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Ni-Co bimetallic catalysts for the simultaneous production of carbon nanofibres and syngas through biogas decomposition

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ABSTRACT

Catalytic Decomposition of Biogas (CDB) is proposed to obtain bio-based materials from biogas in form of valuable carbon nanofilaments together with a syngas in a typical ratio close to 1. NiCo bimetallic catalysts with different Ni/Co ratio were studied in the CDB at different reaction temperatures and WHSV, and the results were related to the catalyst characterization and to the type of carbon formed during reaction. Bimetallic catalyst with an equimolar Ni/Co composition showed the highest carbon yield and sustainability factor at 700 °C and 120 $L_N\,g_{cat}^{-1}\,h^{-1}$. However, if we attend to the carbon efficiency, lower temperatures and WHSV favour carbon formation. Its good performance was related to a synergistic effect between Ni and Co: the presence of Ni favoured surface carbon diffusion while the presence of Co favoured soot and carbon particles oxidation via redox. The combination of both effects allows that the NiCo-33.5-r catalyst was able to produce an important amount of carbon nanofilaments maintaining good catalyst stability.

1. Introduction

Biogas is a renewable energy source composed mainly by CH_4 and CO_2 produced from the anaerobic digestion of the organic matter (agricultural wastes, landfills, urban and industrial wastewaters). Traditionally, biogas has been considered a non-value by-product which was generally burned in flares to prevent human and environmental risks and then released into the atmosphere as CO_2. Most recently, different alternatives for biogas utilization have been proposed such as the generation of heat, electricity, combined heat and power or bio-methane production that can be used as feedstock in different processes [1]. Another interesting option is the production of synthesis gas (syngas), which is composed by a mixture of H_2 and CO and constitutes the base of the C1 chemistry [2]. Among the different processes by which syngas can be obtained from biogas, dry reforming of methane (DRM) is the most promising one due to the presence of both methane and carbon dioxide in biogas. One of the most important challenges of DRM is the deactivation of the catalysts due to the formation of carbon during CH_4 decomposition and CO_2 disproportionation reactions [3–5]. Problems associated with carbon deposition are even of more significance when biogas is used [6]. Biogas generally presents CH_4:CO_2 ratios higher than one, eventually provoking larger amount of carbon depositions that rapidly deactivate the catalysts. However, during hydrocarbons decomposition, different kinds of carbon are formed and not all of them are directly responsible of catalyst deactivation [7–10]. According to Menon et al. [11], the kind and location of carbon atoms are more important than the amount produced when catalytic activity is considered. Generally, only encapsulating carbon is directly responsible of catalyst deactivation due to the covering of the active centres, while other carbon structures, such as carbon nanofilaments, only cause operating problems when they are produced in large quantities since reactor blockage can take place. These problems can be avoided by using a suitable reactor configuration, such a fluidized bed reactor [12]. Carbon nanofilaments, including carbon nanofibers (CNF) and carbon nanotubes (CNT), are filaments with diameters ranging from 1 to 200 nm and lengths of several micrometres formed by the stack of graphene layers and classified by their orientation. Carbon nanofilaments have attracted the interest of the scientific community due to their unique properties [13]. Among them, high thermal and electricity conductivity and interesting textural properties make them a promising material in a number of research areas such as catalysis [14,15], energy storage [16] or additive in polymer composites [17]. The synthesis of these materials from a renewable source such as biogas instead of other non-renewable feedstocks typically used would allow them to be classified as bio-based materials.

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Taking advantage of the possibility of obtaining bio-based materials from biogas in form of valuable carbon nanofilaments together with a syngas in a typical ratio close to 1, a process named Catalytic Decomposition of Biogas (CDB) was recently proposed by our research group [6]. Previous studies focused on the influence of the process variables (space velocity, temperature, CH_4/CO_2 partial pressures) [18,19] using a massive Ni/Al_2O_3, which allowed to stablish the optimum conditions to obtain high CH_4 conversions and carbon in form of fishbone-like CNF avoiding catalyst deactivation. The use of different active phases such as Fe and Co revealed the formation of different carbon structures (parallel and chain-like CNF), although catalytic performance in terms of methane conversion and filamentous carbon yield was significantly lower as compared to the Ni based catalysts mainly due to the formation of encapsulating carbon [20].

The utilization of bimetallic catalysts in the dry reforming of CH_4 has been extensively studied during the last years [21,22]. The promising results obtained have been related to a synergetic effect between the two metals [23–25] that leads to a better dispersion and reduction of the active phase and to the modification of the physicochemical properties of the resulting catalyst due to the formation of a solid solution. In particular, it has been reported that NiCo bimetallic catalysts presented higher cooking rates in the DRM than a Co monometallic catalyst [23]. Since the aim of CDB is to obtain high carbon yields, in this work we focused on the performance of NiCo bimetallic catalysts. Their catalytic performance in the CDB was analyzed considering CH_4 and CO_2 conversions, reaction rates, catalyst stability and carbon yield. Additionally, the CNF produced were characterized by transmission electron microscopy (TEM) in order to address the effect of the variation of the Ni/Co ratio.

2. Experimental

2.1. Catalysts synthesis

Three bimetallic catalysts were synthesized by the fusion method, previously described in [26], employing $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ as precursors. Ni and Co act as active phases (AP) and Al_2O_3 as textural promoter. The AP:Al molar ratio was kept at 67:33 and the Ni:Co molar ratio was varied, resulting in three different Ni:Co:Al molar ratios, namely: 50:17:33, 33.5:33.5:33 and 17:50:33. Catalysts are denoted as NiCo-X-s, where "X" refers to the total Ni molar content (50, 33.5 or 17%) and the suffix "s" to the catalyst state: calcined ("c") or reduced ("r"). Thus, NiCo-50-r corresponds to the reduced bimetallic catalyst with a Ni:Co:Al molar ratio of 50:17:33. Additionally, two monometallic catalysts were synthesized by the same method but employing Ni or Co alone as active phase for comparison purposes. These catalysts present a AP:Al molar ratio of 67:33 and are named Ni-67-s and Co-67-s.

2.2. Experimental procedure

To carry out the experiments, a synthetic $CH_4:CO_2$ 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 a weight hourly space velocity (WHSV, defined here as the total flow rate at normal conditions per gram of catalyst initially loaded) of 120 $L_N\,g_{cat}{}^{-1}\,h^{-1}$. Before each test, 0.05 g of oxidized catalyst were loaded in the reactor and in-situ reduced with a H_2 flow of 100 mL min^{-1} for 1 h. Different reduction temperatures were chosen for each catalyst according to experimental data and TPR analysis: 550 °C for Ni-67-c and NiCo-50-c, 600 °C for NiCo-33.5-c and 650 °C for NiCo-17-c and Co-67-c. Then, a synthetic biogas flow rate of 100 mL min^{-1} was fed into the reactor for 3 h. Additional experiments were carried out at 600 and 700 °C and 30 $L_N\,g_{cat}{}^{-1}\,h^{-1}$ with the NiCo-33.5-c and monometallic catalysts.

CH_4 conversions, $X_{CH4,t}$ (Eq. (1)), reaction rates, $(-r_{CH4,t})$ (Eq. (2)) and sustainability factors, $S.F._{CH4}$ (Eq. (3)) were calculated as follows:

$$X_{CH4,t} = \frac{\left(F_{in,CH4,t} - F_{out,CH4,t}\right)}{F_{in,CH4,t}} * 100 \tag{1}$$

$$(-r_{CH4,t}) = \frac{X_{CH4,t}}{W/F_{in,CH4,t}} \tag{2}$$

$$S.F._{CH4} = \frac{(-r_{CH4,180\mathrm{min}})}{(-r_{CH4,5\mathrm{min}})} \tag{3}$$

in Eq. (1), $F_{in,CH4,t}$ and $F_{out,CH4,t}$ represent CH_4 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 used, initially loaded in the reactor (oxidized state). In Eq. 3, $-r_{CH4,180min}$ and $-r_{CH4,5min}$ represent CH_4 reaction rates after 180 and 5 min time on stream (TOS), respectively. CH_4 sustainability factor ($S.F._{CH4}$) was used to compare the stability of the different catalysts over time. If catalyst activity is maintained, the value of the $S.F._{CH4}$ is one. On the other hand, if the catalyst is completely deactivated after 180 min TOS, this value is zero.

Outlet gases composition (syngas composition) was determined by taking bag samples for 2 min and analysing them 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_2, CO, CH_4 and CO_2 concentrations.

2.3. Characterization techniques

The textural properties were measured by N_2 adsorption at 77 K in a Micromeritics Tristar apparatus. The specific surface areas (S_{BET}) and pore volumes (V_p) were calculated by applying the BET method to the respective N_2 adsorption isotherms and the average pore diameter (APD) was calculated with the BJH method based on the adsorption branch of the N_2 isotherm.

XRD patterns of the calcined, reduced and spent catalysts were acquired in a Bruker D8 Advance Series 2 diffractometer equipped with a Cu (λ: 0.154 nm) anode and a secondary graphite monochromator, using a θ-θ configuration. The angle range scanned was 20–80°, using a counting step of 0.05° and a counting time per step of 3 s. The powder XRD patterns were further processed using the accompanying DIFRAC PLUS EVA 8.0 and TOPAS software. For lattice parameter (a) calculations an internal standard (LiB_6) was used to correct the height error.

The reducibility of the calcined catalysts was studied by temperature programmed reduction (TPR) analysis. The respective reduction profiles were obtained in an AutoChem Analyzer II 2920 (Micromeritics) provided with a TCD from a sample amount of 10 mg and using a heat rate of 5 °C min^{-1} within a temperature range from room temperature to 1050 °C and under a flow rate of 50 mL min^{-1} of a H_2 (10%)/Ar mixture.

The morphology of the reduced and spent catalysts was studied by transmission electron microscopy (TEM) in a JEOL-2000 FXII microscope operating at 200 keV. Standard TEM copper grids covered by a lacey amorphous carbon film were used as sample holders. The TEM was coupled to an INCA 200-X SIGHT EDX analyser operating between 136 eV and 5.9 keV.