.1% N_2.

The study of bimetallic catalysts like Co-Cu/CDC is not straightforward because not only the interaction between both metals must be unraveled, but even more importantly, their stability must be determined. To clarify both questions, the Co-Cu distribution on both the fresh and the used catalyst at different temperatures and reaction times was measured by high-resolution HAADF-STEM (**Figure S.I.-6**). During the reaction at temperatures below 800 ºC, it was observed a slight sintering of the metal nanoparticles of smaller size. However, this minor modification probably does not affect the catalyst performance with respect to the CNTs growth. In contrast, it could have a beneficial effect because such small nanoparticles reach the proper size for templating the CNTs. Extremely small nanoparticles are not able to template the growth of CNTs due to the low driving force for the carbon atoms diffusion. In a previous study, it was demonstrated that there is a narrow window of metal particle diameters, around 40-50 nm, where the CNTs growth is allowed [77]. Consequently, the CNTs observed in **Figures 3, 6 and 7 exhibit** also exhibit diameters about 40-50 nm.

Elemental mapping depicted in **Figure 10** and the spectrum line profiles included in **Figure S.I.-7** confirm that the Co-Cu distribution in the bimetallic nanoparticles was maintained after the CDM reaction. Therefore, the observed deactivation under long-term reactions is not attributed to the modification of the interaction of Co and Cu in the bimetallic nanoparticles.

Figure 10. HAADF-STEM images (left) and energy dispersive spectroscopy (EDS) elemental mapping images (right) showing the distribution of Co and Cu in the fresh Co-Cu/CDC catalyst (A) and after exposure to the reaction mixture at 700 ºC for 11 h (B), 725 ºC for 11 h (C) and 750 ºC for 8 h (D).

Consequently, a complementary TEM study was conducted to elucidate the underlying nature of the growth limiting factors at temperatures below 800 ºC. From **Figure 11**, encapsulation of metal nanoparticles and steric hindrance of the CNTs grown were identified as the main causes of catalyst deactivation. Encapsulation of metal nanoparticles by coke deposits or surrounding graphite-like nanolayers has so far been one of the typical causes of catalysts deactivation in CVD reactions involving hydrocarbons as a carbon feedstock [78]. Upon the initial hydrocarbon decomposition stage, carbon atoms, molecular hydrogen, and in some cases, cracking by-products moieties are adsorbed on the surface of the metal nanoparticles. Carbon reacts with the metal surface forming a metastable metallic carbide, and later the incoming carbon atoms diffuse through the bimetallic nanoparticles to finally form the carbon nanotubes. When the hydrocarbon decomposition rate is significantly higher than that of the metallic carbide formation or that of the carbon diffusion, supersaturation of carbon atoms occurs at the surface of the metal nanoparticles, resulting in the cumulative formation of amorphous carbon (coke) or graphite nanolayers that hamper the access to the metal active sites (**Figure 11-(zone a)**). While fouling of the metal surface with coke is a reversible process that can be avoided by using H_2 or another gasifying agent, the encapsulating graphitic shell is more difficult to remove due to its irreversible adsorption to the metal nanoparticles [71]. In any case, the physical structure of the precipitated carbon varies with the carbon precursor, catalyst composition, and reaction conditions [79]. Furthermore, when the accumulation of CNTs is very high, the catalyst activity can also be reduced due to the increase of the steric hindrance limiting the upcoming CNTs growth [36], (**Figure 11-(zone b)**).

Figure 11. TEM study of Co-Cu/CDC catalyst deactivation in long-term experiments at temperatures below 800 ºC: (a) metal nanoparticles encapsulation and (b) steric hindrance of the CNTs grown. Feed gas composition of 28.6% CH_4:14.3% H_2:57.1% N_2.

This behavior was clearly different from that observed at reaction temperatures above 800 ºC, where the main cause of deactivation was the sintering of the bimetallic nanoparticles, see **Figure 3**. The large particles formed in these cases have a very low intrinsic activity to form CNTs and are more prone to form encapsulating carbon graphitic nanolayers. In this situation, the high volume to surface ratio of large particles decreases the available active sites for hydrocarbon decomposition and favors the nucleation of two-dimensional carbon structures. In contrast, spherical and small-sized metal nanoparticles are more active at temperatures below 800 ºC, where the growth of one-dimensional nanomaterials is the preferential path [16,30,31,80]. The activity of the large particles formed during catalyst synthesis is very low under these reaction conditions and their contribution to the total amount of carbon formed is considered negligible. Finally, it must be considered that during the CNTs growth, the catalyst maintains a substantial level of activity at the end of the operation. This is a consequence of the partial regeneration a fraction of active sites on the metal nanoparticles surface by the H_2 present in the reactive atmosphere [75,76].

3.4. Kinetic modelling of carbon growth.

An understanding of the CNTs growth mechanism is required to better control their crystallinity, chirality, and other structural properties. The effect of the operating CVD conditions on the CNTs growth mechanism was evaluated by fitting the carbon mass evolution curves m_C (gC/gcat) of each experiment with the kinetic growth model detailed in **Equation 1**. In all cases the mathematical fitting was quite good, attaining very high Model Selection Criterion values (MSC>7.5) and correlation coefficients (R^2>0.999), which confirms that the kinetic growth model describes well enough the experimental data results.

Figure 12 shows the influence of the operating conditions on the kinetic parameters used to describe the dynamics of carbon growth (j_{C_0}), the power-law parameter related to the diffusional restrictions of methane (n), and the catalyst deactivation and regeneration functions (ψ_d and ψ_r). As can be noted, the kinetic model used was able to capture the main characteristics of the carbonaceous nanomaterials growth, where there is a critical temperature at which the dominant route of CNTs formation changes as a consequence of a multifaceted phenomenon involving the carbon species during the CCVD process.

In **Figure 12 (A,B)**, the variation of the kinetic parameters with the temperature revealed two different growth regimes which is consistent with the transition from CNTs to graphite-like nanomaterials observed at about 800 ºC. At this critical temperature, there is a change in the balance between the nucleation and precipitation steps of the growth mechanism [30]. Below 800 ºC, carbon precipitation seems to be the prevalent route characterized by the presence of few nucleation points, favoring the growth of one-dimensional nanomaterials like CNTs. However, at higher reaction temperatures numerous nucleation points are generated on the surface of the metal nanoparticles, creating many exit points for the diffusing carbon atoms, which eventually results in the formation of encapsulating graphite nanolayers. This phenomenon was also observed with similar catalysts based on supported Ni [30] or Ni-Cu [31] over biomorphic carbons.

The intrinsic carbon growth rate (j_{C_0}) presented in **Figure 12(A)** increased with the reaction temperature, attaining an activation energy E_{C-LT} = 221.7 kJ/mol in the formation regime of CNTs (700−800 ºC, low temperature-LT) and E_{C-HT} = 129.6 kJ/mol in the growth range of the graphite-like nanolayers (850−950 ºC, high temperature-HT). The lower activation energy above 800 ºC explains the more favorable formation of the encapsulating graphite-like nanolayers instead of CNTs because the flux of carbon atoms through the metal nanoparticles is decreased (**Scheme 1; stage iii**). This fact was consistent with the low values of the power-law parameter (n) and the pre-exponential factor of j_{C_0} (k_{C0}= 2.0×10^4 ($min^{-1}\cdot atm^{-1}$)) observed at high reaction temperatures.

Figure 12. Influence of the operating conditions on the kinetics parameters. (A,B) Arrhenius plot of the intrinsic kinetic parameters: j_{C_0}, n, ψ_d and ψ_r; (C) Influence of P_{CH_4} (P_{H_2}=0.143 atm); (D) Influence of P_{H_2} (P_{CH_4}=0.143 atm). Reaction temperature: 750 °C.

The catalyst deactivation parameter ψ_d was also found to increase with the reaction temperature, being more prominent above 800 ºC (**Figure 12(B)**). This corroborates the monotonic decay of the catalyst activity observed in the carbon mass evolution curves in **Figure 2**. As previously explained, the causes of the catalyst deactivation respond to a combination of complex temperature-dependent phenomena involved during the carbon growth mechanism. On the other hand, the parameter ψ_r was not affected by the reaction temperature in the CNTs formation regime (700−800 ºC), while at temperatures above 800 ºC this parameter was gradually increased. In the whole temperature range evaluated, the values of ψ_d were higher than those of ψ_r indicating that the catalyst deactivation was faster than the regeneration process and therefore the catalyst activity was reduced to some extent. The residual activity of the Co-Cu/CDC catalyst in both kinetic growth regimes can be explained as the result of the lower apparent activation energy of the intrinsic carbon growth rate (E_C) with respect to that of the catalyst deactivation (E_d), and therefore the carbon growth is still favored ($E_{C\text{-}LT}$ = 221.7 kJ/mol vs. $E_{d\text{-}LT}$ = 273.7 kJ/mol and $E_{C\text{-}HT}$ = 129.6 kJ/mol vs. $E_{d\text{-}HT}$ = 192.6 kJ/mol, respectively).

Figure 12(C) shows the variation of j_{C_0}, ψ_d and ψ_r with the methane partial pressure in the feed gas composition. All reactions were carried out in the CNTs growth regime at 750 °C using 14.3% H_2 (0.143 atm) and N_2 as balance gas (total flow rate 700 mL/min). As expected, the increase in the methane partial pressure enhanced the intrinsic carbon growth rate (j_{C_0}) because there are more carbon atoms available in the source to react, and therefore both the carbon flux and the CNTs precipitation are improved. On the other hand, while the catalyst deactivation parameter (ψ_d) slightly decreased with the methane concentration, the catalyst regeneration was more strongly affected. As previously noted, high methane contents cause an excessive amount of carbon atoms that cover the metal nanoparticles in the form of amorphous carbon. This fact increases the activation energy of the CNTs growth process and hampers the diffusion of H_2 to regenerate the surface of the metal nanoparticles, resulting in a decrease of the residual activity ratio ($a_S = \psi_r / (\psi_d + \psi_r)$) from 0.2 ($P_{CH_4}$=0.0714 atm) to 7.1x10^{-6} (P_{CH_4}=0.4286 atm).

Regarding the variation of the growth kinetic parameters with the hydrogen partial pressure, it was observed a general decrease in the values of j_{C_0}, ψ_d and ψ_r as the hydrogen content increases (**Figure 12(D)**). Evidently, the increase in hydrogen concentration causes a drop in the intrinsic carbon growth rate

(j_{C_0}) because the amount of carbon atoms available in the source becomes lower. Additionally, although the catalyst regeneration was expected to improve with the augmentation of the hydrogen partial pressure, both the deactivation (ψ_d) and regeneration (ψ_r) parameters were gradually reduced. Nonetheless, ψ_d and ψ_r took similar values along the experiments evaluated, which reflects the role of competitive adsorption between CH_4 and H_2 molecules at the metal nanoparticles surface on the residual activity of the catalyst. An evidence of this is that the a_s ratio did not vary significantly with the increase in the hydrogen partial pressure (a_s= 0.39 and a_s= 0.58 for P_{H_2}=0.0714 atm and P_{H_2}=0.4286 atm, respectively). In summary, the kinetic model successfully fitted the carbon evolution curves in both cases where catalyst did not suffer deactivation (formation regime of CNTs), and those in which the catalyst underwent a severe activity loss at high reaction temperatures.

4. CONCLUSIONS

In this work, a 23.9%Co-6.4%Cu catalyst supported on a carbon derived from cellulose (CDC) was proved to be active for the selective production of CNTs via catalytic decomposition of methane under moderated reaction temperatures (700−800 ºC). A maximum carbon productivity of 0.33 gC/gcat·h was achieved at 800 ºC under 28.6% CH_4:14.3% H_2. The increment of the reaction temperature above 800 ºC caused a transition in the CNTs growth towards the formation of two-dimensional graphite-like nanomaterials, as a result of a change in the balance between the nucleation and precipitation steps of the growth mechanism.

The kinetic model used was able to capture the main characteristics of the carbon growth, where there is a critical temperature at which the dominant route of carbon formation changes as a consequence of a multifaceted combination of the decomposition, diffusion, precipitation and deactivation-regeneration steps of the carbon species involved during the CCVD process. In all the cases studied, the values of the kinetic parameters obtained were consistent with the carbon mass evolution curves and the observations in the electron microscopy studies. This allowed the understanding of the effect of the operating conditions −reaction temperature and feed gas composition− on the mechanistic stages of the carbonaceous nanomaterial growth.

After exploring a large set of growth conditions in the CNTs formation regime it was found that the increase of the reaction temperature and the methane partial pressure enhance both the productivity and the carbon growth rate. Moderated reaction temperatures favor the diffusion of the carbon atoms through the metal nanoparticles and, at the same time, high methane concentrations increase the amount of carbon atoms available to react. This combined effect promotes the carbon driving force through the metal nanoparticles raising the CNTs growth at the metal−catalyst support interface. However, when using an extreme methane concentration, the CNTs grown become shorter and more defective because the formation of amorphous carbon is favored as well. On the other hand, the increase in the hydrogen partial pressure results in low CNTs productivities and lead to the formation of short CNTs with a poorly defined structure. This might be due to a non-homogeneous carbon precipitation along the catalyst metal nanoparticles induced by the competitive surface adsorption between CH_4 and H_2 molecules during CDM reaction.

Investigation on the catalyst deactivation was found to be dependent on the reaction temperature. Thus, below 800 ºC, the main causes of deactivation were the formation of fouling coke on the exposed surface of the metal nanoparticles at CNTs tip, and the steric hindrance caused by the large amounts CNTs grown. However, at high reaction temperatures, the deactivation was mainly a consequence of the reconstruction and sintering of the metal nanoparticles, which cause the formation of encapsulating graphite-like nanolayers and the decay of the CH_4 diffusion rate through them.

Electron microscopy and Raman characterization results suggest that CNTs productivity and quality are inversely correlated factors, in which high productivity involves an increase in the defects of the nanomaterials obtained, either due to amorphous carbon accumulation or CH_4/H_2 excess limiting the catalyst surface accessibility. Considering both factors, the best-operating conditions for growing CNTs with high productivity (0.29 gC/gcat·h) and quality (I_D/I_G=1.10, I_{2D}/I_G=0.13) were found at 750 °C under 28.6% CH_4:14.3% H_2:57.1% N_2.

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