



# Synthesis of graphenic nanomaterials by decomposition of methane on a Ni-Cu/biomorphic carbon catalyst. Kinetic and characterization results

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## ARTICLE INFO

### Keywords:

Graphene  
Few layer graphene  
Biomorphic carbon  
Ni-Cu  
Kinetic model  
Methane decomposition

## ABSTRACT

This work addresses the preparation and application of the synthesis of graphene in Ni-Cu catalysts supported on carbonaceous materials. The catalysts have been prepared by a biomorphic mineralization technique which involves the thermal decomposition, under reductive atmosphere, of commercial cellulose previously impregnated with the metallic precursors. The characterization results indicate that the preparation method leads to the formation of carbonaceous supports with a moderate microporosity (ca. 33% pore volume) and adequate surface area (343 m<sup>2</sup>/g), maintaining the original external texture. The catalytic performance of these materials was previously tested in liquid phase reactions (Zampieri et al., 2007 [7]). In order to extend the use of these catalysts, in this work we present a study corresponding to a gas phase reaction: the synthesis of graphenic nanomaterials by catalytic decomposition of methane (CDM). The influence of the reaction temperature and of the feed composition (i.e. %CH<sub>4</sub> and %H<sub>2</sub>) has been studied. The graphenic nanomaterials obtained after reaction were characterized by nitrogen adsorption-desorption isotherms, Raman spectroscopy and transmission electron microscopy (TEM). The results indicate that the carbonaceous nanomaterial with the highest quality is obtained operating at 950 °C and feeding 28.6% of CH<sub>4</sub> and 14.3% of H<sub>2</sub>. The evolution of the carbon mass during the reaction time was analysed using a phenomenological kinetic model that takes into account the main stages involved during the formation of carbonaceous nanomaterials (NCMs). The results obtained from the kinetic model along with the characterization results enable the influence of the operating variables on each stage of the carbonaceous nanomaterial formation to be discerned.

## 1. Introduction

Carbonaceous materials are widely used as catalysts [1] or catalytic supports [2,3] for a large variety of chemical reactions due to their textural and chemical properties: large surface area and porosity, good electrical conductivity, presence of a large variety of surface functional groups and relative chemical inertness [4]. An advantage of carbonaceous materials is that they can be prepared from renewable residual lignocellulosic biomass [3]. In this context, it has been suggested [3] that the success of processes derived from the biorefinery concept will require the design and preparation of new types of multifunctional catalysts, probably derived from emerging carbonaceous materials such as graphene (or graphene related materials), carbon nanotubes and carbon monoliths. In this context, biomimetic mineralization is one of the more interesting tools that uses the structures formed by a biological process, e.g. wood and lignocellulosic biomass, as templates for the synthesis of inorganic functional materials [5,6]. It offers the advantage of fabricating materials that are difficult to produce by top-down methods and/or have chemical compositions which cannot be

produced by self-assembly [7,8]. Thus, considering that wood is a multifunctional material structured on several levels of hierarchy, a large variety of ceramic microstructured materials can be prepared using different lignocellulosic materials as templates [9]. The preparation of these kinds of materials has been carried out by thermal decomposition in a reducing (or inert) atmosphere, at high temperature and high heating rates, of several lignocellulosic raw materials (e.g. cellulose, lignin, paper, cotton, fibres, etc.) that can be previously impregnated with catalytic metallic precursors [10]. Using this technique, it is possible in a single step to obtain catalysts formed by a biomorphic carbonaceous (BC) support with the metallic nanoparticles dispersed on its surface. This method of catalyst synthesis has outstanding versatility because it allows the use of different lignocellulose raw materials with a large variety of compositions and metal contents [11].

The catalytic decomposition of methane (CDM) can be used to obtain pure hydrogen and, depending on the operating conditions selected, very high value-added carbonaceous nanomaterials such as single or multi-wall carbon nanotubes or graphene [12–14]. This

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<http://dx.doi.org/10.1016/j.cattod.2017.03.056>

Received 2 November 2016; Received in revised form 27 February 2017; Accepted 27 March 2017  
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process can be applied in the production of CO<sub>x</sub> free hydrogen for use, for example, in fuel cells, where the presence of CO is a poison for the electro-catalyst [15]. In this work, we use the CDM process to study the feasibility of Me/BC catalysts to synthesize specifically graphene and/or graphenic materials, such as few layer graphene (FLG) [16,17]. Nowadays, graphene and graphenic nanomaterials are attracting substantial research interest due to their exceptional properties such as high electrical conductivity, good thermal stability and excellent mechanical strength [18]. Given these properties, the use of graphene is being intensively studied for a large number of potential fields and applications such as electronics [19], photonics [20], sensors [21], catalysts [22], energy storage [23], or the manufacture of composite materials [24].

A key factor for the controlled production of graphene and graphenic nanomaterials is to understand the formation mechanism. In recent years, our research group has developed kinetic models to investigate the kinetics of growth of carbon nanotubes and carbon nanofibers [25–32]. The phenomenological models developed are based on the following steps: i) hydrocarbon decomposition over the exposed surface of the metallic nanoparticles dispersed on the support, ii) diffusion and precipitation of carbon atoms along the metallic nanoparticles, iii) nanocarbonaceous material growth, and iv) catalyst deactivation. These models have been successfully applied to study the data obtained from different reactions using different carbon sources and catalysts [25,27,31].

In this work, we present the results of graphene and FLG formation by the decomposition of methane on a catalyst of Ni-Cu supported on Biomorphic Carbon. The composition of the active phases, Ni-Cu, was chosen in order to combine the high productivity of Ni based catalysts, due to the high carbon solubility in this metal [33], and the excellent graphene quality obtained with Cu based catalyst resulting from the low carbon solubility in this metal [28,34,35]. In order to optimize the CDM process, the effect has been studied of the main operational conditions (reaction temperature, feed composition and reaction time) on the growth rate and on the quality of the graphenic nanomaterials obtained. Finally, the application of the kinetic model to analyse the data obtained in a thermobalance is discussed in the context of the reaction mechanism.

## 2. Experimental

### 2.1. Materials

The raw material used to prepare the biomorphic catalyst was cellulose provided by Sigma Aldrich (ref: C6288). The metal precursors used were Ni(II) nitrate hexahydrate supplied by Alfa Aesar (ref: 10816) and Cu(II) nitrate hydrate provided by Sigma Aldrich (ref: 61194).

### 2.2. Catalysts preparation

For the preparation of the Ni-Cu/Biomorphic carbon catalyst, the cellulose was dried at 100 °C overnight and then impregnated by incipient wetness with the appropriate amounts and concentrations of Ni and Cu aqueous solutions. After impregnation, the solid was dried at 80 °C overnight and then thermally decomposed in a reducing atmosphere (15% H<sub>2</sub>, 85% N<sub>2</sub>) at 800 °C during 75 min. The decomposition temperature was reached at a heating rate of 42 °C/min. Finally, the catalyst was milled and sieved to obtain a homogeneous particle size distribution, ranging between 80–200 micrometres, and stored under N<sub>2</sub> atmosphere.

### 2.3. Catalytic decomposition of methane

The CDM reaction was carried out at atmospheric pressure in a thermobalance (CI Electronics Ltd., UK, model MK2) operated as a

differential reactor (i.e. methane conversions less than 10%), and equipped with mass flow and temperature controllers. This experimental system allows continuous recording of the variations of sample weight and temperature during reaction. The reaction conditions were as follows: sample weight: 25 mg; total flow-rate: 700 mL/min.; temperature range: 850–975 °C; feed composition range: %CH<sub>4</sub>: from 1.4% to 42.9%, %H<sub>2</sub>: from 0% to 28.6% and N<sub>2</sub> until balance; reaction time: from 1 to 120 min.

### 2.4. Catalysts and carbonaceous nanomaterials characterization

The catalysts and carbonaceous nanomaterials were characterized in order to know their textural and structural properties and the type of carbon structures formed (e.g. graphene, few layer graphene (FLG), graphite, etc.). The thermogravimetric analyses in air (TGA-Air) were carried out with a Mettler Toledo TGA/SDTA 851 analyser, using 50 mL/min. This technique allows the calculation of the amount of Ni and Cu deposited on the biomorphic carbon support after the thermal decomposition of the cellulose. After the combustion in the TGA-Air experiment the solid residue consists of NiO, CuO and ashes. Knowing the initial amount of Ni and Cu, the final percentage of each component can be calculated. This protocol was repeated three times with each carbonaceous catalyst in order to determine the variability of this procedure. Specific area and porosity were obtained from nitrogen adsorption–desorption isotherms at 77 K using a TriStar 3000 instrument (Micromeritics Instrument Corp.). BET specific surface areas were measured from the adsorption branches in the relative pressure range of 0.01–0.10. The micropore volume estimation was made by means of the Dubinin-Radushkevich method [36].

The X-ray diffraction (XRD) patterns were recorded within the range of 5–90° (2θ) with a Rigaku D/Max 2500 apparatus operated at 3.2 kW (40 kV, 80 mA) and with a rotatory anode of Cu using Cu K<sub>α</sub> radiation. For the graphenic materials formed during the reaction, the crystallite size along the c-axis, L<sub>c</sub>, and the interlamellar distance, d<sub>002</sub>, were obtained from the (002) reflection at 2θ = 26° of the XRD patterns [37]. From this value, the number of graphene layers of each sample, n, was calculated as:  $n = (L_c/d_{002}) + 1$  [38,39].

Transmission electron microscopy (TEM) micrograph images were recorded in a FEI Tecnai T-20 microscope, operated at 200 kV. Scanning electron microscopy (SEM) micrograph images were captured in a FEI Inspect F50 microscope, operated at 10 kV. The carbonaceous nature of the catalyst support and of the materials formed during the reaction was characterized by Raman spectroscopy using a WiTec Alpha300 Confocal Raman Microscope, with a 532 nm laser excitation beam.

## 3. Results and discussion

### 3.1. Characterization of fresh catalyst

The Ni-Cu/BC catalyst was prepared with nominal contents (wt.%) of 5% Ni and 1% Cu regarding to the initial amount of cellulose. After preparation, the final amounts of metal, calculated from the TGA-air data, were ca. 40% and 8% with in relation to the final amount of biomorphic carbon formed. Replicated TGA measurements gave metal composition values with variations of less than 3%, confirming the validity of this procedure. Obviously, due to the loss of carbonaceous material during the thermal decomposition stage, the weight percentages of Ni and Cu are substantially increased (8 times in this case) in the final catalysts. In fact, the thermal decomposition is a key factor for controlling the final content and dispersion of the metal(s) on the surface of the catalyst.

Fig. 1 shows the N<sub>2</sub> adsorption/desorption isotherm for the Ni-Cu/BC catalyst. According to the IUPAC classification, the isotherm corresponds to I- and II-types, with a hysteresis loop of type H3 or H4 [40,41]. These types of hysteresis loops are characteristic of disordered

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