New Three-Phase Catalytic Reactors based on Carbon Nanotubes Grown over Structured Metallic Supports

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Introduction

Catalytic multiphase reactions account for more than 85% of industrial chemical processes and about $ 1000 billion of chemical sales per annum in USA. Catalytic gas-liquid reactions are usually carried out in reactors type “slurry” or “trickle bed”. However, these reactors present serious problems that limit their applications.

In order to overcome these problems, the development of a new type of structured catalytic reactors, based on metallic supports such as monoliths, filters, foams or mesh, is proposed. These reactors combine conventional reactor´s advantages because they have an elevated contact surface, favour the internal diffusion and do not need an additional stage of catalyst separation. To achieve these properties, a layer of nanocarbonaceous material, NCMs (carbon nanotubes and nanofibres) must be created by an “in situ” growth (immobilization) which serves as reactor catalyst support [1-3]. This new type of structured catalytic reactors has good prospect as catalyst support for several environmental applications such as cleaning of pollutants in water, H_2 production, e.g. by NH_3 decomposition, and intensification of chemical processes by increasing selectivity and reducing by product generation.

In this work, we have grown a CNF layer over monoliths via catalytic chemical vapor deposition (CCVD). The CNF coating properties have been optimized by studying different variables such as pretreatment of the monoliths.

Materials and Methods

Monoliths made of steel mesh were used as metallic support. Before the experiment, the monoliths (42×20 mm) were pretreated with HCl at room temperature for 30 minutes. After, they were oxidized and impregnated in different metallic nitrates. The experiments were carried out in gas phase in a thermobalance (C.I. Electronics, UK). The operating conditions were: oxidation: 800ºC (1 h), 100Nml/min air / 100Nml/min N_2; reduction: 700ºC (1 h), 100Nml/min H_2 / 100Nml/min N_2; reaction: 800ºC (30 min), 100Nml/min C_2H_6 / 500Nml/min N_2. The samples were characterized by SEM after each step with the aim of observing the changes in the structure and the type of deposited carbon.

Results and Discussion

Figure 1 shows the activity results obtained with the different monoliths. The impregnation of the steel mesh with metallic nitrates enhances the carbon content (C_C) and the carbon formation rate (r_C), obtaining the highest activity after the impregnation with Nickel (II) nitrate. After reaction, the monoliths are completely covered by nanocarbonaceous material (Figure 2). SEM micrographs show the formation of a large quantity of carbon nanofibres.

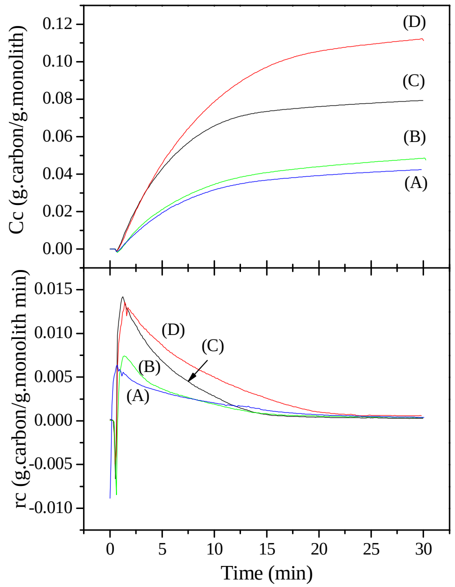

Figure 1. Evolution with time of the carbon content (Cc) and carbon formation rate (rc). A) Mesh without impregnation, B) Fe (III) nitrate impregnation, C) Co (II) nitrate impregnation, D) Ni (II) nitrate impregnation.

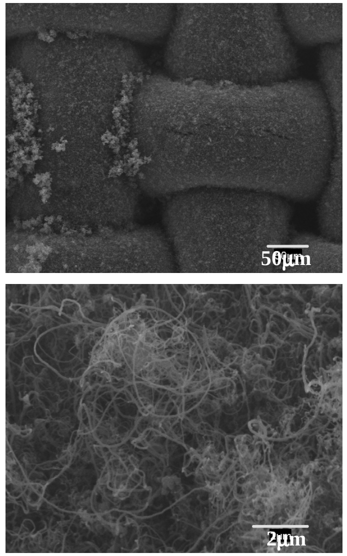

Figure 2. SEM micrographs after reaction of the sample impregnated with Ni.

Significance

An appropriate CNF layer can be created over monoliths of steel mesh via CCVD for the development of new catalytic reactors. The CNF coating properties can be optimized by studying different variables such as impregnation of substrate. After reaction, to check the adhesion of nanocarbonaceous material layer to substrate, its porosity and uniform thickness is necessary.

References

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