To link to this article :
URL : :http://dx.doi.org/10.1016/j.apcata.2006.10.039

To cite this version : Cordier, Anne and Rossignol, Fabrice and Laurent, Christophe and Chartier, Thierry and Peigney, Alain (2007) *A new fast method for ceramic foam impregnation: Application to the CCVD synthesis of carbon nanotubes.* Applied Catalysis A General, vol. 319 . pp. 7-13. ISSN 0926-860X

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

Anne Cordier [a], Fabrice Rossignol [b], Christophe Laurent [a], Thierry Chartier [b], Alain Peigney [a,*]

[a] *CIRIMAT, UMR CNRS-UPS-INP 5085, Centre Interuniversitaire de Recherche et d'Ingénierie des Matériaux,*
Université Paul-Sabatier, 31062 Toulouse cedex 9, France
[b] *SPCTS, UMR CNRS 6638, Science des Procédés Céramiques et de Traitements de Surface, ENSCI, 87065 Limoges cedex, France*

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 (≤ 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].

---

* Corresponding author. Tel.: +33 5 61 55 61 75; fax: +33 5 61 55 61 63.
E-mail address: peigney@chimie.ups-tlse.fr (A. Peigney).

doi:10.1016/j.apcata.2006.10.039

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*),

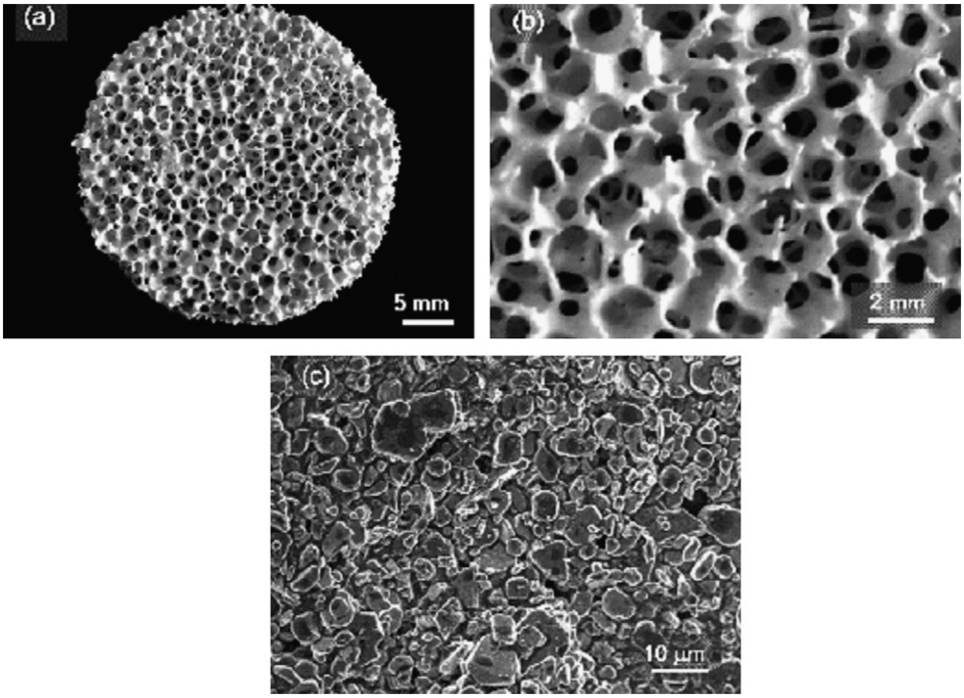

Fig. 1. (a) Macroscopic view of the commercial ceramic foam; (b) macroscopic view of the commercial ceramic foam porosity; (c) SEM image of the pore wall.

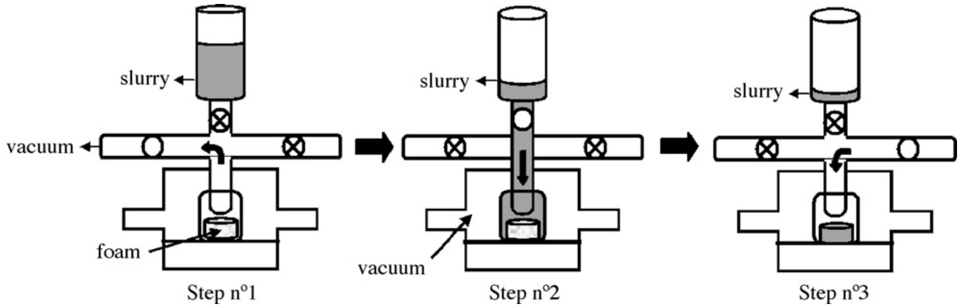

Fig. 2. Scheme of the process used for the impregnation.

- PVA 30/5: aqueous solution of RHODOVIOL 30/5 (diluted at 4 wt.% *Prolabo-VWR*).

The slurries are kept under constant magnetic stirring during 1 h to reach a good homogeneity. The flowchart of the process is shown in Fig. 2. At first, the glass containing the foam is submitted to vacuum using a water jet filter pump, so that the slurry is allowed to flow down into the box. However, since the viscosity is too high to penetrate satisfactorily within all the pores of the ceramic foam, a complete impregnation is performed upon the admission of air until the atmosphere pressure is reached. This process is performed alternatively for each side of the foam without any intermediate drying steps. Then, the impregnated foam is dried at room temperature and calcined in air at 600 °C (150 °C h^{-1}, 60 min). The four impregnated foam will be designated in the following as F1, F2, F3 and F4, prepared using DEG, PEG, PVA 4/125 and PVA 30/5, respectively. The best one will be selected for use as the catalytic material for the CCVD formation of CNTs.

2.5. CCVD synthesis of carbon nanotubes

The selected impregnated foams are transformed into a nanocomposite foam by a CCVD treatment, which consists in a heating under a H_2–CH_4 gas mixture (20 mol.% CH_4, heating and cooling rates at 5 °C min^{-1}, maximum temperature 1025 °C, no dwell) [17]. By this process, a CNT-Fe/Fe_3C–Al_2O_3 composite foam is obtained, with a very homogeneous dispersion of the CNTs around the oxide grains.

2.6. Characterisations

The specific surface area of the α-$Al_{1.8}Fe_{0.2}O_3$ powder before and after attrition was measured by the BET method using N_2 adsorption at liquid N_2 temperature (Micromeritics Flow Sorb II 2300). The particle size distributions of powders are determined using a laser particle size analyser (Malvern mastersizer 2000). The viscosity of the slurry is measured at 20 °C for different shear rates (from 65 to 775 s^{-1}) using a viscometer (TVe-05 Lamy) and following the DIN 53 019 and NF EN ISO 3219 standards. The starting commercial ceramic foams and the impregnated foams (F1–F4) are observed by SEM (JEOL JMS 35CF) in order to evaluate the washcoat quality. The washcoat amounts are measured by weighting the foams before and after the impregnation and calcination steps. Then, after the CCVD treatment, the resulting nanocomposite foams are observed by FEG-SEM (JEOL-6700F) in order to evaluate both the quantity of CNT and the overall quality of the deposited carbon (we consider that a high carbon quality is reflected by a high proportion of CNT compared to other carbon forms). The carbon content is measured by flash combustion.

3. Results and discussion

3.1. Attrition-milling

As shown in a previous paper, the product obtained by combustion and further calcinations is monophased and composed of a α-$Al_{1.8}Fe_{0.2}O_3$ solid solution [16]. This powder

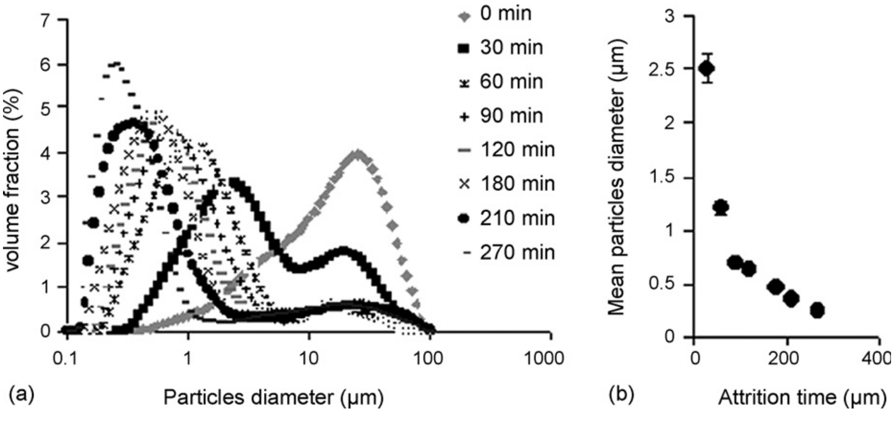

Fig. 3. (a) The particle size distribution for different attrition-milling times. (b) The mean particle size vs. the attrition-milling time.

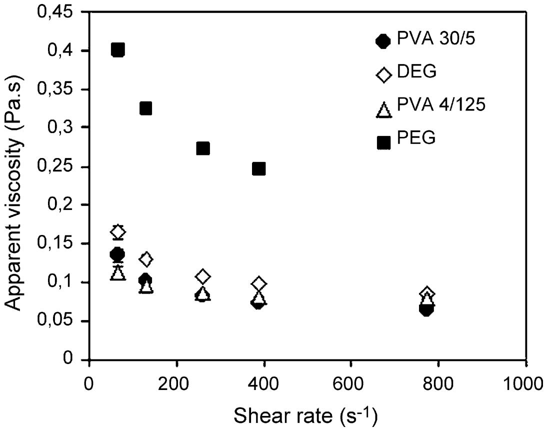

Fig. 4. The apparent viscosity of the different slurries vs. the shear rate.

consists of a few tens of micrometers veil-like agglomerates with a specific surface area of 2.7 ± 0.3 m^2 g^{-1}. Since Agrafiotis et al. [5] have shown that the adhesion of an alumina deposit on a honeycomb ceramic is greatly improved by a slurry composed of fine particles, we intend to decrease the grain size while increasing at the same time their specific surface area by implementing an attrition-milling treatment. The evolution of the grain size during durations of attrition-milling up to 270 min is reported in Fig. 3(a). Up to $t = 60$ min, a spectacular decrease of the particles size is observed. For longer attrition-milling times, the decrease is much lower and progressively the mean grain diameter tends to a minimum value around 250 nm at $t = 270$ min (Fig. 3(b)). There are about four orders of magnitude between this mean particle size and the pore size of the foam walls, which allow a good adhesion and prevent from obstruction of the porosity. The 270 min attrition-milling treatment was selected as the most appropriate for this work. After drying the milled powder, the specific surface area is 25.1 ± 0.7 m^2 g^{-1}, that is to say ten times larger than that of the non-milled powder.

3.2. Viscosity of the different slurries

The apparent viscosities of the different slurries made of 30 wt.% of attrited powder in the conditions described in Section 2.4, are reported in Fig. 4. The observed apparent viscosity variations as a function of the shear rate can be fitted by the Ostwald–De Waele model:

$$\eta = K\gamma^{n-1}$$

where, η is the apparent viscosity (Pa s) and γ is the shear rate (s^{-1}). The constant K (Pa s^n) represents the flow consistency index and n is the flow behaviour index, which traduces the deviation from the behaviour of a Newtonian fluid.

Table 1
Values of the flow consistency index K and the flow behaviour index n for the different slurries

Dispersion medium	K (Pa s^n)	n
DEG	0.472	0.7387
PEG	1.229	0.7286
PVA 4/125	0.206	0.8480
PVA 30/5	0.445	0.7011

The values of K and n are reported in Table 1. Whatever the slurry, the flow behaviour indexes n are less than unity, which indicates a shear-thinning behaviour. The values of n are almost equivalent, excepted for the slurry prepared with PVA 4/125, showing a less pronounced deviation from Newtonian fluid (Table 1). Such a shear-thinning behaviour is common for solutions made of large polymeric molecules in a solvent. Indeed, on increasing shear rate, long molecular chains gradually align themselves and produce less resistance. However, the slurries differ by the values of their flow consistency index K (Table 1). K corresponds to the value of the viscosity for a shear rate equal to 1 s^{-1}. Thus, the higher this value, the more viscous the slurry is at low shear rates. The K value for the slurry prepared with PEG is three times higher than for those prepared with DEG or PVA 30/5 and six times higher than for the one prepared with PVA 4/125 (Table 1). Shear rates, imposed to the slurry during impregnation in the commercial ceramic preform pores with diameters around a millimeter, are expected to be low. Thus, the most efficient impregnation should be obtained for slurries prepared with PVA 4/125.

3.3. Influence of the dispersion medium on the oxide deposits

The commercial ceramic foams are impregnated by the slurries as described in Section 2. Then, they are dried and calcined at 600 °C for 1 h, with a heating rate of 150 °C h^{-1}. The as-obtained F1, F2, F3 and F4 samples are weighted, observed by SEM, and the characteristics of the oxide deposits are compared (Table 2). The relative weights (wt.%) of the deposits, calculated for 100 g of dry impregnated foam, are reported in Table 2. The thickness of the deposits, their homogeneity and the possible presence of cracks, which are evaluated upon several SEM images (see examples in Fig. 5),

Table 2
Macroscopic and microscopic characteristics of the impregnated ceramic foams

Sample	Dispersion medium	Deposit (wt.%)	Deposit thickness (μm)			Cracks	Microscopic homogeneity
			Minimum	Average	Maximum		
F1	DEG	36.6 ± 3.7	0	29	52	Many	Poor
F2	PEG	24.1 ± 2.4	5	22	44	Few	Acceptable
F3	PVA 4/125	24.5 ± 2.5	15	30	47	Very few	Good
F4	PVA 30/5	29.4 ± 2.9	0	35	52	Few	Poor

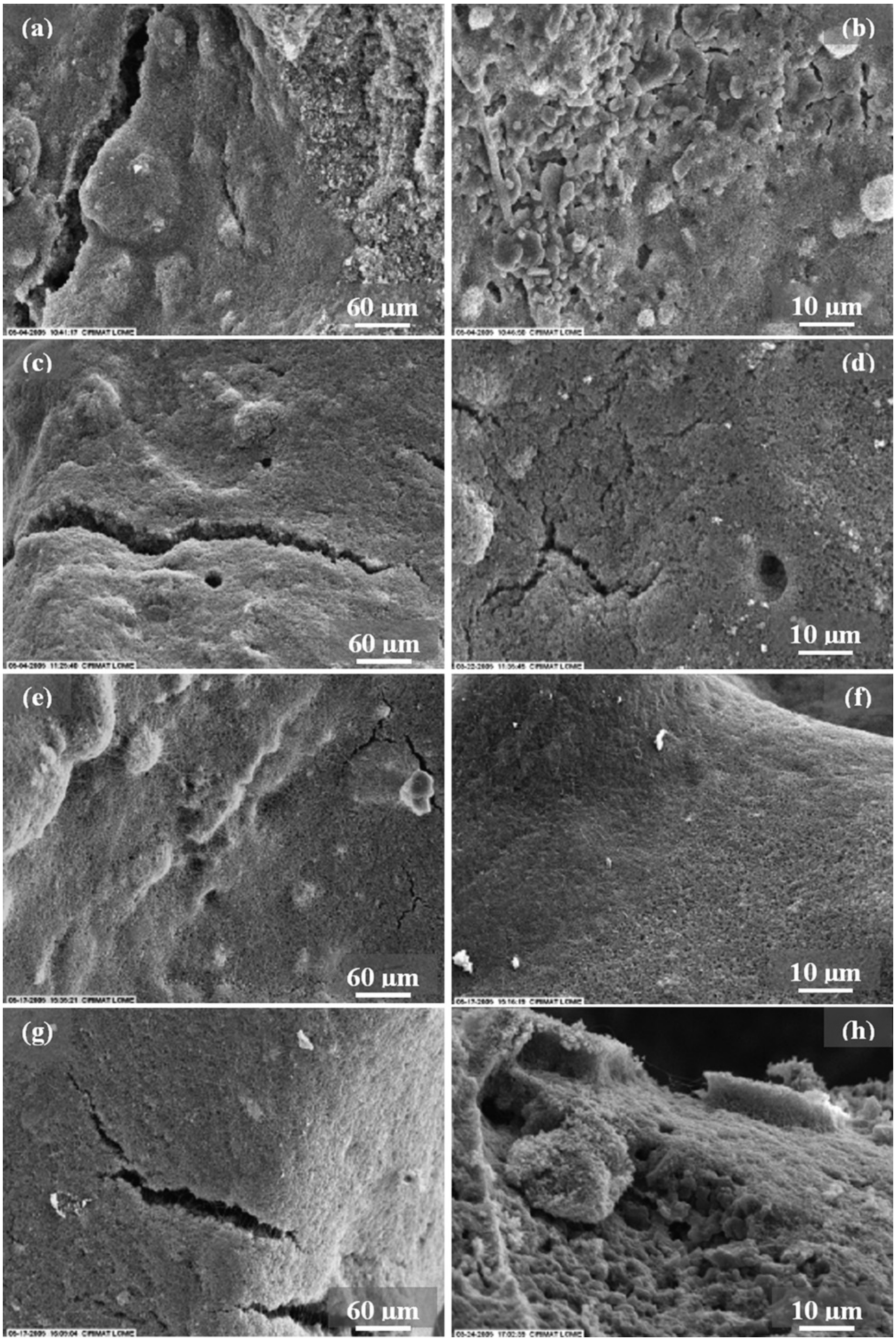

Fig. 5. SEM images of the deposits obtained using different dispersion media: (a) and (b) DEG, (c) and (d) PEG, (e) and (f) PVA 4/125, (g) and (h) PVA 30/5.

are also given in Table 2. It is to be noticed that the average, the minimum and the maximal values of the thicknesses are given to give an idea of the regularity of the oxide layer.

For the F1 foam, the relative weight of the deposit (36.6%) is slightly higher than that of the other foams (between 24.1 and 29.4%), but its thickness appears to be very irregular (between 0 and 52 μm). The zero value corresponds to non-covered areas of the foam walls (Fig. 5(b)). Moreover, many large and small cracks can be observed on this deposit (Fig. 5(a) and (b)). The F1 sample, obtained with a slurry prepared with DEG, is hence of poor quality in term of homogeneity. On the contrary, the deposit of the F2 foam covers all the wall surfaces of the foam (thickness between 5 and 44 μm), although it still contains both large and small cracks (Fig. 5(c) and (d)). The deposit in the F2 sample, corresponding to a slurry prepared with PEG, has globally some acceptable characteristics. However, all the characteristics of the deposit in the F3 sample are clearly better than those of the other samples. Indeed, the deposit thickness is more regular (thickness between 15 and 47 μm) and all the surface of the foam substrate appears to be covered by the oxide layer with only very few small cracks detected (Fig. 5(e) and (f)). The microscopic homogeneity is also better than that of the other foams. Instead, for the F4 foam, the deposit appears to be rather irregular (thickness between 0 and 52 μm) and many areas of the foam substrate are not covered by the oxide layer (Fig. 5(h)), although this deposit contains few cracks (Fig. 5(g)). Thus, in spite of the presence of less numerous cracks and good microscopic homogeneity, the deposit in the F4 sample, corresponding to a PVA 30/5 slurry, is considered to be globally of poor quality. Thus, we conclude that the increasing order of quality of the deposits in the impregnated foams is the following F1, F4, F2, F3.

The poor homogeneity of F1 and F4 deposits cannot be attributed to a too high viscosity of the slurries at low shear rate, as a better deposit is obtained with the more viscous slurry prepared with PEG (Table 1). The new one step impregnation process proposed in this paper is thus, suitable for the foam impregnation by slurries of consistency index up to 1.2 Pa s^n. So, we can infer that most of the defects come from a powder re-agglomeration during the process, likely because of the use of the phosphate ester dispersant that may not be suitable for DEG and PVA 30/5 dispersion media. Agglomeration can lead to the blocking of a part of the pores of ceramic foams, and thus, to a non-complete deposition during impregnation. The foams impregnated by the slurries prepared with PEG or PVA 4/125 have a homogeneous deposit. The foams F2 and F3 could in principle be used for the CCVD synthesis of CNT. However, as the deposit in the F3 sample, corresponding to a slurry prepared with PVA 4/125, exhibits the best characteristics among the four samples, we have retained this impregnated foam to perform the synthesis of CNT.

3.4. Application to the CCVD synthesis of CNT

A Mössbauer spectrometry study [16], both at room temperature and 80 K, of the starting oxide (α-$Al_{1.8}Fe_{0.2}O_3$) after calcination at 1100 °C showed that the spectra could be adequately fitted with a ferric quadrupole doublet representing Fe^{3+} ions substituting for Al^{3+} ions in the corundum lattice. Another study in the attrited powder [23] revealed no change, and there is no reason to suspect that the deposition process used in the present work in order to obtain this material as a washcoat produced any change in the distribution of the Fe^{3+} ions.

The CCVD treatment, a selective reduction of α-$Al_{1.8}Fe_{0.2}O_3$ in H_2–CH_4 atmosphere, leads to the formation of nanometric Fe particles at a relatively high temperature [13,17,18] and those located at the oxide grain surface immediately catalyse the decomposition of CH_4 and the subsequent nucleation and growth of CNT. Each active particle leads to one CNT, no more than a few nanometers in diameter. Post-reduction Mössbauer spectrometry studies [17,21] have revealed that the reduced species present in the specimen are α-Fe, Fe_3C and a γ-Fe–C alloy and a correlation of the proportion of theses species with the proportion of CNT allowed to show that the nanoparticles responsible for the formation of the CNT are in γ-Fe–C form at high temperature but are found as Fe_3C by post-reduction Mössbauer analysis. It has been shown that the majority of the CNTs are double-walled, which is discussed elsewhere [18,22] along with the CNT formation mechanisms. The fact that the solid solution is in the form of a washcoat should not basically change this, although one may expect that the reduction may be easier than when it is in the form of a powder bed. This could cause the formation of metal surface particles at slightly lower temperatures.

The CCVD treatment, performed on the impregnated foam F3, leads to a nanocomposite foam. The global carbon content measured is 1.9 ± 0.1 wt.%. When this value is reported to the proportion of catalytic material (24.5 ± 2.5 wt.%, Table 2), the carbon content becomes 7.6 ± 1.2 wt.%. This value can be compared to those obtained using the same solid solution (α-$Al_{1.8}Fe_{0.2}O_3$) as catalytic material in the form of a powder bed. It is similar to that obtained with a non-milled powder [18] and slightly higher than that obtained with an attrited-milled powder (7.6 versus 5.8 wt.%) [19]. This latter result probably reflects a better CH_4 supply to the catalytic material when deposited as a washcoat.

The quality of the carbon was investigated by SEM. Some examples of the obtained images are given in Fig. 6. The low magnification image of the nanocomposite foam surface (Fig. 6(a)) shows a large amount of filaments covering that surface. The observation at high magnification (Fig. 6(b))

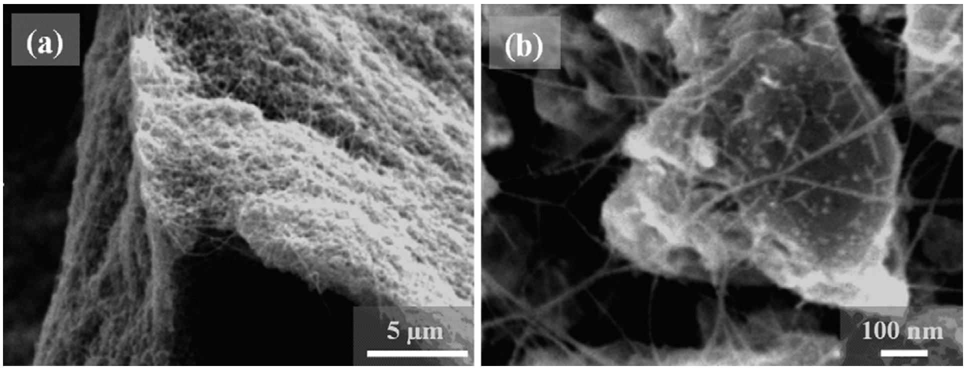

Fig. 6. SEM images of CNT grown on the nanocomposite foam made with PVA 4/125 dispersion medium: (a) low magnification image, (b) FEG-SEM high magnification image.

shows that these filaments have the usual morphological characteristics of bundles of CNT [18], between 10 and 20 nm in diameter, which interconnect the oxide grains. The small species appearing at the surface of the oxide grains (white dots Fig. 6(b)) are metallic nanoparticles, which have not been activated for the CNT synthesis and which are usually covered by carbon capsules [18]. The carbon synthesised during the CCVD treatment of the impregnated foam is, however, mostly in the form of CNT. No nanofibers are observed. The large amount of CNT and the good quality of carbon prove that, during the CCVD treatment, the CH_4 and H_2 supply to the oxide grains was efficient.

The new process proposed in this paper allows to impregnate a reticulated ceramic foam in only one step without decreasing the catalytic material activity. These results are in good agreement with those obtained using a $Mg_{0.9}(Co_{0.75}Mo_{0.25})_{0.1}O$ oxide as the washcoat [11], in spite of the fact that the CNT content remains much smaller in the present work. However, this large difference is similar to what is already observed when using these materials as powder beds [18–20]. In fact, the main advantage of using α-$Al_{1.8}Fe_{0.2}O_3$ lies more in its better compatibility with the α-alumina foam and its subsequent better adhesion than in a gain in the CNT quantity. Although a detailed study of the CNT number of walls distribution was not attempted here, it is worth noting that it appears [23] that using an oxide catalyst as a foam instead of using it as a powder bed favours the formation of single-walled nanotubes over double-walled. This phenomenon is under study and will be reported elsewhere.

4. Conclusion

In this paper, we introduce a new process to prepare, in only one step, a good washcoat of catalytic oxide material in a reticulated ceramic foam to be further used for the synthesis of CNT by CCVD. In a first step, the attrition-milling of the catalytic material allows to obtain a finely divided powder (mean particle size of 250 nm, specific surface area of $25\ m^2\ g^{-1}$), resulting in an increased catalytic activity and allowing a good adhesion of the oxide to the wall surface of the foam. In a second step, the impregnation of reticulated ceramic foams by slurries are performed by a process including successively the setting of the foam under vacuum, pouring of the slurry and then penetration within the foam caused by air admission. Four slurries, with a shear-thinning behaviour and flow consistence indexes ranging from 0.2 to $1.2\ Pa\ s^n$ are prepared using different dispersion media based on DEG, PEG, PVA 4/125 and PVA 30/5. Only impregnation by slurries based on the use of PVA 4/125 and PEG allows getting homogeneous deposits, covering the total surface of the foam. Other slurries lead to poor quality deposits, mostly due to the use of a non-appropriate dispersant in these systems rather than to a viscosity that would be too high. The catalytic activity of the foam impregnated by the slurry based on PVA 4/125 is finally tested with regards to the CCVD synthesis of CNT. A large amount of CNT bundles, without nanofibers, is obtained, in relation with the high reactivity of the catalytic material and the efficient supply in H_2 and CH_4. Thus, this new fast process is suitable for the impregnation of reticulated foams for heterogeneous catalysis application.

References

[1] H. Ogawa, H. Horie, In Jpn Kokai Tokkyo Koho, (Nissan Motor Co., Ltd., Japan), Jp, 1991, , 4 pp..
[2] M. Haruta, Y. Souma, H. Sano, Int. J. Hydrogen Energy 7 (1982) 729.
[3] J.T. Richardson, Y. Peng, D. Remue, Appl. Catal. A 204 (2000) 19.
[4] J.T. Richardson, D. Remue, J.K. Hung, Appl. Catal. A 250 (2003) 319.
[5] C. Agrafiotis, A. Tsetsekou, I. Leon, J. Am. Ceram. Soc. 83 (2000) 1033.
[6] A. Sirijaruphan Jr., J.G.G. Rice, R.W. Wei, D. Butcher, K.R. Roberts, G.W. Spivey, J. Appl. Catal. A 281 (2005) 11.
[7] R.A. Clyde, In U.S, (USA), Us, 1975, , 8 pp..
[8] Y. Peng, J.T. Richardson, Appl. Catal. A 266 (2004) 235.
[9] A. Worner, C. Friedrich, R. Tamme, Appl. Catal. A 245 (2003) 1.
[10] P. Avila, M. Montes, E.E. Miro, Chem. Eng. J. 109 (2005) 11.
[11] A. Cordier, E. Flahaut, C. Viazzi, Ch. Laurent, A. Peigney, J. Mater. Chem. 15 (2005) 4041.
[12] P. Jiang, G. Lu, Y. Guo, Y. Guo, S. Zhang, X. Wang, Surf. Coat. Technol. 190 (2005) 314.
[13] A. Peigney, Ch. Laurent, F. Dobigeon, A. Rousset, J. Mater. Res. 12 (1997) 613.
[14] K.C. Patil, Bull. Mater. Sci. 16 (1993) 533.
[15] J.J. Kingsley, L.R. Pederson, Mater. Res. Soc. Symp. Proc. 296 (1993) 361.
[16] A. Cordier, A. Peigney, E.D. Grave, E. Flahaut, Ch. Laurent, J. Eur. Ceram. Soc. 26 (2005) 3099.
[17] Ch. Laurent, A. Peigney, A. Rousset, J. Mater. Chem. 8 (1998) 1263.
[18] A. Peigney, P. Coquay, E. Flahaut, R.E. Vandenberghe, E. De Grave, Ch. Laurent, J. Phys. Chem. 105 (2001) 9699.
[19] Ch. Laurent, A. Peigney, E. Flahaut, A. Rousset, Mater. Res. Bull. 35 (2000) 661.
[20] E. Flahaut, A. Peigney, W.S. Bacsa, R.R. Bacsa, Ch. Laurent, J. Mater. Chem. 14 (2004) 646.
[21] A. Cordier, V. Gonzaga, A. Peigney, E.D. Grave, Ch. Laurent, in press.
[22] E. Flahaut, A. Peigney, Ch. Laurent, J. Nanosci. Nanotechnol. 3 (2003) 151.
[23] S. Rul, A. Peigney, W.S. Bacsa, Ch. Laurent, in press.