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Growth of carbonaceous nanomaterials over stainless steel foams. Effect of activation temperature

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ABSTRACT

Some of the problems that occur during the operation of chemical reactors based of structured catalytic substrates, as monoliths, foams, membranes, cloths, fibres and other systems, are related to the preparation of long term stable coatings. Frequently, the deposition of the catalytic layer is carried out by washcoating, requiring this step a cautious attention, especially in the case of complex geometries, like of that of foams or cloths. In the case of the deposition of layers of carbonaceous materials (CNMs), an alternative route, avoiding the washcoating, it is their direct growth by catalytic decomposition light hydrocarbons (also called CCVD), over the surface of the metallic substrate. In this case, if the metallic substrate is of stainless steel, it already contains the catalytic active phases like Fe and Ni.

In order to optimize the process of CNMs growth over structured metallic substrates, we are studying the effect of the main operational variables of the ethane decomposition reaction on stainless steel foams. In this contribution we present a study of the influence of the temperature of the activation (oxidation and reduction) stage on the type and morphology of the carbonaceous materials formed. The results obtained allow us to determine the optimal operating conditions to maximize the amount and the selectivity of the process to obtain a given type of CNM.

1. Introduction

The potential possibilities of application of the outstanding properties of carbonaceous nanomaterials (CNMs), like carbon nanotubes (CNTs), carbon nanofibers (CNFs) or graphene, have motivated the huge research effort carried out during the last twenty five years in practically all fields of nanoscience and nanotechnology [1–3]. These carbonaceous nanomaterials are compounds with unique mechanical, electronic, chemical and physical properties [4–6].

Among the different technologies used, catalytic chemical vapour deposition (CCVD) has become the main technique for the synthesis of CNMs, due to its easiness of scale-up, reducing significantly the costs of production [7]. During the CCVD process of decomposition of light hydrocarbons over the surface of the metallic nanoparticles (e.g. Ni, Co, Fe) dispersed on a high surface area carrier, the CNMs are obtained in a powdered form [2,8], which is a major drawback in many applications as for example, as catalytic supports in structured reactors.

The structured catalytic substrates, as monoliths, foams, membranes, cloths, fibres and other systems, due to their flexibility, have been applied to two- and three-phase reactions, showing substantial improvements of mass and heat transfer, pressure drop and productivity [9,10]. However, these systems present problems related to the preparation of long term stable coatings [9,10]. Frequently, the deposition of the catalytic layer over the surface of metallic substrate is carried out by means of a washcoating stage, requiring this step a cautious attention, especially in the case of complex geometries, like of that of foams or cloths [11–16].

In the case of the deposition of layers of carbonaceous materials, an alternative route, that avoids the washcoating, it is their direct synthesis over the surface of the metallic substrate, e.g. stainless steel (SS), taking advantage of the stainless steel contains some of the active components, like Fe and Ni, that are able to catalyse the hydrocarbon decomposition [17–25].

The hybrid system formed by CNMs grown over monoliths, foams or meshes has been used as filters, adsorbents, sensors, reinforcements of polymers or composites for enhanced heat transfer [26–32]. For example, the CNFs grown by CCVD on the surface of

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Table 1
Composition of the stainless steel AISI 316L foam.

	%Ni	%Cr	%Mn	%Fe	%Mo	%C
Bulk (before rxn.), by A.A.	10.8	13.6	1.44	70.4	n.d.	n.d.
Surface (after activation, [a]), by EDX	5.3	10	1.2	76	0.7	1.56

[a] Oxidation and reduction at 800 °C.

SS foam boost the heat transfer efficiency from 30% to 75%, due to the enlargement of the surface area provided by the CNFs. Therefore, the combination of metallic filters with CNFs coatings results in composites with a high thermal conductivity [33].

Recently, Reichelt et al. have studied the use of this type of devices as catalytic reactors in several reactions [9]. In an example of their application during the reaction of ozone oxidation using SS meshes [20], the electrodeposition of Co nanoparticles over the surface of MWCNT, previously grown on the SS, increases notoriously the kinetic constant of the reaction. This fact was due to the higher dispersion attained by the Co particles, compared with the case of deposition over the bare mesh [20]. In the same framework, recently we have developed a study of the selective oxidation of CO in the presence of H_2, using Pt nanoparticles deposited over CNFs. The CNFs was directly grown, by catalytic decomposition of ethanol, over the inner surface of the channels of microreactors, made of stainless steel [34]. The results obtained with the Pt/CNF/microreactor system clearly outperformed those obtained with a typical fixed bed configuration, operated at the same space velocity, attaining total CO conversion at lower temperatures (ca. 50 °C).

With the aim of developing these devices in order to be used in new applications, our main goal is the optimization of the CNMs growth process over structured metallic substrates. With this goal, we are studying the kinetics of growth of carbonaceous nanomaterials during the reaction of ethane decomposition over foams of stainless steel. In this contribution we present a study of the influence of the temperature of the activation stage on the type and morphology of the carbonaceous materials formed. The activation of the fresh foam was made carrying out consecutive treatments of oxidation and reduction at high temperature. The foam and the CMNs obtained have been characterized, before and after reaction, to know the changes on the foam structure, and also the type and characteristics of the carbonaceous nanomaterials formed. The results obtained allow us to determine the optimal operating conditions to maximize the amount and the selectivity of the process to de desired type of CNMS.

2. Material and methods

The stainless steel foam used (AISI 316L) was supplied by Goodfellow® (www.goodfellow.com, ref: FE243825). The foam is a rigid three-dimensional structure with large pores that allows the feed stream easily flow with low pressure drop, and showing large superficial surface. The main characteristics are: thickness: 6.35 mm; density: 0.55 g cm^{-3}; porosity: 93%; pores/cm: 24. The foam was cut in 10 mm × 10 mm pieces to be placed inside the reactor.

The bulk chemical composition of the foam was measured by atomic absorption in a VARIAN spectrophotometer (model SPECTRAA 110). In Table 1 is presented the bulk composition, determined by atomic absorption (AA) of the foam. As mentioned above, the presence of large amounts of Fe (ca. 70%) and Ni (ca. 10%) allows to the foam be used as a suitable catalyst to carry out the reaction of ethane decomposition [35–40].

After reaction, the foam as the carbonaceous materials obtained were characterized by transmission and scanning electron microscopy, X-ray diffraction, Raman spectroscopy and Energy dispersive X-ray spectroscopy (SEM-EDX).

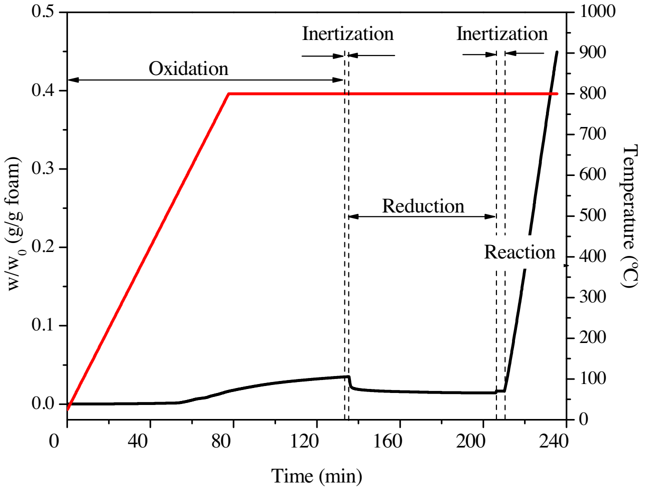

Fig. 1. Evolution of weight along the stages of a typical CCVD experiment.

TEM images were recorded in a FEI Tecnai T-20 microscope, operated at 200 kV. Scanning electron microscopy (SEM) micrographs images were captured in a FEI Inspect F50 microscope, operated at 10 kV. This microscope was also used to measure the weight ratio of the components in the surface of the stainless steel foam with an energy dispersive X-ray (EDX). The X-ray diffraction (XRD) patterns were recorded within the range of 10–90° (2θ), in a Rigaku/Max Cu rotatory anode equipment, operating at 40 kV and 80 mA using Cu Kα radiation. Raman spectra were taken using the 532 nm laser excitation beam on a WiTec Alpha300Confocal Raman Microscope.

The adherence of the carbon coatings was evaluated using a method described by Yasaki et al. [41] that is based in the measurement of the weight loss caused by exposure to ultrasound. This method was also applied by Valentini et al. [42] for alumina layers on ceramic and metallic monolithic supports to comparatively measure changes in the washcoating adherence when silica was used as a binder. Boix et al. [43] also used the method for PtCoFerrierite-washcoated cordierite monoliths. The coated foam was immersed in water inside a Pyrex vessel and then kept in an ultrasound bath at 50 °C for 1 h. After that, the sample was dried during 24 h at 393 K. The weight of the sample was measured after and before the ultrasonic treatment.

Ethane decomposition reaction was carried out in gas phase at 800 °C and at atmospheric pressure, using a thermobalance (CI Electronics Ltd., UK, model MK2) as differential reactor. The experimental set-up, equipped with mass-flow and temperature controllers, allows the continuous recording of mass and temperature variations along all the stages: oxidation, reduction and reaction, see Fig. 1. Previous to the reaction of ethane decomposition, the metallic foam is oxidized and reduced in-situ (activation steps). The reaction was carried out feeding 600 N mL/min of a mixture of $1.67\%H_2/33.33\%C_2H_6/65\%N_2$. The operating conditions used during activation stages were: (i) Oxidation: Temperature: from 700 to 900 °C; time: 60 min at final temperature (heating rate: 10 °C/min); mass flowrate: 200 N mL/min; feed composition: $50\%air/50\%N_2$; (ii) Reduction: Temperature: from 700 to 900 °C; mass flowrate: 200 N mL/min; feed composition: $50\%H_2/50\%N_2$.

3. Results and discussion

Fig. 1 shows the variations of the weight of the sample along the successive stages (oxidation, reduction and reaction) of a typical