



# Effect of the synthesis conditions of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts on the biogas decomposition to produce H<sub>2</sub>-rich gas and carbon nanofibers



S. de Llobet, J.L. Pinilla, R. Moliner, I. Suelves\*

Instituto de Carboquímica, CSIC, C/Miguel Luesma 4, 50018 Zaragoza, Spain

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## ABSTRACT

The utilization of biogas as carbon source for the co-production of filamentous-like materials and syngas is proposed. Catalysts with different Ni:Al molar ratios, Al<sub>2</sub>O<sub>3</sub> supports and preparation methods were synthesized. The suitability of the catalysts was analyzed considering activity, stability and carbon yield. Catalysts showed a good performance and similar results according to syngas compositions were obtained. However, some differences related to stability over time and carbon yields were detected. TPR analysis and TEM micrographs of the fresh catalysts revealed the presence of two different Ni particles: large Ni particles with low metal support interaction (MSI) that favoured the formation of encapsulating carbon and small Ni particles inserted in the Al<sub>2</sub>O<sub>3</sub> structure with a greater MSI that lead to nanofilamentous carbons formation. Generally both kinds of Ni particles were observed in all catalysts, however their relative abundance was dramatically affected by the Al<sub>2</sub>O<sub>3</sub> employed, the preparation method and the Ni:Al molar ratio.

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## 1. Introduction

Biogas is generated from the anaerobic digestion of the organic matter (agricultural wastes, landfills and urban and industrial wastewaters). Commonly, biogas is released into the atmosphere or directly burned in an internal combustion engine [1]. Most recently, different alternatives for biogas utilisation have been proposed such as bio-methane production [2], combustion in a dual fuel diesel engine [3,4] or as feedstock in the dry reforming of CH<sub>4</sub> (DRM) [5,6]. In the latter case, high CO<sub>2</sub> concentration, up to 50%, makes biogas a perfect choice to be used as feedstock, resulting in a suitable syngas that can be used for hydrogen production [7,8], to feed a solid oxide fuel cell [9] or for hydrocarbons synthesis via the Fischer–Tropsch process [10]. Besides this, DRM using biogas can be classified as environmentally friendly due to the renewable character of the feedstock. However, the utilization of biogas in the DRM faces many challenges, being the energy required to carry out the process (CH<sub>4</sub> + CO<sub>2</sub> → 2H<sub>2</sub> + 2CO, ΔH° = 247 kJ mol<sup>-1</sup>), catalyst poisoning caused by biogas minor compounds [11–13] and catalyst deactivation by carbon deposition [14] among the most important.

Catalyst deactivation is commonly associated to carbon deposition, and efforts in DRM are focused on the synthesis of catalysts

with low amounts of active metals in order to generate small crystallites that inhibit carbon formation [15]. However, only encapsulating carbon is responsible of catalyst deactivation [16,17]. During DRM, other carbon structures can be obtained [18,19], being the nanofilamentous carbons (NCs) of special interest. Even though NCs are not directly responsible of catalyst deactivation, they can cause reactor plugging [20]. This situation can be solved by using a fluidized bed reactor instead of a fixed bed reactor [21]. NCs are high valuable materials [22] that depending on their structure and surface properties can be employed in different applications [23,24]. The condition of the DRM using biogas as feedstock can be adjusted so that the formation of NCs without catalyst deactivation can be achieved. Therefore, biogas is used as carbon source for the co-production of filamentous-like materials and a H<sub>2</sub> rich gas with very interesting combustion properties [25]. This biogas valorization route has been previously studied by our group [25–27] and it is known as catalytic decomposition of biogas (CDB). Conceptually, this process is similar to the catalytic decomposition of methane (CDM) [21,28–30]. Metals belonging to groups 8–10 (Ni, Co and Fe) and supported on different metal oxides (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> or MgO) have been traditionally used in the CDM to generate NCs [31]. From the carbon yield point of view, catalyst metal content plays an important role. High metal loading catalysts are favorable for hydrogen and NCs production [30]. Ermakova et al. [32] and Li et al. [33] observed that carbon yield was proportional to the Ni concentration in the catalyst. However, Takenaka et al. [34]

\* Corresponding author. Tel.: +34 976 73 3977; fax: +34 976 73 3318.  
E-mail address: [isuelves@icb.csic.es](mailto:isuelves@icb.csic.es) (I. Suelves).

reported a great carbon yield ( $491 \text{ gC g}_{\text{Ni}}^{-1}$ ) with a 40% Ni/SiO<sub>2</sub> catalyst. Support also plays an important role. Unsupported Ni catalysts barely generate NCs when CH<sub>4</sub> is decomposed [33,35], while a production up to  $385 \text{ gC g}_{\text{Ni}}^{-1}$  was reported when using a 90% Ni/SiO<sub>2</sub> catalyst [32]. Many studies have also related NCs growth with Ni crystal domain size. Chen et al. [36] observed an optimal Ni crystal size of 34 nm while Pinilla et al. [37] obtained the best results with catalysts with a Ni crystal domain size after reaction between 10 and 20 nm. Little information considering NCs production from biogas has been published. Besides previous works carried out by our research group [26,27,38], for the best of our knowledge, only Corthals et al. [39] considered biogas as an interesting source for NCs generation. Carbon yields up to 37.2 and  $19.1 \text{ gC g}_{\text{Ni}}^{-1}$  were achieved with a Ni(30)SrTiO<sub>3</sub> catalyst when decomposing biogas at 600 °C with a CH<sub>4</sub>:CO<sub>2</sub> ratio of 2 and 1, respectively.

The purpose of this work is to synthesize different Ni/Al<sub>2</sub>O<sub>3</sub> catalysts to study how their properties can affect its performance in the CDB. Thus, two different Ni:Al molar ratios (30:70 and 67:33), two different Al<sub>2</sub>O<sub>3</sub> and two different preparation methods (impregnation and fusion) were used to prepare catalysts with different characteristics. The suitability of the catalysts was analyzed considering activity, stability and carbon yield. Additionally, the NCs produced were characterised by different techniques (XRD, N<sub>2</sub> adsorption, TEM) in order to address the effect of the different catalysts characteristics on the NCs properties and morphology.

## 2. Experimental

### 2.1. Aluminas synthesis

Two aluminas with different surface properties were used as support. An organized mesoporous alumina (OMA-Al<sub>2</sub>O<sub>3</sub>) was synthesized according to a procedure available in [40]. Briefly, aluminium isopropoxide was dissolved in ethanol and propanol with 1, 8 and 6 molar ratios, respectively. Then, a non-ionic surfactant (Pluronic F127) was added in a 0.01 molar ratio to the mixture with constant stirring at 50 °C. When the surfactant was dissolved, water was added in an 11 molar ratio to create an emulsion. All molar ratios are expressed in reference to aluminium isopropoxide. The surfactant and solvents were later removed by subsequent drying steps at 150 and 350 °C and through calcination at 600 °C for 4 h. The second alumina (SIG-Al<sub>2</sub>O<sub>3</sub>), was directly obtained after the calcination of Sigma–Aldrich aluminium nitrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) at 450 °C for 8 h.

### 2.2. Catalysts synthesis

Four different catalysts were synthesized, two with a Ni:Al molar ratio of 67:33 and two with a Ni:Al molar ratio of 30:70. Catalysts with a high Ni content (67 mol.%) were prepared by the fusion method previously described in [41]. Summarizing, nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) was mixed and crushed with one of the aforementioned aluminas (OMA-Al<sub>2</sub>O<sub>3</sub> or SIG-Al<sub>2</sub>O<sub>3</sub>), followed by calcination of the resulting mixture at 450 °C for 8 h. Catalysts with a low Ni content (30 mol.%) were prepared by the incipient wetness impregnation method with impregnation of an aqueous solution of the nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O). The resultant slurry was dried at 110 °C during night and calcined in air flow at 450 °C for 8 h. In all cases, the powder samples obtained after calcination were ground and sieved to allow the selection of 100–200 μm particle size.

Calcined catalysts were named as NiO-X-Y, where “X” refers to the Ni molar content (30 or 67) and “Y” to the alumina employed (OMA or SIG). Therefore, NiO-30-OMA stands for a catalyst with a Ni:Al molar content of 30:70 and prepared with the OMA-Al<sub>2</sub>O<sub>3</sub>.

**Table 1**  
Synthesis parameters of the prepared catalysts.

Name	Ni:Al molar ratio	Al <sub>2</sub> O <sub>3</sub>	Method
NiO-30-OMA	30:70	OMA	Impregnation
NiO-30-SIG	30:70	SIG	Impregnation
NiO-67-OMA	67:33	OMA	Fusion <sup>a</sup>
NiO-67-SIG	67:33	SIG	Fusion <sup>a</sup>
NiO-67-SIG2	67:33	SIG	Fusion <sup>b</sup>

<sup>a</sup> Prepared by mixing Ni nitrate with the previously calcined Al<sub>2</sub>O<sub>3</sub>.

<sup>b</sup> Prepared by mixing at the same time Ni and Al nitrates.

Reduced catalysts are named in the same way but substituting “NiO” by “Ni”.

Results obtained with the NiO-67-SIG catalyst were very poor as compared with the other catalysts, especially in terms of carbon yield. For that reason, a fifth catalyst with a Ni:Al molar ratio of 67:33 and named NiO-67-SIG2 was synthesized. The preparation method was similar to that employed to prepare the NiO-67-SIG catalyst but in this case both nitric salts of Ni and Al were crushed and mixed together, followed by calcination of the mixture at 450 °C for 8 h. A summary report of the different catalysts synthesized is shown in Table 1.

### 2.3. Experimental procedure

To carry out the experiments, a synthetic CH<sub>4</sub>:CO<sub>2</sub> mixture with a volume ratio of 60:40 was used. This volume ratio was chosen in order to mimic biogas composition. Catalytic experiments were carried out in a fixed-bed quartz reactor, 15 mm i.d, 750 mm height, fed by the top and heated by an electric furnace. A Peltier cooler was placed after the reactor to condense steam formed during the reaction. Tests were performed at a reaction temperature of 700 °C and 0.05 g of catalyst were loaded in the reactor. Before each test, catalysts were in-situ reduced with an H<sub>2</sub> flow of 100 mL min<sup>-1</sup> at 550 °C for 1 h. Then, a synthetic biogas flow rate of 100 mL min<sup>-1</sup> was fed into the reactor for 3 h. The weight hourly space velocity (WHSV, defined here as the total flow rate at normal conditions per gram of catalyst initially loaded) was 120 L<sub>N</sub> g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>.

In order to determine the outlet gases composition (syngas composition), bag samples were taken and analysed by means of gas chromatography in a micro GC Varian CP4900 equipped with two packed columns (Molecular Sieve and Porapack) and a TCD detector to quantify H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub> concentrations.

CH<sub>4</sub> conversions,  $X_{\text{CH}_4,t}$  (Eq. 1), reaction rates,  $(-r_{\text{CH}_4,t})$  (Eq. 2) and sustainability factors,  $S.F._{\text{CH}_4}$  (Eq. 3) were calculated as follows:

$$X_{\text{CH}_4,t} = \frac{(F_{\text{in,CH}_4,t} - F_{\text{out,CH}_4,t})}{F_{\text{in,CH}_4,t}} \times 100 \quad (1)$$

$$(-r_{\text{CH}_4,t}) = \frac{X_{\text{CH}_4,t}}{W/F_{\text{in,CH}_4,t}} \quad (2)$$

$$S.F._{\text{CH}_4} = \frac{(-r_{\text{CH}_4,180 \text{ min}})}{(-r_{\text{CH}_4,5 \text{ min}})} \quad (3)$$

In Eq. (1),  $F_{\text{in,CH}_4,t}$  and  $F_{\text{out,CH}_4,t}$  represent CH<sub>4</sub> molar flow rates entering (in) or leaving (out) the reactor at a certain reaction time ( $t$ ). In Eq. (2),  $W$  represents the grams of catalyst or the grams of Ni, depending on the basis of calculation used, initially loaded in the reactor. In Eq. (3),  $-r_{\text{CH}_4,180 \text{ min}}$  and  $-r_{\text{CH}_4,5 \text{ min}}$  represent CH<sub>4</sub> reaction rates after 180 and 5 min time on stream (TOS), respectively. CH<sub>4</sub> sustainability factor ( $S.F._{\text{CH}_4}$ ) was used to compare the stability of the different catalysts over time. If catalyst activity is maintained, the value of the  $S.F._{\text{CH}_4}$  will be one. On the other hand, if the catalyst is completely deactivated after 180 min TOS, this value will be zero.

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