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A new fast method for ceramic foam impregnation: Application to the CCVD synthesis of carbon nanotubes

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Abstract

A new process that allows preparing, in a single step, good washcoats of catalytic materials for the catalytic chemical vapour deposition (CCVD) synthesis of carbon nanotubes (CNTs) in reticulated ceramic foams is reported. It is shown that the washcoats, obtained by impregnation using viscous slurries made of finely divided powders dispersed in different media, cover the total surface of foams with good adhesions. The catalytic activity with regards to the CNT synthesis is finally verified, showing that our new fast impregnation process makes possible to get materials with final architectures suitable for heterogeneous catalysis applications.

Keywords: Ceramic foam; Impregnation process; Washcoat; Synthesis of carbon nanotubes

1. Introduction

Several studies have shown the interest to use consolidated ceramic foams as catalyst supports instead of packed powders [1,2]. Indeed, the low-pressure drop and the high geometrical surface area of ceramic foams lead to a better gas turbulence and thus, to a higher catalytic efficiency [3,4]. However, ceramic foams usually exhibit a low specific surface area ($\leq 1\ m^2\ g^{-1}$) after consolidation by sintering at high temperature. In order to overcome this problem, they can be impregnated by a slurry made of finely divided powders that are characterised by a high specific surface area like γ-Al_2O_3 powders [5,6]. This so-called washcoat is then decorated by the catalytic nanoparticles.

In this method, the main difficulty is to deposit the washcoat on the whole foam surface with a homogeneous thickness and a good adhesion and without closing the foam porosity. The coating process currently used consists in: (i) dipping the ceramic foam into a slurry containing the powders, water and additives [7,8], (ii) removing the excess of slurry by draining or by blowing air through the foam pores and (iii) drying the impregnated foam. These three steps may be repeated as much as it is necessary before calcination [9]. The thickness and the homogeneity of the washcoat depend on the foam characteristics (material, walls porosity and thickness, pores size, porosity architecture) and on the intrinsic characteristics of the slurry (powder grain size and shape, powder loading, nature of dispersion medium) [10]. Thus, an optimum slurry viscosity has to be found in order to get a homogeneous coating of the foam using a minimum number of impregnations, while preventing from pores obstruction. In most of previously reported studies, three successive impregnations were needed to obtain a good deposit when a reticulated foam was used [11,12], which means a rather long process due to all the necessary drying steps.

In this study, we propose an original process allowing the deposition of homogeneous layers of catalytic materials on reticulated ceramic foams in only one step using high viscosity slurries. Four different powder dispersion media are tested to get the slurries. After characterisation, one among the impregnated foams is chosen and a catalytic chemical vapour deposition (CCVD) treatment is conducted in order to *in situ* synthesise carbon nanotubes (CNT) [13].

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2. Materials and experiments

2.1. Commercial ceramic foams

The commercial ceramic foams (Aluminium Martigny, France) are mainly composed of α-alumina (more than 80%) and in lower proportions of mullite and cristobalite. Their shape is cylindrical (diameter = 35 mm; height = 22 mm) (Fig. 1(a)), with an opened porosity of 50 pores per inch (ppi), which corresponds to pore diameters between 0.5 and 1.5 mm (Fig. 1(b)). The wall surface is rough and porous, with a pore size of less than 1 μm (Fig. 1(c)). The ceramic foams are impregnated using a slurry made of the chosen catalytic material powder and they are further dried in air. Then, the impregnated foams are calcined under flowing air in order to remove the dispersant and any other organic compounds.

2.2. Preparation of catalytic material powder

The combustion route [14,15], which is used to prepare the catalytic material composed of an oxide solid solution ($Al_{1.8}Fe_{0.2}O_3$), has already been described in details in a previous paper [16]. $Al(NO_3)_3$, $9H_2O$ and $Fe(NO_3)_3$, $9H_2O$ are dissolved in deionised water together with the required amounts of citric acid and urea. The mixture of citric acid and urea (25% citric acid and 75% urea) is used as the fuel, in a quantity equal to the double of the so-called stoichiometric ratio. A Pyrex dish containing the solution is placed in a furnace preheated at 550 °C. The solution immediately starts to boil and undergoes dehydration. The resulting paste froths and then blazes. No flame occurs and a rather light material is produced which swells to the capacity of the Pyrex dish. The total combustion process proceeds in less than 10 min. The combustion product is first calcined during 1 h at 600 °C to remove remaining carbon residues. Then, an α-alumina-type phase is obtained after calcination at 1100 °C (900 °C h^{-1}, 30 min).

2.3. Attrition-milling of the powder

The α-$Al_{1.8}Fe_{0.2}O_3$ solid solution powder is milled by attrition at 2000 rpm for various durations using a vessel and a rotor made of Nylon. High purity α-alumina balls of a diameter in the range from 200 to 300 μm are used as milling agent. The operation is performed in ethanol in which 1 mg of dispersant (BEYCOSTAT C213, CECA, France) per meter square of powder surface is initially introduced. The ratio between the powder volume and the milling ball volume is fixed at 0.5. After attrition-milling, the α-alumina balls and the powder are separated by rinsing in ethanol. Finally, after a filtering step, the powder is dried in air.

2.4. Preparation of slurries of catalytic powder and impregnation of ceramic foams

The different slurries are prepared by simply mixing with the help of ultra-sounds the attrited oxide powder in the dispersion medium in the presence of the above-mentioned C213 dispersant. The different tested dispersions media are:

- DEG: pure diethylene glycol (*Prolabo-VWR*),
- PEG: mixture of 50 wt.% of aqueous solution of polyethylene glycol 6000 (diluted at 50 wt.% *Prolabo-VWR*) and 50 wt.% diethylene glycol,
- PVA 4/125: aqueous solution of RHODOVIOL 4/125 (diluted at 10 wt.% *Prolabo-VWR*),

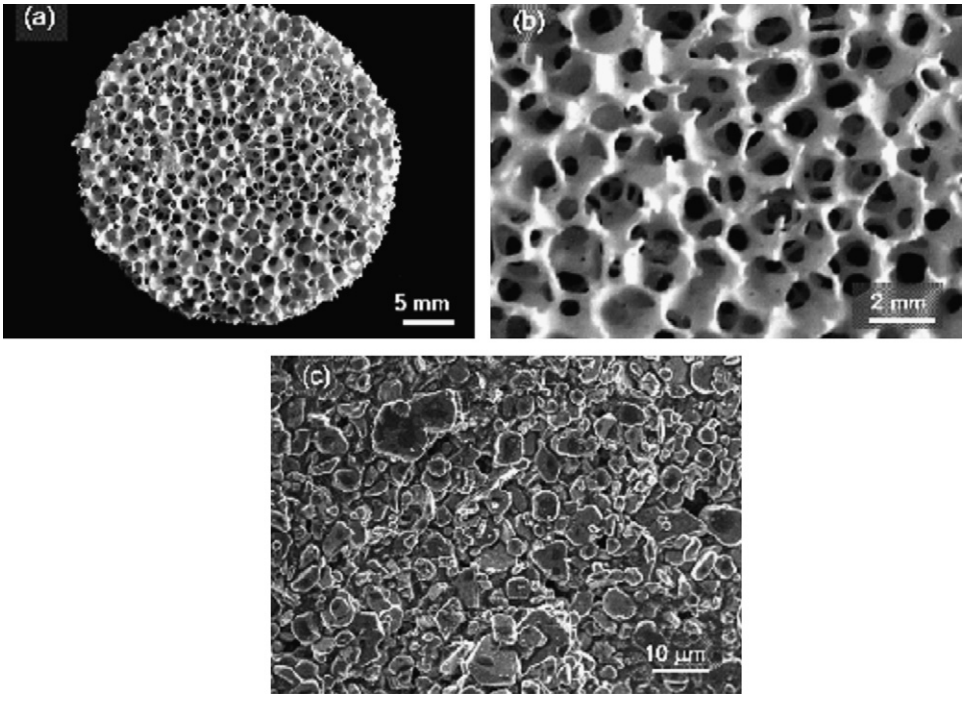

Fig. 1. (a) Macroscopic view of the commercial ceramic foam; (b) macroscopic view of the commercial ceramic foam porosity; (c) SEM image of the pore wall.