Hierarchically structured reactors containing nanocarbons for intensification of chemical reactions

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Abstract

Carbon nanomaterials, such as carbon nanotubes, carbon nanofibers and graphene, featured functional properties and tailored nanoscale dimension have been widely used in different research fields, especially for the catalysis and sustainable chemistry. The hierarchically structured reactors, combining nanoscopic coating carbon layer to disperse the active phase or even directly as metal-free catalysts, with controlled macroscopic shapes, have been extensively developed since the last decades for numerous relevant catalytic processes, where mass and heat transfers are easily optimized for better catalytic performance and stability. The 3-D structuration enables to fully exploit the intrinsic activity of the catalyst and its industrial deployment without drawbacks linked with nanomaterials. In this review article, we will summarize the recent developments involved in the field of hierarchically structured reactors, i.e. monolith, foam and others, containing carbon nanomaterials, and interests will be shared among large scientific communities. It is expected that such structured reactors will face high scientific and industrial interests in the future not only in the field of catalysis but also to those linked with wastewater purification or aerosol filtration processes. It will also be evidenced how the hierarchically structured materials have contributed to the intensification of catalytic processes compared to conventional reactors, thus paving the way to the enhancement of other chemical reactions and its industrial deployments.

Keywords Hierarchically structured reactor, nanocarbon materials, macroscopic shaping, catalysis, carbon nanotubes, carbon nanofibers

I. Introduction

Catalysis is receiving increasing academic and industrial interests as about 90 % of chemical processes, to produce food and goods, involves at least one or more catalytic steps.¹⁻² Catalysis is a critical step for developing new processes to reduce waste and by-products with respect to the environmental legislations in place nowadays. It is expected that catalysis will become more and more important in the decades to come due to the need for improving environmental impact, i.e. low waste release, and also to reduce as much as possible the energy input in the different chemical processes.³ The improvement in catalysis field stems from the development of new and optimized catalysts as well as catalytic processes based on the advances in the field of characterization techniques and chemical engineering. The development of new catalyst support represents another aspect for the improvement of the catalytic performance by providing adequate structure with high effective surface area for improving dispersion and anchoring of the active phase, reduced diffusion limitations along with low pressure drop which significantly contribute to the enhancement of the selectivity of the process as well as to the long-term stability of the catalyst by reducing deactivation through active phase sintering and poisoning by secondary products.

For using very active catalyst effectively, it is crucial to design reactors in which reaction is not controlled by mass transfer. This is even more dramatic for liquid phase reactions in which the diffusion coefficients are typically 4 orders of magnitude lower than in gas phase.¹ In the application of heterogeneous catalysts in liquid phase reactions, the rate of reaction as well as selectivity, are often negatively influenced by mass transfer limitations in the stagnant liquid in the pores of the catalyst support leading to a loss of the overall selectivity and deactivation with time on stream. Internal mass transfer limitations can be reduced by maximizing the porosity and shortening the diffusion path of the catalyst support. Currently, nanocarbon supports, i.e. nanotubes or nanofibers, represent adequate supports for different catalytic processes in both gas- and liquid-phase reactions. Nanocarbons are promising catalyst supports because of the combination of large pore volume (0.5–2 cm³/g) and extremely open morphology with low tortuosity, i.e. lack of ink-bottled pores, and significant high external surface area (100–200 m²/g). The nanoscopic dimension of these nanocarbons, typically few tenths to hundred nanometers, also significantly reduces the problem of diffusion of the reactant towards the active sites. This enhances the diffusion of the liquid and minimizes the amount of stagnant liquid by the refreshment of the liquid in the pores by the convective flow. The high external surface area of these nanocarbons ensures a high density of exposed active sites and, as a consequence, the improvement of the intrinsic catalytic performance. The short diffusion path also allows the high desorption rate of intermediate products which contribute to the high selectivity of the process reducing by such a way secondary products. The

nanocarbon supports surface can also be functionalized with different heteroelements in order to improve the anchorage of the active phase and also to reduce its sintering during operation. Another aspect concerns the problem linked with heat transfer through the catalyst bed, *i.e.* exothermic catalytic processes where heat release by the reaction itself is not well dispersed to the entire matrix of the catalyst which leads to the formation of local hot spots. These hot spots contribute to the modification of the overall selectivity of the process through secondary reactions, *i.e.* multiple cracking or total oxidation or also to coke formation. Hot spots could also induce temperature runaway which compromises the safety of the process. Nanocarbons display relatively high thermal conductivity which could reduce to a large extent the problem of hot spot formation inside the catalyst bed which significantly improves the overall selectivity of the reaction as well as the security for operating the plant. For the endothermic reactions the heat transfer facility allows one to reduce the catalyst temperature gradient.

Nevertheless, carbon nanotubes (CNTs) and carbon nanofibers (CNFs) in powder form have a number of drawbacks for industrial applications, including the problems of transport and handling, high-pressure drop for gas phase processes and agglomeration with time on stream.⁴⁻⁵ Coupled with health and safety concerns related to large-scale airborne presence of CNTs, these aspects have, so far, limited the applicability of such catalysts in industrial grounds. It is worthy to note that carbon nanotubes or nanofibers have also a high tendency to agglomerate upon drying due to the presence of van der Waals forces. Such phenomenon leads to the diminution of the accessible catalyst surface after deposition of the active phase and thermal treatment. To mitigate some of these limitations, a number of groups have recently tackled the growing CNT or CNF on structured supports where the macroscopic shape provides, in turn, an easy way for handling and transport. The anchorage of the CNTs or CNFs onto a macroscopic support also prevents excessive agglomeration upon drying step as discussed above for the bulk materials. The structure of macroscopic host supports can also be tuned at will in order to cope with the catalytic process downstream with the aim of improving heat and mass transfer, increasing the effective contact surface through the generation of micro-turbulences through the catalyst bed, accelerating the escaping rate of intermediate products and shortening the diffusion path. The macroscopic shape reduces also the pressure drop through the catalyst bed which is one of the most important prerequisite for industrial implementation. In addition, carbon-based supports are chemically inert which could significantly reduce or suppress the possible reaction between the active phase nanoparticles and the support (strong metal-support interaction), which significantly improves the reducibility of the active phase and thus keeping a high exposed metal active surface.

Another approach to increase the efficiency of a catalyst in liquid phase is by reducing the diffusion path. Thin layers of CNFs coated on structured materials is an interesting approach as

it would combine the advantages of slurry phase operation (short diffusion length), fixed bed operation (no catalyst separation is required, no catalyst attrition, and no catalyst agglomeration) and application of CNT or CNF aggregates (high porosity and low tortuosity). In addition, it allows one to take advantage of the use of structured reactor packing for optimizing hydrodynamics and especially gas–liquid mass transfer to improve catalytic performance as well as recyclability. The pioneering work of Moulijn et al.² has clearly demonstrated these advantages in the case of monoliths. Later, Schouten et al.³ started to explore similar opportunities in the case of foam materials in many catalytic processes. The recent works reported by Edouard and co-workers^{6–8} highlight also the advantages of structured foam support for different catalytic processes with improved mass and heat transfer. For liquid-phase reactions the use of the structured catalysts instead of slurry catalysts allows one to avoid the costly and time consumption filtration process to separate the catalyst from the final product. Structured catalysts also prevent the problem of fine formation as encountered with slurry reactor due to the attrition of small particles under vigorous stirring which lead to the plugging of the filtration device. Finally, microturbulences generated inside the structured catalyst also contribute to a higher degree of reactant mixing leading to a better catalytic performance.

In the present review, we will report on the developments of hierarchical structured catalysts based on the homogeneous decoration of a macroscopic host matrix, *i.e.* monolith, foam and others, with a layer of carbon nanotubes (CNT) or carbon nanofibers (CNF). Pure nanocarbons have been used as catalyst support for anchoring metal and/or oxides nanoparticles while doped nanocarbons have also been used directly as metal-free catalysts for several relevant catalytic processes. The carbon surface can be also functionalized with different elements in order to finely tune its hydrophilicity/hydrophobicity character for subsequence applications. We also focus our attention on the different catalytic processes, both in gas- and liquid-phase, which involve these structured catalysts. When it is possible, the direct comparison will be made between the structured catalysts and the traditional ones in order to highlight the advantages of the structured catalysts in complex catalytic processes where mass and heat transfers represent a major issue. In this review, the term monolith does not refer to the general meaning of monolith, which is “material made from one single piece”. When we say monolith, we implicitly mean the so called honeycomb monoliths with parallel straight channels while other structures will be explicitly stated. The present review will gather some of the updated developments on hierarchical structured reactor incorporating carbon nanomaterials applied to the catalysis field and it is expected that it will encourage industry to implement them and to R&D researches to find new processes that can benefit from these structured reactors.

2. Structured catalyst preparation

2.1. Monoliths

2.1.1. Growth of CNF/CNT on monoliths

2.1.1.1. Growth of CNF/CNT on ceramic monoliths

Several approaches have been used to growth carbon nanofibers (CNF) on monoliths for being used as catalyst support in different catalytic processes. One of them requires the washcoating of the monolith with a high surface area support and subsequent impregnation of metal catalyst onto the washcoat layer. The deposition of the washcoat layer on the macroscopic host matrix requires precaution in order to reduce as much as possible problems linked with the washcoat mechanical adhesion and dispersion.⁹⁻¹¹ Alumina¹²⁻¹⁵, mordenite¹⁶ or titania¹⁷ have been frequently used as washcoating layers in numerous catalytic processes. Other approaches reduce the number of preparation steps by depositing the CNF growth catalyst directly on cordierite monolith or carrying the CNF growth on bare cordierite monolith using a floating catalyst method, in this later method the growth catalyst was carried in the gas feed as ferrocene.¹⁸⁻¹⁹ The advantage of using CNF or even carbon nanotubes (CNT) as coating layer is that the layer also conveys to the catalyst some thermal conductivity which could reduce the problem of temperature gradient found for other insulator coatings. The possibility to improve thermal conductivity of the catalyst is of great interest for reducing problem of selectivity lost, due to the formation of local hot spots, as discussed above. Tuzovskaya et al.²⁰ have reported that the grafting of a layer of CNFs on stainless steel foam boosts the heat transfer efficiency from 30 to 75% due to the increase of the effective surface contact and also to the thermal conductivity of CNFs. In addition, catalysts with improved thermal conductivity could also be helpful during some oxidative regeneration process where temperature gradient needs to be avoided.

In the washcoating method, monolithic structures are typically washcoated with a high-surface area metal oxide and impregnated with the metal catalyst, usually nickel or iron, and subsequently heated in a flowing carbon-containing gas to perform the growth of CNFs.¹²⁻¹⁵ Using this procedure, the metal catalyst for the growth of CNFs remains behind on the monolith. In most of applications, the metal is not a hindrance for reaction since it is encapsulated by carbon layers deposited during the growth process and thus no longer exposed to reactant molecules. However, as a rule of thumb, it is advisable to perform a blank reaction test with the bare CNF/monolith before depositing other metal catalyst to corroborate that the growth catalyst is inactive in the targeted reaction. A treatment with strong acid for the removal of residual metals is not always feasible, since this may also partially dissolve the monolith structure and affect the attachment of the CNF layer.²¹ Some authors

reported that the washcoating with a TiO_2 layer increased significantly the resistance of the CNF/monolith structure towards acid treatment.¹⁷

The mechanical resistance of the as-growth nanocarbon layer is of great interest for industrial application as low mechanical strength leads to the formation of fine and inhibits in such a way the advantage of the nanocarbon coating. It has been observed that the mechanical stability of CNF/monolith is very sensitive to the CNF growth conditions, which requires optimization based on a trial and error approach. The growth conditions of a CNF layer on monoliths have been optimized previously for a Ni/alumina wascoated monolith.¹²⁻¹³ The optimized CNF layer is very well attached to the monolith, resisting even after very harsh ultrasound treatment. The CNF content in the monolith is typically around 17 wt. % leading to a CNF layer of about 5 μm in thickness. This CNF layer was grown with 50% $\text{C}_2\text{H}_6:\text{H}_2$ mixture at 873 K during 3 hours. Lower CNF loadings were also well attached to the monolith, achieved by diluting the feed hydrocarbon gas with Ar. Alternatively, N-doped CNF were also grown on Ni impregnated alumina coated monoliths by using a gas containing 50% $\text{C}_2\text{H}_6:\text{NH}_3$.²² The mechanism of CNF growth is well documented,²³⁻²⁴ in brief, the fed gases are decomposed on the Ni catalyst leading to carbon diffusion through the metal nanoparticle and precipitation of graphitic layers at the rear to form the CNFs. The precipitation step occurred when the carbon concentration inside the catalyst particle reached a certain value. This process continues until the metal nanoparticle is encapsulated by a carbon layer. The decomposition of C_2H_6 and NH_3 supply carbon and nitrogen atoms, respectively, during the growth of N-doped CNFs. Similar efficiency of the alumina washcoat for nanocarbons growth has also recently been reported by Hosseini et al.²⁵ for the synthesis of CNFs on honeycomb monolith.

The excellent attachment of CNF layer to monolith evidenced by the negligible loss of CNFs in harsh conditions is attributed to the penetration of CNF network inside the cordierite macropores¹⁵ and also to the self-supporting ability of the entangled CNFs network with joints and branches (Figure 1A and B).¹³ The penetration of CNFs into the cordierite monoliths functions as a “root” for the CNF “carpet” as illustrated in Figure 1C and D. The good attachment requires very critical CNF growth conditions. Excessive CNF growth produces the creation of cracks in the cordierite, leading to the bending of the monolith as illustrated in the scheme presented in Figure 1D and eventually to the powdering of the composite through the grain boundary breaking as a consequence of to the penetration of the CNF inside the host matrix. Several reasons can lead to the excessive CNF growth such as fast growth due to high temperature, excessive reactive gas or very large metal nanoparticles.²⁶

Figure 1. (A, B) Representative CNF with branched structure grown on monoliths. Note the presence of exclusive prismatic planes of the CNF with high reactivity. (C) Picture illustrating a good attachment of CNF coating to the monolith due to penetration of CNF on the macropores; (D) Picture illustrating the excessive CNF growth leading to breaking of the cordierite monolith and detachment of CNF layer.

Therefore, the growth of CNF layer must be controlled very carefully because excessive or uneven CNF growth can lead to disintegration or detachment of the CNF coating as shown in Figure 2 a and b, respectively. The growth conditions should be optimized in each case using trial and error feedback. In our case, CNF loadings above 22 wt. % were achieved without damaging or breaking of the monolith. It is worthy to note that such structure damage not only happens with monolith or foam but also with pellets, with higher integrated structure, as well due to the deep penetration of nanocarbons inside the grains boundary which finally disrupt the grains cohesion leading to the macrostructure collapse. Such phenomenon has been reported earlier to be at the origin of some reactor breakdown during high temperature operation.

Figure 2. Digital images of disintegrated monolith after the CNF growth at 1023 K (a) and detached CNF layer from the macroscopic host substrate which compromise the mechanical resistance of the composite (b).

A very crucial step for the preparation of CNF/monolith is the washcoating with alumina layer. One popular method for the washcoating of monoliths with alumina layer is dip coating using a sol of pseudo boehmite precursor. Very thin or very thick alumina washcoating layer are not optimal conditions for the final monolith properties. The thickness of this layer depends on several factors such as sol viscosity and withdrawal speed from sol.²⁶ Very thin washcoating layer ($< 0.1 \mu\text{m}$) may leave some areas of monolith walls without coating, resulting in an uneven growth of CNFs. On the other hand, if alumina washcoating is very thick, the macropores of cordierite are completely filled with alumina preventing the anchorage of CNF within the macropores leading to a poor mechanical anchorage for further catalytic use. In addition, with thick alumina washcoating ($\sim 17 \mu\text{m}$), the thickness of the CNF layer grown was smaller ($\sim 1 \mu\text{m}$) for similar CNF loadings,¹⁵ suggesting that some of the CNFs were buried in the porous alumina washcoating and thus, are not accessible for anchoring active phase. Moreover, the resulting composite may retain significant microporosity due to the pores of the alumina washcoating which enhance the problem of diffusion. In liquid-phase catalytic reactions, the remaining microporosity of alumina layer can give rise to significant diffusion limitations and unexposed metal active phase, often resulting in reduced selectivity and conversions. To avoid microporosity of the underneath alumina support, one option is to coat it with mesoporous alumina. Using the washcoating approach, between 5-6 wt.% of mesoporous alumina with respect to monolith weight was deposited, giving rise to alumina thicknesses of less than $1 \mu\text{m}$.¹² Initially the monolith with the alumina washcoating was mesoporous with pores centered at 6 nm (Figure 3). After CNF growth, the CNFs fill the pores of the alumina leaving almost no pores smaller than 10 nm, only the mesopores larger than 10 nm arise. These later mesopores cannot be attributed to alumina but to the pores left between the entangled CNFs and between these later and cordierite macropore walls. The

overall surface area of the monolith after CNF coating was $\sim 30 \text{ m}^2\text{g}^{-1}$, which is relatively low compared to traditional supports such as alumina or silica, i.e. $> 100 \text{ m}^2\text{g}^{-1}$, but significantly high for ceramic composites. Assuming that all the surface area corresponds to CNFs, the surface area normalized per CNF weight is $170\text{-}200 \text{ m}^2\text{g}^{-1}$, which is in agreement for previous values reported for pure CNFs aggregates.²³ In addition, the nanoscopic dimension of the CNF inside the layer provides a high effective surface area for anchoring of the active phase along with short diffusion path for accelerating the reaction rate and also to improve the escaping of intermediate product.

Figure 3. Pore size distribution determined by the DFT method applied to N_2 physisorption isotherms of the original γ -alumina washcoated monolith and the monoliths after CNFs growth with $\text{C}_2\text{H}_6:\text{H}_2$ mixture at the different temperatures: (○) γ -alumina wascoated monolith, (▲) composite after CNF growth at 873 K, 13.2 wt% CNF ; (■) composite after CNF growth at 923 K, 16 wt% CNF; (◆) composite after CNF growth at 973 K, 17.8 wt% CNF. Reprinted from reference [12] with permission of Wiley.

Concerning the growth metal catalyst, the preparation of Ni nanoparticles of small size is crucial for the integrity of the monolith after CNF growth. In our preparation method, the Ni particles have a mean size of 6 nm. To achieve this small size of Ni nanoparticles, which are uniformly distributed along the monoliths, the strong electrostatic adsorption method was used. Using a pH-neutral buffered solution of $\text{Ni}(\text{NO}_3)_2$, a 20 wt. % of NiO was adsorbed with respect to the weight of alumina. For the uniformity of CNF layer coverage and thickness, it is also pivotal that Ni is evenly distributed on the alumina washcoating (Figure 4). The uniformity of Ni coverage can be visually confirmed by the uniform greenish color in the entire monolith

(Figure 4 b). Zeolites have also been used as a washcoat layer to disperse cobalt nanoparticles for subsequent growth of CNFs.¹⁶ Wang et al.²⁷ have reported that Ni-Cu catalyst was effective for growing CNFs on monolith structure. The addition of Cu to Ni reduces the sintering of the Ni particles which improves the growth rate of CNFs as well as the uniformity of their diameter.

Figure 4. Different preparation stages of CNF/monolith: (a) Al_2O_3 washcoated monolith, (b) monolith after nickel impregnation showing the typical green color, (c) black-colored monolith after CNF growth.

Some authors used a simplified preparation process by depositing the metal directly on the cordierite monolith and thus, avoiding the washcoating step. The metal, Fe or Co, was impregnated directly onto the monolith from nitrate precursor solutions either by adsorption in vacuum²⁸ or dip coating²⁹, respectively. Carbon nanotubes (CNT) were grown using a very reactive hydrocarbon, namely, 50% C_2H_2 in H_2 . Subsequently, the monolith was treated in H_2 atmosphere at 750 °C for 2 h to remove amorphous carbon formed during the growth process. It was demonstrated that the CNT adhesion to the monolith is good since only a 3 wt. % of CNT is lost in the first 20 min of ultrasonic treatment and then remained stable for longer treatment. The cobalt loading has a profound impact on the properties of CNTs/cordierite monoliths.²⁹ For the higher Co loading of 0.7 wt. %, the monolith becomes very brittle, the CNT diameter distribution is non uniform and part of the monolith wall is not covered by CNT. It was proved that the CNT diameter is uniform for 0.3 wt. % Co loading but it is not shown if the coverage of the monolith walls is complete. Measurement of the average thickness of the CNF layer is also omitted in the article which renders the comparison somehow difficult.²⁸ The active sites such as Fe nanoparticle for growing CNFs and CNTs could be also obtained from natural sources, such as minerals, clays, and soils. For example, Su

et al.³⁰⁻³¹ used the lava rocks from Mount Etna, containing abundant Fe_2O_3 with a mass loading as high as 11 wt. %, as growth catalysts and supports to synthesize and immobilize CNTs and CNFs. CNTs/CNFs supported on natural minerals sources without intricate synthetic strategy could also be considered as efficient and economical strategy exploitation for superior and tailored nanostructured carbon supports for large-scale applications, such as catalysis and wastewater treatment.

An even more simplified preparation process is by introducing the growth catalyst directly into the growth area in the form of vapor, *i.e.* the so-called floating catalyst method. Aligned arrays of CNTs were grown on cordierite monoliths via an aerosol based chemical vapor deposition (CVD) of ferrocene dissolved in toluene.¹⁸⁻¹⁹ The resulting CNTs layer is 80–100 μm thick, and represents up to ~5 wt. % by weight of the resulting monolith composite (Figure 5). This method has the advantage that it allows the avoidance of the steps of washcoating and catalyst deposition on the monolith used in the other previous methods. However, the methods are not directly comparable because actually each method gives rise to very different materials. The resulting CNT/monolith composite synthesized by the floating catalyst has substantial differences compared to the CNF/monolith prepared by the fixed catalyst anchored on the alumina washcoating method. First, the microstructure of the carbon material is different, aligned CNT vs. entangled fishbone CNF. The surface area of the CNT/monolith is 8 $\text{m}^2 \text{g}^{-1}$ after activating in air at 550 $^\circ\text{C}$ while that of CNF/monolith is 30 $\text{m}^2 \text{g}^{-1}$. As explained above, this porosity is only ascribable to the voids between the entangled CNFs and between these and cordierite walls. The CNT layer thickness is one order of magnitude larger and the CNT weight loading lower for the monoliths developed by floating catalysts method than for those developed by alumina washcoating method, indicating that less carbon nanomaterial is embedded in the macropores of cordierite for the former method. After 30 min in ultrasonic bath, it is reported a 20 wt. % weight loss of CNT while it is typically lower than 7 wt% for CNF/monoliths prepared by the washcoating method.^{12, 14} In both methods, the looser CNFs are released in the first 30 min in ultrasonic bath and there is no more weight lost for longer durations. These results suggest that the adhesion of some CNTs prepared by floating catalyst method is weaker than that of CNF attached to alumina washcoated monoliths. It is claimed that the attachment of CNT to the substrate occurs through nanoparticle at the base of CNT anchored to the cordierite.¹⁸⁻¹⁹ Unfortunately, no evidences were presented about this. The adhesion of CNT prepared by floating catalyst method might be sufficient for gas-phase application such as the proposed Fisher-Tropsch reaction where low space velocity and low friction was generally encountered.¹⁹ Nevertheless, for applications with harsher mechanical conditions such as flowing liquids or mobile applications, the use of CNT/monoliths prepared by floating catalyst method may release CNTs, giving rise to health concerns. Therefore, the

good attachment of CNTs should be demonstrated for each application under real operation conditions. Cordierite monolith as substrate to support CNF has some drawbacks such as it is insulator and thus, could be damaged by local hot spot formation when operating exothermic reactions. This could be circumvented by using conductive substrates such as metallic monoliths described in next section. The straight channels of the cordierite also offer low effective surface contact for the reactant gas during the process compared to foam structure.

Figure 5. SEM micrographs of CNT grown on bare cordierite monolith. Adapted according to the data from reference 18.

2.1.1.2. Growth of CNF/CNT on metallic monoliths and microreactors

Metallic monoliths have many similarities with microreactors as both display parallel straight channels where reaction takes place. The main difference is the width of the channels that is in the range of millimetres for monoliths while it is in the range of hundreds of microns for microreactors. The main advantage of metallic monolith and microreactor is that they display a very good thermal conductivity which prevent or suppress the formation of temperature gradient inside the reaction zone leading to the improvement of selectivity by reducing thermal induced secondary reaction. The smaller channel size of microreactors favors heat and mass diffusional processes and endows microreactors a higher volumetric surface area than the monolith. The heat transfer can be also improved by coupling the microreactor with a heat exchanger where a fluid circulation ensures the heat exchange with the reactor itself. The manufacture of chemicals in catalytic micro-structured reactors has become recently a new branch of chemical reaction engineering focusing on process intensification and safety.³²⁻³³

The integration of a solid catalytic phase (heterogeneous catalyst) in microreactors is a challenging task. One of the options is filling microchannels by catalyst powder³⁴ but this leads to high pressure drop and increases residence time distribution, spoiling some of the advantages of the microreactors. Another option is using a thin layer of catalyst coated on the inner wall of a microchannel to increase surface area and to reduce the problem linked with pressure drop.³⁵ There is a limitation in the layer thickness for several reasons. Typically, it should be thinner than 100 μm because thicker layers may encounter adherence problems. In

exothermic reactions, the catalyst layer should be $<1\text{-}2\text{ }\mu\text{m}$ to avoid temperature gradients. Due to the limitation of thickness the mass of catalyst is too small which renders process intensification an elusive goal, especially for fast reactions. In addition, the channel can be plugged during the coating process which calls for reactor replacement in order to avoid excessive pressure drop through the channel. Most of these problems can be overcome by introducing nanoscale structural features in the microchannels. An exciting option in this regard is the use of rigid, porous and orderly arranged catalyst supports based on carbon nanostructures, such as carbon nanofibers, onto which a metallic catalytic active phase can be deposited.

In principle, it would be also possible to grow CNF/CNT layer directly on stainless steel monoliths or microreactors without additional metal deposition for CNF/CNT growth because the metals contained in stainless steel can be able to decompose a hydrocarbon source to yield CNF/CNT. However, the coating of a layer of CNFs or CNTs on stainless steel surface requires preliminary thermal treatment of the substrate, *i.e.* oxidation and reduction, before the growth process. Stainless steel foils after a suitable thermal pretreatment have been used to grow CNFs.³⁶⁻³⁹ Metallic monoliths are usually produced from corrugated stainless steel foils.⁴⁰⁻⁴¹ Therefore, it seems to be feasible to develop stainless steel monoliths coated with CNFs. Nevertheless, as far as we know, this has scarcely been reported. One of the reasons could be that the growth of CNF/CNT on stainless steel foils is less controllable, as well as less effective, than on well-defined metal nanoparticles and leads to inhomogeneous growth, leading eventually to the deformation of the metallic monolith. Another approach has been proposed by Pham-Huu and co-workers⁴² using vertically aligned CNTs grown by floating catalyst to fill-up the microreactor volume.

A possible approach could be coating the monolith with a metal oxide support on which size-uniform metal nanoparticles (Ni, Co or Fe) are anchored. This approach has been used to grow a layer of CNF on stainless steel microreactors coated previously with an alumina washcoating layer and impregnated with Ni.⁴³⁻⁴⁴ For optimized growth conditions, the CNF coating was homogenous and the adhesion was good due to the well attached alumina layer (Figure 6). High growth temperatures led to inhomogeneous coating and to the growing of not only CNFs but also other non-filamentous carbonaceous species.

Figure 6. SEM images of CNF coating grown at 853 K with $C_2H_6:H_2$ (60:40): (a) transversal image of the border of a microchannel, (b) high magnification top-view of entangled CNF coating and (c) transversal view of a place where the CNF layer is slightly detached and it is possible to measure the CNF-layer thickness between 1 and 2 μm (arrows in the figure). Reprinted with permission of ⁴⁴.

Silica microreactors have been coated with carbon nanomaterials such as aligned carbon nanotubes by thermal chemical vapor deposition (CVD) using ferrocene and xylene diluted in inert gas.⁴⁵ The reactors were tested in the hydrosilylation of an olefin. The aligned nanotubes were found to greatly improve the catalytic activity as well as its lifetime. CNFs have also been grown on closed channel of fused silica microreactor coated with Ni/alumina and nickel thin film catalyst.⁴⁶ By directly flowing reactant gases over a catalytic coating inside the microchannels, a mechanically stable and porous CNF-alumina composite was formed with high surface area (160 m^2/g) along with significant exposed effective contact surface. In adhesion test using 40 kHz ultrasound, the alumina layer was completely removed after 10 min when there is no CNFs remained on the microreactor. However, in the case of CNF-alumina composite, only about 18 wt. % of the composite was removed and the rest remained stable after 2 h of treatment showing that CNF incorporation resulted in higher mechanical stability of catalyst support layer in the microchannel. The penetration of some CNFs inside the microreactor wall could also be responsible for such mechanical strength improvement. Using also fused silica substrates,⁴⁷ it was demonstrated that the presence of a metal adhesion layer is necessary for the stability of the deposited Ni thin-film on the substrate, and the choice of a proper adhesion material (*i.e.* TiW and Ta) not only improves the attachment of synthesized CNF-coating, but also helps to tune morphological properties such as the diameter of CNFs. Furthermore, an approach was used to efficiently utilize the microchannel volume for reaction, *i.e.* micromachined channels filled with arrays of pillars covered with a CNF-coating,⁴⁸ as shown in Figure 7.

Figure 7. Cross-sectional SEM images showing arrays of micromachined silicon pillars (a) prior to CNF-synthesis, (b) post to CNF-synthesis without hydrogen (25 vol.% C_2H_4 for 1 h), (c) post to CNF-synthesis with 6.25 vol.% H_2 added to C_2H_4 (growth time 2 h): the CNF layer fills the complete pillar spacing, and (d) the grown CNF-coating exhibits the open structure of entangled CNFs. Reprinted from Ref 47 with permission of Wiley.

In another attempt, vertically aligned and strongly attached multi-walled carbon nanotubes (VA-CNTs) were grown on the inner wall of a cylindrical silica reactor (20 mm, inner diameter, 200 mm, length) which can be efficiently used as a catalyst support as well as stirrer in liquid-phase reactions (Figure 8).⁴⁹ The aligned carbon nanotubes film was grown by injecting a mixture of ferrocene/toluene and argon into the decomposition zone at 800 °C. After depositing Pd on the as-growth CNTs, the reactor was used as catalyst and mechanical stirrer and tested in the liquid phase hydrogenation of cinnamaldehyde (Figure 8A). The selectivity towards the hydrocinnamaldehyde, *i.e.* C=C bond hydrogenation, remained high and constant regardless of the level of conversion, *i.e.* selectivity of 90% at a conversion of about 80%. It is worthy to note that the vertically-aligned CNTs (VA-CNTs) display an extremely high mechanical strength which allows them to withstand high stirring rate without structural damage or fine formation during the catalytic tests. An example of such high mechanical strength is illustrated in Fig. 8B where the quartz ring used for the growth of the VA-CNTs was further dissolved in an HF solution in order to recover the VA-CNTs. The VA-CNTs can be manipulated without damage thanks to its high mechanical strength.

Figure 8. (A) Vertically-aligned CNTs (VA-CNTs) growth on the inner surface of a quartz cylinder for being used as stirrer in liquid-phase reactions.⁴⁹ (B) The VA-CNTs ring recovered after dissolving the quartz ring by HF showing the high mechanical strength of the material.

Scanning electron microscopy (SEM) was used to investigate the microstructure of the VA-CNTs and the representative results are presented in Figure 9. According to the SEM analysis, the CNTs were well aligned perpendicularly to the quartz surface in a dense structure (Figure 9A and B). The same VA-CNTs can be also grown on planar quartz surface as evidenced in Figure 9C and D with the same arrangement along the growth axis. The height of the VA-CNTs carpet can also be precisely controlled by adjusting the synthesis duration as shown in Figure 9E. Such control is of high interest when VA-CNTs were grown directly inside a microreactor channel. The control of the growth rate allows one to fill-up the microreactor channel with a homogeneous carpet of CNTs without leaving empty space in the channel which could lead to a heterogeneous flow distribution. The diameter of the VA-CNTs is relatively homogeneous as shown by the SEM micrographs which pointed out another advantage of the synthesis method. The density of the CNTs inside the carpet can be controlled by changing the floating growth catalyst concentration during the synthesis.

Figure 9. (A) Sheet of parallel carbon nanotubes forest with a height of 1200 mm grows on the inner surface of the silica reactor. (B) High magnification SEM micrograph showing the perfect alignment of the tube and the average diameter. (C, D) SEM micrographs of the CNT forest synthesized on a planar quartz plate with a perfect alignment of the CNT along the growth direction. (E) SEM micrograph showing the CNTs carpets at different reaction duration displaying various length. Reprinted from Ref.⁴⁹ with permission of Elsevier.

The benefit of a CNF layer on microreactors was also demonstrated by Schouten et al.⁵⁰⁻⁵¹ using nickel as growth catalyst deposited on carbon plates. Subsequently Pd was deposited on CNF and the microreactor was used for a three-phase reaction, namely hydrogenation reaction of 3-methyl-1-pentyn-3-ol. It was demonstrated that the observed rate of reaction of the liquid-phase selective hydrogenation of an alkyne is higher for an open and rough carbon nanofiber (CNF) layer positioned on a microchannel wall than for an unsupported flat plate catalyst or dense and smooth CNF layers. The CNF layer with the most open structure and the largest CNF layer thickness showed an increase of the overall reaction rate with a factor of approximately 3.5 to 4 in comparison with the unsupported flat plate catalyst, whilst keeping the selectivity towards the intermediate product over 95%. It was stated that a further increase in the overall reaction rate per channel volume could be achieved by a frequent refreshment of the liquid in the CNF layer by a continuous flow of liquid into the layer. These results highlight the good prospects of CNF coating on microreactors. However, more research is needed to improve the preparation of CNF on microreactors surface channel in

order to obtain an optimized CNF layer in terms of adhesion and porosity for the subsequent catalytic processes. The difficulty encountered with the re-use of the microreactor partly hampers the development of such kind of reactor.

2.1.2 Growth of CNF/CNT on bulk and structured carbons

The bulk carbon materials with macroscopic shape could also be used as substrate for hosting the nanocarbon materials. The bulk carbon is defined as carbon without any structuring at nanosize dimension, such as active carbon (AC), carbon felt (CF) and carbon paper, which are widely available but are not highly efficient in catalytic application in its macroscopic shape. AC is a typical example, which is derived from natural precursors. Su et al.⁵²⁻⁵⁴ synthesized hierarchical monolith containing CNF on the outer surface and nested inside of the AC through the CVD of organic molecules. One more advantage is that the introduction of nanocarbon on the AC matrix could also overcome the drawbacks of AC such as low electric and thermal conductivity.⁵⁵ It is known that AC consists of sp^2 - and sp^3 -bonding with a turbostratic structure.⁵⁶ These bioinorganic/bioorganic polymers are well structured in several dimensions, amenable to modifications (functionalization/activation) and mass available.⁵⁷⁻⁵⁹ The fiber fabric-like AC, with large amount of micropores that are beneficial for the dispersion of catalytic nanoparticles, is also adopted as the substrate to grow the CNFs to form a hierarchically structured CF cloths.⁶⁰ Zhou et al.⁵⁷ fabricated a 3D CNT/AC hybrid architectures with pen-tipped CNTs on the surface of bamboo-derived AC. The bamboo-derived AC were activated for anchoring sites on metal catalyst using KOH as an activating agent and then surface functionalized through concentrated HNO_3 treatment. The AC as substrate has structural advantage, however complex pretreatments are needed to increase the oxygenated functional groups as well as the porosity, which is required to develop active catalyst to grow CNFs by CVD.

CNFs have also been immobilized on graphite felt, as proposed by Pham-Huu and co-workers⁶¹⁻⁶² for being used as catalyst support in several reactions. First, Ni as growth catalyst (1 wt %) was deposited on the graphite felt and CNFs were synthesized at 680°C using a reaction mixture of ethane and hydrogen with different concentrations. The CNFs are strongly anchored to the felt as no matter loss could be detected during ultrasonic treatment in ethanol solution during several minutes. It was speculated that the anchoring of CNFs was due to penetration of CNFs into the graphite matrix of the graphite felt during the growth process. The felt microfilamentous were homogeneously covered by a dense network of CNF after synthesis as shown by the SEM micrographs presented in Figure 10A and B. The high coverage degree of the host carbon felt by the CNF was explained by a so-called “octopus growth” model where several CNF were grown from a single metal center as shown in Figure 10C and

D and thus, providing a high coverage surface from a limited number of growth centers which provide an efficient coverage of the macroscopic host matrix within a relatively short synthesis duration.⁶³

Figure 10. (A) Microfilamentous graphite felt covered with a homogeneous and dense network of CNF after CVD synthesis. Inset: Pristine graphite felt with smooth surface reprinted with permission of ⁶⁴. (B) High resolution SEM micrograph of the as-synthesized CNF with homogeneous diameter and high entanglement. (C, D) SEM micrographs with different magnifications showing the “octopus growth” of CNFs from a single nickel particle.⁶⁵

The introduction of CNF in the carbon felt leads to the formation of micro- and nano-bridges between the CNFs, as evidenced by SEM and TEM analysis, which acting as solid glue to connect the different structures together (Figure 11A and B). These bridges provide a significant improvement of the mechanical strength of the composite as depicted in Figure 11C and D. Such property is of high interest to prevent structure collapse during operation as well as fine formation leading to a gradual activity lost with time. The bridges also significantly improve the electrical and thermal conductivity through the composite. Shen et al.⁶⁶ also

reported 3D CNF on the graphite felts (GF) using methane as carbon source, which was subsequently used as efficient adsorbing materials for the removal of Pb^{2+} , Congo red, organic solvents, and oils from aqueous solutions. The secondary CNF arrays were well anchored to the primary carbon microfibers (the diameters around 10 -15 μm) for the fabrication of well-defined geometry shape and excellent chemical stability 3D monolith composite. The nanocarbons such as CNT or nitrogen-doped CNT were also introduced in the macroscopic GF structure as reported by other groups.⁶⁷⁻⁷⁰

Figure 11. (A) SEM micrograph showing the presence of bridges between microfilamentous graphite felt after CNF synthesis. The CNF play the role of “solid glue” for bridging the microfilamentous together. (B) TEM micrograph showing the formation of bridge at nanoscale between the CNFs. (C) Digital photos showing the improvement of the mechanical strength of the composite CNF/C felt after incorporation of the CNF.

Schouten and co-workers⁷¹ have reported the growth of CNFs on carbon paper using nickel as growth catalyst for use as electrode in proton exchange membrane fuel cell. The nickel salt was deposited on one side of the carbon paper through a homogeneous deposition precipitation (HDP) method which took advantage of the hydrophobicity of the carbon paper (Figure 12). The CNFs were homogeneously grown on the surface of the carbon paper and the final specific surface area of the composite was $> 150 \text{ m}^2/\text{g}$ along with a high porosity ≥ 60

%. The catalyst displays a high mechanical stability due to the strong binding of the CNF to the carbon paper host matrix which prevents CNF detachment during reaction, similar to those reported by other groups.⁷²⁻⁷⁴

Figure 12. (A) Low magnification SEM micrograph of the CNF-grown on carbon paper surface after 24 h of homogeneous deposition precipitation of nickel hydroxide. Inset: Photo of the whole CNF-grown carbon paper with a diameter of 40 mm. (B) SEM micrograph of the CNFs on the carbon paper showing the homogeneous diameter and high aspect ratio.

2.1.3. Unsupported nanocarbon monoliths and microreactors

Micro-channelled structures resembling that of the honeycomb monolith have been prepared based on self-supporting multi-walled CNT (MWCNT) within a ceramic supporting substrate.⁷⁵ Employing a method called ISISA (ice segregation induced self-assembly), materials with well-defined macroporous 3D architectures were prepared. The ISISA process was applied to water suspension of MWCNTs (2-8 wt %) and chitosan (1 wt %). The MWCNT/Chitosan suspension is unidirectionally frozen by immersion in liquid nitrogen. Subsequent freeze-drying results in highly porous and self-supported monoliths mostly composed of MWCNTs (up to 89%) with a chamber-like architecture in the form of interconnected MWCNT/Chitosan sheets arranged in parallel layers. Liu et al.⁷⁶⁻⁷⁷ prepared self-macronized MWCNTs and nitrogen atoms doped MWCNTs with controlled macroscopic shape and fully accessible surface area through the gelation process (Figure 13A-F). The macroscopic shape of MWCNTs beads is beneficial for mass diffusion, thus avoiding the drastic pressure drop across the solid bed compared to that of unshaped carbon nanotubes powder. The nitrogen-doped carbon nanotube beads with macroscopic shaping were then applied as metal-free catalyst for the selective oxidation of H₂S into sulfur. It displays a relatively high

catalytic performance and also high stability, which is comparable to the reported high active metal base catalyst, i.e. $\text{Fe}_2\text{O}_3/\text{SiC}$.⁷⁷ A self-standing nanocarbon monolith containing MWCNTs and nitrogen doped mesoporous carbon with controlled size and shape was synthesized through physical mixtures of CNTs and food-grade components (D-glucose, citric acid and ammonium carbonate) as the starting materials, and then went through further thermal treatment under air and inert gas, respectively.⁷⁸⁻⁷⁹ In this process, the macroscopic composites with different pore size distributions and specific surface areas ($> 350 \text{ m}^2/\text{g}$) could be adjusted by changing the mass ratio of MWCNTs and food-grade components, depending on the downstream applications of the monolith materials.

The self-standing CNT or CNF monoliths either with or without nitrogen element doping have been developed in recently by using polymer, organic compounds or hydrogencarbons as carbon sources.^{10, 80-81} Zhang et al.⁸² fabricated prismatic structure material composed of multiwalled CNTs using the commercial styrene–divinylbenzene copolymer resin as carbon precursor (Figure 13G-J). The produced CNTs sphere presented BET surface area and the pore volume as $224 \text{ m}^2 \text{ g}^{-1}$ and 0.42 mL g^{-1} , respectively, which consisted mostly by open-ended CNTs with inner diameter of the tubes ranges from 60 to 90 nm. Metal-organic frameworks (MOFs) have also been used as precursor for both nanocatalysts and carbon sources for the general oriented formation of CNTs with high yield at low-temperature of around 430°C in pyrolysis process.⁸³ The different morphologies and components (with nitrogen doping and transition metals) of MOF-derived CNT monoliths were synthesized by various MOF crystals.

Figure 13. (A-D) Sequential steps for the preparation of N-doped 3D self-standing composites (N-C/CNT) (D), from a physical mixture (wt/wt) of commercially available food-grade components and pristine MWCNTs (A) to their physical crushing (B) up to their thermal treatment in a selected shape-inducing sample holder.⁷⁸⁻⁷⁹ (E, F) SEM micrographs of N-C/CNT monolith at various magnifications. (G) Schematics of the formation process of N-CNTs from zeolitic imidazolate frameworks (ZIF-67). (H-J) SEM and TEM images of N-CNT-assembled hollow dodecahedra.⁸³

A self-supporting microreactor consisting of parallel carbon nanotubes sandwiched between a top and bottom carbon layer was prepared using porous alumina as the template and propylene as the precursor gas (Figure 14).⁸⁴ Continuous flow around the individual tubes

is accomplished which makes it possible to perform catalytically driven chemical reactions on a sub- μm to nm scale. The concept was proved after depositing Pd in the hydrogenation of p-chloronitrobenzene to p-chloroaniline achieving a yield of p-chloroaniline of 2.6 % without performing any optimization of the process.

Figure 14. a) Nanostructured reactor with macroscopic scale. b) The skin like, flexible, all-carbon structure can be handled with tweezers. c) SEM view of the top carbon layer. The tubes are embedded between top and bottom layers. d) A close-up side view of the structure showing the straight and parallel tubes in a three-dimensional array. Reprinted from ⁸⁴ with permission of Wiley.

Foam-like monoliths consisting only of graphene have been recently synthesised. Several methods have been used such as the use of a sacrificial template such as nickel or iron sponges⁸⁵⁻⁸⁸ for the growth of graphene sponges by CVD. Graphene foams have also been prepared by soaking alumina or silica with graphene oxide dispersions.⁸⁹⁻⁹⁰ Graphene foams or aerogels have been attained without the use of sacrificial template, by autoassembling of graphene oxide nanosheets and subsequent freeze drying.⁹¹⁻⁹⁶ Using unidirectional freezing, ice acts as a template leading to aerogels with parallel channels resembling those of honeycomb monoliths.⁹⁷⁻⁹⁸ To our knowledge, graphene aerogels have been used in absorption or energy storage applications but not yet as structured reactor for chemical reactions. The problem of active phase loading per volume of catalyst in the case of light weight aerogels could represent a drawback in the industrial development.

2.1.4. Deposition of active phase on the CNF/CNT monolith

For the development of catalyst supported on CNFs/CNTs in powder form, it is a common practice to perform an oxidation treatment of CNFs/CNTs to create oxygenated surface groups to anchor the metal catalyst precursor. HNO_3 is usually the oxidizing agent of choice.⁹⁹⁻¹⁰⁰ However, harsh treatments with HNO_3 under boiling conditions should be avoided because leaching of metals from cordierite substrate are very likely to happen, which is detrimental for the mechanical stability of the monolith and for the adhesion of the CNF coating.²¹ On the other hand, it was observed that H_2O_2 is a milder oxidizing agent that creates oxygenated surface groups on CNF without compromising the mechanical stability of the CNF/monolith.

For the impregnation of the metal precursor, methods such as incipient wetness impregnation are not feasible for a uniform deposition on a monolith. To guarantee a uniform deposition along CNFs, suitable methods are based on some kind of interaction between the precursor and functional groups on CNF surface for the anchorage of the active phase. This interaction can be of different nature, such as electrostatic, van der Waals or covalent attachment. It is important that the active phase does not become mobile after the subsequent calcination or reduction treatment to prevent sintering.

In addition, to ensure the uniform distribution of metal along the monolith walls, the precursor solution must wet completely the monolith surface as well as its porosity. To this end, usually the liquid precursor is flowed through the monolith channels for long time. One impregnation method used very often for CNF/monoliths is equilibrium impregnation, also called equilibrium adsorption. This method leads to a uniform deposition of the metal on all the CNFs on the monolith surface. This procedure is carried out using a continuous circulation of the precursor solution through the channels of the monolith for several hours until equilibration.^{12, 101-102}

If the interaction between the precursor and the CNFs surface is electrostatic, the metal loading is controlled by the amount of oxygenated acid surface groups and the pH of solution. The electrostatic adsorption is maximized for certain pH of solution which leads to the so called strong electrostatic adsorption.¹⁰³⁻¹⁰⁵ The strong electrostatic adsorption occurs for pH of solution higher than the PZC (point of zero charge) of the CNF/CNT when using a cationic metal precursor and for pH of solution lower than the PZC of the CNF/CNT when using an anionic metal precursor. It was found that nitrogen atoms substituting carbons on CNFs also contribute to enhance the adsorption of a cationic Ru precursor compared to undoped CNFs.

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Another strategy to deposit metal nanoparticles on CNFs coating a monolith in a homogeneous fashion is the homogeneous deposition-precipitation method (HDP). In this

method, the pH is gradually and homogeneously increased from 3 to 6 by hydrolysis of urea. This makes that the cationic precursor is gradually bound to the deprotonated oxygenated acidic groups of carbon surface. Toebe et al.¹⁰⁷ compared the deposition precipitation method with the adsorption method at a constant pH using cationic precursors, namely $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ and $\text{Ru}(\text{NO}_3)_3(\text{H}_2\text{O})_2$. With both synthesis techniques, homogeneously distributed, highly dispersed and thermally stable metal particles were obtained with an average particle size of 1–2 nm. Nevertheless, it was demonstrated that using HDP procedure higher platinum loadings (4 wt %) can be achieved than using the ion adsorption procedure (<2 wt %). Using the HDP method for the Pt/CNF catalysts, a linear relationship between the number of acidic oxygen-containing groups on the surface of activated CNF and the metal loading has been found, corroborating the anchoring of the precursor to the acidic oxygen-containing groups. Consequently, the metal distribution reproduces the uniform distribution of oxygenated acidic groups on CNFs along the entire monolith surface. Liu et al.¹⁰⁸ prepared cobalt nanoparticles on the monolith supports containing CNT layer and $\alpha\text{-Al}_2\text{O}_3$ host for the Fischer-Tropsch synthesis (FTS) process. The homogeneous, highly entangled and structure-opened CNT thin shell was beneficial for the cobalt nanoparticle dispersion and also for the mass diffusion during the FTS reaction which resulted the highly selectivity towards liquid hydrocarbons and stability. Furthermore, they introduced single crystal TiO_2 nanoparticles on the surface of CNT- $\alpha\text{-Al}_2\text{O}_3$ monolith in order to avoid the mobility of the cobalt nanoparticles in the FTS reaction.¹⁰⁹ They concluded that the high FTS activity on cobalt deposited $\text{TiO}_2/\text{CNT-}\alpha\text{-Al}_2\text{O}_3$ monolith could be attributed to the presence of TiO_2 -promoted surface which displayed a high interaction with the deposited cobalt phase leading to the formation of small cobalt nanoparticle sizes from 4 to 10 nm. The effective surface area of CNT network on the monolith surface again provided high accessibility of the reactant toward the active sites even in the presence of some liquid phase generated during the reaction.

2.2. Foams

Structured foams, ceramic or metal, are widely studied in the last decades due to their outstanding physical properties such as high open porosity, low diffusion path, high tortuosity, interconnected structure and low pressure drop across the catalyst bed. Foams are also commercially available in several shapes regarding the downstream applications as well as with different materials, i.e. metallic, ceramic, carbon. Foam materials have already been used as catalytic stirrer in several catalytic applications with improved liquid-solid mass transfer.¹¹⁰⁻¹¹³ Compared to the honeycomb monolith foam displays an extremely high degree of radial mixing of the flow passing through its porous matrix, being it gaseous or liquid, which considerably improves the reactant mixing and also the heat transfer for the reaction (using

thermal conductive support). It is expected that structured foam catalyst will become more and more important in the heterogeneous processes, when diffusion limitations become critical, i.e. fast gas-phase and liquid-phase reactions, compared to the others catalysts.¹¹⁴⁻¹¹⁵ The digital photo and the reconstructed volume of foam through X-ray tomography¹¹⁶ are presented in Figure 15A and B showing the high open porosity and the randomly distribution of the struts along the foam axis. The high efficiency of the foam to perform high mixing degree of liquid is presented in Figure 15C. The struts of the foam are also relatively thin which significantly improve the reactant access to the deposited active phase and thus, reduce the problem of mass transfer or pore plugging during the reaction. This section will deal with the synthesis of a medium to high specific surface area (10 to 70 m²/g) porous beta SiC foam and washcoated Al₂O₃/Al foam as a new catalyst supports platform for developing hierarchical catalyst support or directly as metal-free catalysts in some relevant catalytic processes. The hierarchical catalysts display high catalytic performance in some catalytic processes where traditional catalysts have evidenced weakness, i.e. selective oxidation, fine chemical synthesis and synthetic fuel production, just to cite a few. Those supports present a relatively high thermal conductivity, thanks to the interconnected structure, through the entire matrix which could efficiently prevent the formation of hot or cold spot within the catalyst bed when operated with exothermic and endothermic reactions. In addition, the foams can be produced with different window sizes and shapes, which can be efficiently adapted for downstream applications. An example of SiC foams with different pore window size and dimensions is presented in Figure 15D.

Figure 15. (A) Scanning electron micrograph of the SiC foam struts and windows with high open porosity and interconnected structure. (B) Reconstructed structure of the polymeric foam by X-ray tomography method.¹¹⁶ (C) Dye dispersion in liquid medium through foam structure. (D) SiC foams with different windows size (Courtesy from <https://sicatcatalyst.com>).

2.2.1 CNF/CNT on SiC foam

The CNF decorated SiC foam has been developed by the group of Pham-Huu and co-workers for different catalytic processes including gas- and liquid-phase reactions.^{62, 117-119} The growth catalyst, nickel nanoparticles, is relatively well anchored and dispersed on the SiC foam thanks to the presence of a thin natural washcoat layer constituted by a mixture of SiO₂ and SiO_xC_y.¹¹⁴ The SiO₂/SiO_xC_y layer with a thickness of about 2 to 3 nm covers almost 60% of the SiC surface (Figure 16) according to the analytical TEM analysis and XPS.¹¹⁴ The SiO₂/SiO_xC_y layer was expected to be formed during the calcination step after the SiC synthesis in order to remove the unreacted carbon inside the material. Such natural washcoat displays an extremely high mechanical stability as it has been grown directly from the native surface of the support which allows the avoidance of problems of washcoat breaking and detachment, as usually encountered.

Figure 16. (A) Low magnification transmission electron micrograph of the SiC synthesized by a gas-solid reaction covered by a thin layer of $\text{SiO}_2/\text{SiO}_x\text{C}_y$ (indicated by arrow). (B) High resolution TEM micrograph showing the $\text{SiO}_2/\text{SiO}_x\text{C}_y$ layer with a thickness of 1-2 nm on the SiC surface.

The growth process is similar to that developed in the CVD one for the production of CNF and CNT from the literature using either nickel or iron nanoparticles. In Figure 18 are presented the representative SEM micrographs of the CNT/SiC foam composite obtained using iron as growth catalyst and ethane as carbon source (Figure 17A and B). The CNTs can be synthesized either in a pure form or doped with nitrogen, using NH_3 as nitrogen source, for further used as metal-free catalyst. The ferrocene has also been used as floating catalyst to growth vertically-aligned CNTs on the foam surface as shown in Figure 17C and D. Such VA-CNTs provide a relatively high effective surface for the reactant during the catalytic process which is somehow lower than those provided with entangled CNT or CNF due to the high density of CNT per surface unit. However, the main drawback is linked with the low mechanical anchorage of the VA-CNTs layer on the SiC foam surface. Such problem could be due to the porous structure of the SiC foam compared to that of quartz.

Figure 17. (A, B) SEM micrographs of the CNT layer on the SiC foam with a homogeneous coverage using Fe as growth catalyst. (C, D) SEM micrographs of the VA-CNTs growth from a floating ferrocene catalyst on the SiC foam. The alignment of the CNT is less straight along with a lower mechanical strength on SiC surface than that obtained on the quartz surface which could be attributed to the porous surface of the SiC.

Similar reports focused on the synthesis of CNTs or CNFs on SiC foam have been published in the recent literature.¹²⁰ The additional coating of a silica washcoat layer on the SiC foam seems to have a little effect on the growth rate and yield of the CNFs. Chizari et al.¹²¹ have also synthesized nitrogen-doped carbon nanotubes (N-CNT) by CVD method on the SiC foam for being used as metal-free catalyst in the partial oxidation of H_2S into elemental sulfur. The N-CNTs were homogeneous dispersed on the SiC foam surface which endows the composite a high effective surface area and low diffusion path, thanks to the nanoscopic dimension of the N-CNTs, for the reaction (Figure 18A-D). TEM analysis indicates that the SiC-supported N-CNTs display a similar microstructure as those in a bulk form with a periodical bamboo-like arrangement along the tube axis (Figure 18E). TEM tomography carried out on such material indicates that the compartments are closed by carbon cap with high nitrogen concentration.¹²² The main drawback of such bamboo-like structure is that only the nitrogen sites on the surface are accessible for the reaction while those present inside the structure are not in contact with

the reactant. The N-CNT also displays lower defect density compared to that encountered with undoped CNT.

Figure 18. (A, B) Photographs of the SiC foam and N-CNT/SiC foam composite synthesized in a mixture of $\text{C}_2\text{H}_6/\text{NH}_3/\text{H}_2$, which show the high accessibility of the macroscopic structure. (C, D) SEM images of the N-CNT/SiC composite, which show the detailed microstructure of the N-CNTs on the surface of the SiC support and the average diameter of the N-CNTs. (E) TEM micrograph of the N-CNTs with a periodical bamboo-like structure along the tube axis.

The same synthesis was also used for producing N-CNT decorated SiC pellets as hierarchical metal-free catalyst in the gas-phase selective oxidation of H_2S .¹²³⁻¹²⁴ The introduction of N-CNT onto the SiC pellets leads to a significant increase of the overall specific surface area thanks to the high intrinsic specific surface area of the N-CNT. The specific surface area decreases for the composites synthesized at temperature higher than 750°C as evidenced in Figure 19A. The optimum synthesis temperature is 750°C where a highest surface area was obtained. In Figure 19B is presented a comparison of the diameter between the unsupported N-CNT and the N-CNT/SiC pellets. According to the results, the supported N-CNTs display a broad range of diameter distribution compared to that of the unsupported one. Such difference could be explained by the fact that the N-CNTs were synthesized from a $\text{Fe}/\text{Al}_2\text{O}_3$ which presents higher metal-support interactions than that of the Fe/SiC . The lower metal-support interaction in the Fe/SiC leads to a higher metal sites sintering during the thermal treatment and, as a consequence, to N-CNTs with broader diameter distribution. The hierarchical N-CNT/SiC catalyst has also succeeded applied as metal-free catalyst in the direct dehydrogenation (DDH) of ethylbenzene to styrene.¹²⁴ The N-CNT/SiC (with a N-CNT loading of 40 wt. %) catalyst was applied in the DDH reaction, which showed slightly higher activity compared to commercial $\text{K-Fe}_2\text{O}_3$ -based catalyst. The specific reaction rate at steady state (expressed as the amount of styrene produced per g of N-CNT per hour) of the N-

CNTs/SiC catalyst was 2.3 times higher than that of the N-CNTs unsupported catalyst, indicating that the highly accessible macroscopic structured N-CNT/SiC enhanced the contact between the active site and reactant.

Figure 19. (A) Specific surface area of the pristine SiC and the same after decorating with different N-CNT as a function of the synthesis temperature. (B) Average tube diameter of the unsupported N-CNT (Fe/Al₂O₃ as growth catalyst) and SiC-supported N-CNT synthesized at 750 °C.

Su and co-workers have recently reported the high efficiency of CNT coated SiC foam as monolith catalyst and catalyst support in several relevant catalytic processes such as oxidative and direct dehydrogenation reaction.¹²⁵⁻¹²⁷ The CNTs with diameter of around 20 nm are grown randomly and entangled on the SiC foam surface, and then used as efficient metal-free monolithic catalyst for the oxidative dehydrogenation reaction of 1-butene into butadiene.¹²⁵ The CNT-SiC foam monolith was further decorated with Pd nanoparticles, exhibiting a superior catalytic activity in the Suzuki cross-coupling reaction compared to that of Pd/CNTs catalyst.¹²⁷ More favourable performances of Pd/CNT-SiC monolith are anticipated for the potential application in industrial processes, where more easily separation and recovery from reaction solutions are highly searched for.

2.2.2 CNF/CNT on metallic or oxide ceramic foam

The Schouten group is pioneer and the most involved in the development of structured aluminum foam for catalytic applications in several liquid-phase processes.¹²⁸⁻¹²⁹ The catalytic stirrer developed was based on aluminum metal foam coated with an alumina wash-coat layer. The reactant and product diffusion rates are closely depended to the thickness of the alumina wash-coat layer.¹⁴⁻¹⁵ Metallic foams are mechanically resistant and thus, can be easily shaped in

various forms depending to the downstream applications. Structured catalysts also prevent the problem of fine formation as encountered with slurry reactor due to the attrition of small particles under vigorous stirring which lead to the plugging of the filtration device. Indeed, in liquid-phase reaction the stirring rate has a significant influence on the homogenization of the reactant within the medium which conditioning the catalytic performance of the catalyst. The influence of the foam stirring rate on the hydrogenation activity has also been reported by Tschentscher et al.¹¹⁰ for the oxygen/water system with rotating foam catalyst and could be explained by the following fact: at increasing stirring rate, the number of bubbles breaking when passing the foam window is increased and could led to the formation of finer dispersed bubbles which enhance the gas–liquid mass transfer and also the contact between the reactant and the active sites localized on the CNFs surface. However, it is worthy to note that up to a certain rotating speed problem of catalyst accessibility becomes predominant conducting to an activity decrease (see discussion in the Catalytic applications section).

Hierarchical structured reactors based on the growth of CNTs and CNFs on different metallic host matrix has been reported by several groups nowadays.¹³⁰⁻¹³⁶ The advantages of using metallic foams as macroscopic host matrix are the possible avoidance of washcoat and metal growth catalyst deposition, as the metal contained in the foam is directly used as growth catalyst, while the drawbacks are that the metallic phases inside the foam could participate in the reaction and the low ratio between the deposited carbon nanomaterials and the foam itself. Impurities containing in the metal matrix could also underwent segregation leading to an enrichment of the surface which could initiate active phase modification or deactivation with time on stream. Chinthaginjala et al.¹³³ revealed how the CNFs attached to Ni foam by decomposition of ethylene. They found that two distinctive carbon layers were deposited on the surface of Ni foam and then generated an apparently dense layer ('C-layer') at the carbon-Ni interface, as well as the subsequently growth of CNF on surface of Ni foam.

However, in order to efficiently growth CNTs or CNFs directly on metallic foam surface, without a layer of washcoat, thermal treatments such as oxidation and reduction, are usually required in order to activate the metal surface,¹³⁷ while the second option is to depositing a washcoat layer on the metal surface prior growing process. Alumina washcoated nickel foam decorated with carbon nanotubes for use as stirrer in liquid-phase catalytic aerobic oxidation of cumene has recently been reported by Mu et al.¹³⁸ The alumina wascoat had a high influence on the quality and yield of the CNTs as low alumina washcoat leads to the formation of large nickel particles while thick layer prevents nickel diffusion to generate CNTs. Alumina washcoat could also prevent the formation of amorphous carbon during the growth process on the metal substrate. Several authors^{39, 139} also growth carbon nanomaterials on stainless steel foam, after sequential oxidation and reduction steps, at different temperatures. **The optimum weight**

of active phase per weight of catalyst should be fine in order to improve the specific catalytic performance of the system.

As specified before the use of metallic substrates has the advantage that it is not necessary to deposit additional metal catalyst for CNT/CNF growth. The metallic substrate itself after appropriate pre-treatment, such as calcination, is able to catalyze the growth of CNTs/CNFs.¹⁴⁰ Tribolet et al.¹⁴¹⁻¹⁴² synthesized CNFs on metal fibers for gas phase applications in order to achieve efficient heat transfer. Sintered metal fiber filters (SMF) consist of fibers with 8 μm diameters made of Inconel 601, containing 60% Ni. Thermal pretreatment of the filters was found to be important for the final result (oxidized at 650°C for 3 h, reduction in hydrogen at 600°C for 2 h). CNFs were synthesized using ethane at 655°C which yielded composite with specific surface area of 22 m^2/g . The attachment of the CNFs to the metal filters was stable against ultrasonic treatment at 30 W in methanol for 5 min. It is reported that increasing CNF loading caused increased pressure drop over the composite due to some plugging. Therefore, an optimum CNF loading has to be maintained to balance the maximization of surface area with the minimization of pressure drop. The materials were tested for hydrogenation of acetylene, after depositing Pd on CNFs activated in boiling 35% aqueous hydrogen peroxide for 4 h. It is reported that the activity of Pd/CNF/SMF Inconel was one order of magnitude higher as compared to that of Pd on activated carbon. Such improved activity could be attributed to the absence of micropores in the Pd/CNF/SMF system which displays higher accessibility to the reactant. CNFs on Inconel sintered metal fibers with Pd-Sn and Pd-Cu have been also used in a liquid phase reaction such as nitrate reduction in water¹⁴³ and for simultaneous bromate and nitrate reduction.¹⁴⁴ However, in such structured metal supports the active phase concentration is relatively low compared to the total weight of the final catalyst which is mostly due to the weight of the metal support. Such drawback could hinder the extensive use of structured metal-based catalysts.

Stainless steel meshes have been also coated with aligned carbon nanotubes layers (Figure 20). The mesh itself was used as catalyst to growth CNTs after the appropriate treatment (acid attack, oxidation and reduction).¹⁴⁵⁻¹⁴⁶ Mesh coated with CNT have been employed for phenol degradation in water by ozonation.¹⁴⁶

Carbon nanofiber was also coated uniformly on the surface of alumina–silica foam catalyzed by homogeneous distribution of Ni compounds.¹⁴⁷ Thanks to the high specific activity of the Ni-catalyst on such Al/Si ceramic foam results to superior carbon yield of 30 $\text{g}/\text{g}_{\text{nickel}}$ and uniformly of mesoporous CNF-layer with specific surface 500 m^2/g of CNF by chaotic interlacing of the nanofibers. This hierarchical structure with efficient specific surface area of CNF could be considered as promising adsorbents for immobilization of enzymatic active substances.¹⁴⁸

Figure 20. SEM micrographs of the CNT/CNF composite coated stainless steel substrates: (a) 5 wt% CNF on sintered metal fibers (Inconel) reprinted with permission of Ref. ¹⁴³. Inset: High-resolution SEM micrograph of the composite showing the homogeneous coating of the stainless steel fiber by a layer of CNT/CNF. (b) CNT growth on stainless steel mesh reprinted with permission of Ref. ¹⁴⁵.

2.2.3 CNF/CNT on other material foams

Schouten grown CNF on reticular vitreous carbon after Ni deposition.³ A critical Ni concentration was found for a complete coverage with CNF. They supported Pd and tested in a fast liquid phase oxidation reaction. Similar or higher mass transfer rates were obtained but at a considerably lower pressure drop than for random packings.¹⁴⁹

Recently Liu et al.¹⁵⁰ developed hierarchical structured carbon composites as catalyst supports by combining electrospinning (ES) fibers and CVD process to generate CNFs decorating the ES fibers with high effective surface area. The nickel salt was electrospun with the polymer to form a polymer fibers containing nickel phase. The sample was further carbonized at different temperature under argon to generate porous carbon fibers with nickel nanoparticles (Figure 21A and B). In this process the nickel salt was reduced in the presence of reductant gases generated from the thermal decomposition of the polymer precursor during the carbonization step. The CVD process was carried out on the as-carbonized Ni@CF to generate CNFs as shown in Figure 21C and D. The former ES carbon fiber is homogeneously decorated with a dense layer of CNFs as shown in Figure 21E. The optimization of the annealing and CVD temperature as well as they duration allow the authors to obtain controlled macroscopic hierarchical carbon-based structures with high effective surface area (> 200 m²/g). Such hierarchical composite can be shaped in different forms depending to the downstream applications. The main advantage of this preparation route is that the weight of the nanocarbon is relatively high compared to that of the inactive host matrix which could

improve the active density per unit volume of the catalyst. The same synthesis can be combined with the electrospinning and electrospraying described above to generate controlled hierarchical structured composites with micropatterning form for different downstream applications.

Figure 21. (A, B) Ni/ES carbon composite after different carbonization temperature. The nickel can be visualized as bright spots in the micrographs. (C, D) Ni/ES carbon composite decorated with a dense network of CNFs after a CVD step at 700°C in C_2H_6/H_2 mixture. (E) High resolution SEM micrograph showing the carbon fiber decorated with a dense and homogeneous hairy structure of CNFs. Reprinted from Ref.¹⁵⁰ with permission of RSC.

In another method the authors have synthesized 3D structure consisted of interconnected ES polymer fibers (poly(acrylonitrile)/poly(vinyl pyrrolidone), noted as PAN/PVP) and periodically nodes containing nickel nanoparticles via electrospraying process (Figure 22A and B). The PAN/PVP sample decorated with periodical islands of nickel was subsequently carbonized under argon atmosphere at 800°C followed by a CVD step in the presence of C_2H_6/H_2 at 700°C leading to the formation of 3D carbon fibers periodically decorated with CNF as shown in Figure 22 C and D. Such combined process could be used to deposit CNT or CNF growth catalyst on a specific area leading to a final hierarchical carbon composite decorated periodically with CNTs or CNFs. The selective deposition of active phase on such high reactive carbon material could allow one to control the distance between different catalytic centers. The growth of CNFs within periodical areas could also give rise to an improvement of the overall mechanical resistance of the composite.

Figure 22. (A) Low magnification SEM micrograph of the patterned ES/EP carbon composite after carbonization and CVD steps. One of the nickel localization periodically in the composite is schematized by a circle. (B) SEM micrograph of the composite with higher resolution. (C) SEM micrograph of the area containing only pure carbon fibers issued from ES process. (D) SEM micrograph of the area where carbon fibers are decorated with CNFs growth from the nickel catalyst during the CVD step.

Ismagilov et al.¹⁵¹ studied CNF growth on silica glass fibers. CNFs were grown on nickel/alumina coated silica fibers by decomposing methane. CNF loading up to 55 wt % was reported, with typical diameters of the CNFs ranging from 20 to 50 nm. However, no details on the stability of the CNFs under operation conditions were reported. Schlatter and co-workers¹⁵²⁻¹⁵³ have used modified electrospinning (ES) process to synthesize honeycomb-like hierarchical structure on patterned metallic substrate (Figure 23A and B). In the first ES process the polymer was electrospun directly on the patterned substrate leading to the formation of thin polymer interwoven structure on the pattern. In a modified ES process the polymer solution was electrospun first followed by an electro spraying to generate particles with higher conductivity on the first ES layer. These steps were repeated several times in order to obtain a honeycomb structure with 3D morphology for the targeted applications. The structure of the composite can be finely tuned through nanofabrication processes to generating different host patterns for depositing the polymer fibers. The electro sprayed

particles ensure the charge transfer to the collector and maintain the structure electrically conductive for subsequent electrospinning (Figure 23C) leading to a final 3D hierarchical structure (Figure 23D). The polymer fibers localized between the columnar are not well connected and thus, are positively charged as evidenced in Figure 23C which push the subsequent deposited layers onto the part where particles are present. A homogenous CNF layer of 25 μm thickness was prepared on reticular vitreous carbon (RVC) which was designated as “Hairy Foam”.³ The existence of CNFs significantly enlarged the surface area of the RVC foam from 0.12 m^2g^{-1} 146 m^2 , resulting in a superior catalyst support that can be used in a multitude of chemical reactions.

Figure 23. (A) Honeycomb pattern decorated with electrospinning polymer fibers through electrospinning process. (B) The same honeycomb structure decorated by combined electrospinning and electrospraying to generate 3D structure. (C) Schematic representation of the charge transfer and conductivity through columnar structure containing nanoparticles. (D) Final 3D honeycomb structure synthesized through combined electrospinning/electrospraying with open and interconnected meso- and macroporosity. ¹⁵²⁻¹⁵³

Han et al.¹⁵⁴ have reported the synthesis of SiC nanowires within SiC matrix using an ice-growth template (Figure 24). During the freeze-drying process of columnar ice, pores were easily formed by sublimation. The unique SiC(nanowires)/SiC ceramics can be generated by

chemical vapour infiltration (SiC), where SiC was readily infiltrated into the neat channels in the initial SiC networks. The specific mechanical properties, morphologies and composition were investigated by means of compression tests, scanning electron microscopy, XRD techniques, etc.

Figure 24. SEM images displaying the as-synthesized SiC nanowire aerogel from the view of the plane: (a) parallel to the macroscopic ice growth, (b) perpendicular to the macroscopic ice growth, (c) starting SiC nanowire, and (d) the enlarged images of the SiC nanowire “walls”. Reprinted from Ref. ¹⁵⁴ with permission of Elsevier.

3. Catalytic applications

The preceding sections were more focused on the synthesis aspects of the different types of structured reactors. In this section, the focus is put on the use of these structured reactors in different catalytic reactions divided in two categories in gas phase and liquid phase. Emphasis will be placed in comparing the catalytic behavior of the CNF/structured reactors to conventional reactors and, whenever possible, highlighting the benefits of CNF/structured reactors.

3.1. Gas phase reactions

The diffusion coefficient of reactants is about four orders of magnitude larger in gas phase reactions than in liquid phase reactions.¹ Therefore, the pore size distribution of the

structured reactor has only a little effect on the catalytic performance. For gas phase applications, the main advantage of using CNF/monoliths is the robustness, lower pressure drop and the high external effective surface area as well as strong mechanical resistance through immobilization of CNFs on a structured support. Otherwise, loose CNFs would hardly be used in gas phase reaction due to the high pressure drop and the swept of nanostructures with the gas flow. Airborne CNT powders have potential toxicity due to the dispersion of fine in atmosphere during the transport and handling, which has, so far, limited its use in industry. Thus CNFs immobilized on monoliths would pave the way to the implementation of CNT/CNF based catalyst in industry because such anchorage avoids the release of these nanomaterials to the atmosphere. These advantages have been exploited for instance in NH_3 decomposition to generate H_2 , which is free of CO_x . NH_3 has been recently proposed for chemical storage of H_2 . The monolithic structure entailed higher conversions than a fixed bed of the monolith crushed to powders, which was attributed to the enhanced removal of produced H_2 , which inhibits NH_3 decomposition.¹⁵⁵ Ru nanoparticles have been dispersed in monoliths coated with either CNFs or N-CNFs and used in the NH_3 decomposition for in-situ H_2 generation.¹⁵⁶ Nitrogen doping of CNFs was demonstrated to increase the metal uptake on CNF/monoliths and to promote the reductive adsorption of the precursor during catalyst preparation by equilibrium adsorption.¹⁰⁶ Moreover, the N-CNF supported catalyst afforded higher NH_3 decomposition than the un-doped CNF counterpart. The former keeps Ru nanoparticles in a more reduced state upon exposition to oxidant atmosphere than the later support, which was put forward as the reason to explain the catalytic results.

The reverse reaction, i.e. ammonia synthesis has also been performed using CNT anchored on cordierite monoliths as hierarchical support.²⁹ Barium promoted ruthenium catalysts supported on the as-synthesized materials showed much higher activity for ammonia synthesis than their counterparts deposited on bare cordierite monoliths. Furthermore, the catalytic activity linearly increased with the BET surface area of CNTs-cordierite monoliths. No clear conclusions can be derived about the effect of the support since the detailed characterization of Ru particle sizes on the several supports is lacking and there is no comparison with the catalyst in powder form. The higher dispersion of the metal active phase on the hierarchical support could be advanced to explain the enhancement of the reaction rate.

CNT/monoliths have also been used as **Fe catalyst support** for CO_2 hydrogenation to **C1-C4 hydrocarbons via Fischer-Tropsh synthesis (F-T)**.¹⁹ CNTs grown on cordierite monolith using ferrocene and toluene have iron nanoparticles encapsulated by carbon according to TEM analysis. The encapsulated carbon was removed by oxidation in air at 470 °C during 10 min

and the activated Fe/CNT/monolith turn out to be an active catalyst for CO₂ conversion to hydrocarbons. The Fe/CNT/monolith furnished poorer performance than the powdered catalyst at atmospheric pressure, but achieved similar conversions and a higher rate of reaction under high pressure conditions (Figure 25). Experimental evidences suggested that when pressure is increased beyond 7.5 bar, the reaction is mass-transfer limited, rather than rate-limited.

Figure 25. Comparison of the powder and monolith supported Fe@CNT for total conversion and rate of reaction (conditions: 7.5 bar, 370 °C for 6 hours). Reprinted with permission of 19.

The macroscopic structure containing nanocarbon materials for the application in Fischer-Tropsch synthesis have been summarized in previous reviews.^{114, 157} The necessity of using these nanocarbon materials as support is based on two essences superiorities. One the one hand, the nanocarbon materials such as CNT and CNF are basically materials with both mesopores and macropores. The unique structure of these materials can largely facilitates the transfer of mass and heat, which can help to reduce the bed pressure as well as to enhance the catalytic performances. Zarubova et al.¹⁵⁸ have synthesized the specific Co/FB-CNF/carbon-felt catalyst by using the chemical vapor deposition and subsequently used for F-T reaction. The result suggested that by using the hierarchically structured composite, the reaction temperature was considerably stable without obvious thermal runaway in the catalyst bed. However such advantages were not observed by using the catalyst with similar composition but platelet structure (Co/P-CNF/carbon-felt) or the CNF in powder form. A hierarchically structured Co-based F-T catalyst was fabricated containing α -Al₂O₃ grain covered

homogeneously by a layer of carbon nanotubes with high specific surface area ($76 \text{ m}^2 \text{ g}^{-1}$) and fully accessible effective surface.¹⁰⁸⁻¹⁰⁹ The nanoscopic size of CNTs on the surface of $\alpha\text{-Al}_2\text{O}_3$ grain provided short diffusion pathway for the reactant to get access to the active site during F-T synthesis process. Thus, The introduction of a carbon layer led to a significant improvement of F-T activity compared with that of the pristine $\alpha\text{-Al}_2\text{O}_3$ -supported catalyst. Ba et al.¹⁵⁹ also decorated the few-layer graphene (FLG) with a dense network of carbon nanofibers, which was then used to dispersed the NDs for the direct dehydrogenation of ethylbenzene. It was suggested that more anchorage sites were able to be provided to disperse ND, which can be accounted for the higher density of active sites per weight as well as the promoted effect of mass transfer. The as-designed catalyst displayed outstanding DH activity as $56.9 \text{ mmol}_{\text{STGND}}^{-1}\text{h}^{-1}$ with 91.3% selectivity of styrene at 600°C , and no deactivation was observed during the tested 70 h. On the other hand, one of the problems causing the difficulty of nanocarbon materials to be industrially used is the swelling volume due to their powdered form, which makes the delivery and storage uneasy to be accomplished. On the contrary, the hierarchically structured nanocarbon catalysts are more readily to be synthesized as macroscopically shaped monolith,^{126, 160} which makes the reduction of the volume available. The silicon carbide-based foams coated with a nitrogen-rich mesoporous carbon matrix (NMC) were for the first time synthesized by Ba et al.¹⁶¹ and subsequently used as a non-innocent glue for highly dispersed nanodiamond (ND) fillers. The catalyst was even designed based on cheap and non-toxic food-grade components, which displayed suitable reactivity at the similar conditions of industrial plants ($9.9 \text{ mmol}_{\text{STGND}}^{-1}\text{h}^{-1}$) with only low ND loading. It was suggested that by using 40 kg of these macroscopically shaped monolith (ND@NMC/SiC), containing less than 5.0 kg of the ND@NMC active phase, are sufficient to produce up 1 ton of ST per day under industrial conditions (600°C and 10 vol.% of EB).

CNF-graphite felt composite was used as a catalyst support for iridium in the catalytic decomposition of hydrazine (N_2H_4) for satellite maneuvering, **reaction which is used for satellite maneuvering**.¹⁶² CNF-based Ir catalysts outperformed the commercial alumina based catalyst because of the faster mass transport which allows complete conversion of all hydrazine. In addition, the high thermal conductivity of the CNF-graphite composite allows faster heating of the catalyst bed which also contributed to a fast and powerful response to the introduction of hydrazine to the engine. The conductive nature of the CNF composite catalyst allows a rapid and homogeneous dispersion of heat in the catalyst bed, assisting complete decomposition of the reactants. The rapid heat transfer also prevents hot spot formation which could induce excessive sintering of the metal active phase during long-term operation. In short, mass and heat transfer limitations were overcome by using a CNF-based catalyst thanks to the nanoscopic dimension of the support and the high thermal conductivity of the

composite. Other authors also grew platelet-type CNF on carbon felts after depositing bimetallic Cu and Ni.⁶⁴ The initial dispersion of the catalyst was not found critical since bimetallic nanoparticles were generated in-situ by fragmentation during the CNF growth process. The resulting platelet-CNF/CF composite (Figure 21) is mechanically stable and displays a relatively high surface area of 250 m²/g. CNF/CNT supported on carbon felts have been used successfully as catalyst support in several reactions, for example, in Fischer-Tropsch synthesis,¹⁵⁸ in oxidative dehydrogenation of ethylbenzene,¹⁶³ in H₂S oxidation,¹⁶⁴ in catalytic ozonation of oxalic acid,¹⁶⁵ in batteries as electrode¹⁶⁶ and in hydrogenolysis of sorbitol.¹⁶⁶⁻¹⁶⁷

The reactions mentioned above take place in reducing atmosphere, in which carbon materials are more resistant than in oxidative atmosphere. Nevertheless, CNFs on monoliths have been also used in reactions carried out under oxidative environment. Due to the relative high resistance of CNFs towards combustion in oxygen atmosphere compared to other carbon materials, they have been used as support of Pt and Pd in gas phase catalytic combustion of BTX (benzene, toluene and xylene) at low temperatures (< 200 °C).^{17, 168} **This reaction is useful for environmental protection to clean air from these volatile organic compounds.** The behavior of Pt or Pd supported on CNF/ γ -Al₂O₃/monolith was compared to the counterpart supported on CNF/ γ -Al₂O₃. When water vapor was supplied to the reactant flow, the activity of the Pt catalysts supported on the γ -Al₂O₃ was more affected than that of the catalysts supported on CNF. The CNF-coated monolithic catalysts were the most active, independently of the metal or the type of the tested aromatic compound. This was attributed to the fact that the CNF surface is more hydrophobic than that of γ -Al₂O₃, and the release of water molecules produced during the combustion is favored, reducing its inhibiting effect on the reaction. The hydrophobicity also allows the catalyst to be less affected in the presence of steam in the feed due to the decrease of competitive adsorption.

Pham-Huu and co-workers¹²¹ have reported catalytic results in the partial oxidation of H₂S into elemental sulfur on the metal-free N-CNT/SiC foam catalyst. According to the reported results, the desulfurization activity of the N-CNT was significantly improved on the foam supported catalyst under similar reaction conditions (Figure 26A). The improvement of the catalytic performance of the supported catalyst was attributed to the high effective surface area of the supported N-CNT, and the high degree of gas mixing through the foam structure which provide high contact surface with the reactant. The catalytic activity improvement could also be attributed to the nanoscopic dimension of the N-CNT, which provides high effective surface area for the reactant adsorption and reaction. The high effective surface area also enables to operate the process at much higher gaseous velocity than on the bulk N-CNT catalyst where pressure drop becomes predominant. On the other hand, the sulfur selectivity is lowered on the N-CNTs/SiC foam catalyst compared to that obtained on the unsupported

N-CNTs (Figure 26B). The authors have attributed the sulfur selectivity lost to the longer sojourn time of the formed sulfur through the catalyst bed which favors the secondary reaction with the excess of oxygen leading to SO_2 formation.

Figure 26. (A) H_2S conversion and (B) sulfur selectivity as a function of the Weight Hourly Space Velocity (WHSV) on the N-CNTs and N-CNTs/SiC foam catalysts. Reaction conditions: ^[21]

3.2. Liquid phase reactions

Monoliths incorporating CNFs offer good potential for catalysis involving liquid phase reactants and for biocatalysis, as a consequence of the excellent accessibility of the active phase, which is present at the external surface of the fibers, without any microporosity which could hinder the diffusion of reactants to the active sites.¹ The CNF/structured reactors display similar performance compared with conventional reactors and supports such as packed bed of particles for fast reactions. In contrast, for slow reactions, due to the lower solids

holdup, and thus lower catalyst concentration, of the structure reactors larger reactors are needed, resulting in a higher total pressure drop.¹⁶⁹ .

Despite the favorable properties anticipated for the combination of CNFs and monoliths in liquid phase reactions, their application has been scarcely reported which could possibly due to difficulties encountered during the preparation procedure to obtain mechanically resistant CNF/monoliths.

Monoliths coated with CNFs have proved to be a stable support for the immobilization of enzyme (lipase) in organic solvents.^{2, 170-171} **The immobilization of enzymes on a support keeping its activity has significant industrial interest due to the easiness of catalyst separation from reaction medium.** The CNF/monoliths with immobilized lipase were tested in acylation reaction as a test reaction using a monolithic stirred reactor free of diffusional limitations. Monoliths coated with CNFs showed higher enzyme adsorption capacity than monoliths coated with other porous carbons derived from sucrose or polyfurfural alcohol. This higher capacity for enzyme adsorption is attributed to the mesoporous open structure of CNFs with high anchorage sites density. On the basis of simple calculations, it was concluded that about one monolayer of enzyme could be accommodated on the CNFs. The activity in acylation reaction per unit of enzyme was the same for all the carbon materials tested. However, the higher enzyme capacity led to the enhanced performance per reactor volume for CNF coated monolith (Figure 27).

A special type of monolith developed by Dow Chemical Company with the same macroscopic geometry as classical cordierite monoliths but with open walls named as highly porous acicular mullite ceramic (ACM) was also used for this application (Figure 28).¹⁷⁰ CNF were grown on ACM and subsequently used for lipase adsorption. It was observed that CNF penetrated the monolith open walls (Figure 29a). The open structure of the ACM monolith walls suitable for a higher enzyme loading and leads to a higher activity per monolith volume compared to classical cordierite monoliths (Figure 27).

Figure 27. Comparison of activity per unit monolith volume for the cordierite monolith and acicular mullite ceramic (ACM) biocatalysts studied. The main figure is for immobilized lipase activity. The inset is for immobilized lactase on PEI-coated supports. Reprinted with permission of reference ¹⁷⁰.

Figure 28. (a) Photomicrograph of ACM1 ("small" pore) honeycomb and (b) photomicrograph of ACM2 ("large" pore) honeycomb. Adapted from the data from reference 2.

Figure 29. SEM micrographs of supported CNF on γ -alumina washcoated monoliths (a) ACM-CNF, (b) Cordierite-CNF 400 cpsi.¹⁷¹

Pd supported on CNF/TiO₂/monolith has been used for the selective hydrogenation of cinnamaldehyde (CAL).¹⁷ In CAL molecule, there are two functionalities amenable to be hydrogenated. If the aldehyde group is hydrogenated cinnamylalcohol (COL) is produced, which is an important fine chemical used in for the fragrance industry. On the other hand, if the conjugated double bond is hydrogenated the product is hydrocinnamaldehyde (HCAL). The challenge is to produce selectively only one of the products, specially COL which is thermodynamically less favorable product. The selectivity to the hydrogenation of the double bond (hydrocinnamaldehyde, HCAL) increased from 82% to 90% after treatment with N₂ at 773 K for removal of oxygenated surface groups. Using this structured catalyst, the selectivity to HCAL remained very high (about 90%) at 95% of CAL conversion. The same as that over powdered Pd/CNF (about 93%) and much higher than that over Pd on activated carbon (about 45%) and Pd on mesoporous carbon (82%), which was attributed to the elimination of internal diffusion limitation on Pd/CNF/TiO₂/monolith. Pd/CNF/SiC foam catalyst was also tested directly as catalytic stirrer for the selective hydrogenation of cinnamaldehyde.¹¹⁹ In such case, the high effective contact surface between the reactant and the active phase was assumed by the nanoscopic dimension of the CNF decorating the foam surface. The high interaction between the prismatic planes of the CNF and the palladium active phase also provided a high dispersion of the metal as well as sintering resistance (Figure 30A and B). The foam windows also play a role of bubbles breaker to finely disperse the hydrogen gas inside the reaction medium. The authors have observed that the reaction rate was more efficient with the catalytic foam stirrer than with the magnetic stirrer, indeed, for the foam stirrer, the same conversion rate was obtained at much lower stirring rate (300 rpm) compared to that of the magnetic stirrer (625 rpm). The hydrogenation rate on the Pd/CNF/SiC composite catalyst is about twice of the one obtained on the Pd/SiC catalyst under similar reaction conditions. Such

an improvement in terms of the hydrogenation activity can be attributed to the high dispersion of the palladium particles on the prismatic planes of the CNF and also to a higher effective surface area of the catalyst which provides a higher contact surface between the reactants and the active sites. The results evidence the high hydrogenation activity, along with the high selectivity, which are directly linked to the high effective surface, low diffusion path and high mixing degree of the hybrid catalyst.

In addition, the Pd/CNF/SiC exhibits a constant hydrogenation activity as a function of the cycling tests while a deactivation was observed on the Pd/SiC catalyst (Figure 30C) during the cycling tests. The deactivation could be attributed to the lower metal-support interaction between the Pd nanoparticles and the pristine SiC surface which ultimately leads to the sintering or leaching of the metal particles into the reaction medium.

Figure 30. (C) Cycling tests on the Pd/CNF/SiC and Pd/SiC foam catalysts showing the high stability of the Pd/CNF/SiC catalyst as a function of tests.

The most interesting fact is that the catalyst with macroscopic shape can be easily recovered from the reaction medium without any need for filtration step as generally encountered with powdered catalyst. Such results are of great interest as catalyst recovery from liquid phase reactions represents time and energy costs for the process. Part of the catalyst could also be lost during the filtration step leading to a gradual activity loss with time.

Alumina washcoated nickel foam decorated with carbon nanotubes for use as stirrer in liquid-phase catalytic aerobic oxidation of cumene has recently been reported by Mu et al.¹³⁸

Cumene oxidation to cumene hydroperoxide (CHP) is a key step of the three-step process

from benzene to phenol and acetone, which contributes more than 90% phenol in the world. Moreover, the oxidation with molecular O_2 (aerobic oxidation) has economic and environmental advantages over the use of other oxidants such as peroxides. The foam catalyst was fixed on the stirrer as shown in Figure 31A and B. The nickel foam surface is well decorated with an entangled layer of CNTs (Figure 31C). The structured foam catalyst displays slightly higher cumene conversion compared to that obtained on the unsupported CNT, *i.e.* 25 % instead of 22 %, along with a high stability as a function of cycling tests. The high cycling test stability was attributed to the high mechanical anchorage of the CNT layer on the Ni foam substrate. In addition, the most important fact is that the macroscopic shape of the foam catalyst allows an easy recovery of the catalyst after reaction where no filtration is needed as encountered with the powdered CNTs. The authors have also pointed out an important fact for operating the rotating foam stirrer reactor (RFSR) which is the negative influence of the high rotating speed on the liquid reactant circulation through the foam matrix and, as a consequence, the decrease of the accessibility of the catalytic phase localized inside the catalyst foam. Such results pointed out the importance of chemical engineering parameters control on the optimization of hierarchical structured reactors.

Figure 31. (A) Schematic representation of the rotating foam stirrer reactor (RFSR) using

CNT-grown on nickel foam as catalyst for the oxidation of cumene. (B) Photo of the CNT/Ni foam fixed on a rotating axis. (C) SEM micrograph of the CNTs showing the homogeneous diameter and high aspect ratio. Reproduced from ref. ¹³⁸.

Unsupported CNT and CNF with and without nitrogen doping have demonstrated high efficiency as metal-free catalyst or catalyst support for catalytic water treatment.¹⁷²⁻¹⁷³ CNF/monolith was applied as catalyst in the catalytic ozonation of emerging organic micropollutants.¹⁷⁴⁻¹⁷⁵ Atrazine, Bezafibrate, erythromycin, metachlor and nonylphenol were selected as contaminants representative of pesticides, pharmaceuticals and endocrine disruptors.¹⁷⁵ The use of this catalyst was demonstrated to improve the mineralization degree compared to single ozonation. The application of the monolith in a triphasic system (monolith placed inside reactor 1 in Figure 32), in which liquid, gas bubbles and solid co-exist, was demonstrated to be favorable when compared to a biphasic system (monolith placed inside reactor 2 in Figure 32), in which ozone was first dissolved in water and subsequently flushed through the monolith channels, *i.e.* there aren't gas bubbles. The triphasic system followed the so-called Taylor flow or segmented flow, which combines a low-pressure drop with very high transport rates and near plug-flow behavior.^{1, 176} The enhanced performance of the triphasic system over the biphasic system confirms the benefits of Taylor flow for the mass transfer of both ozone and water pollutants to the catalytic sites. To attain this type of flow regime, it was necessary to generate gas bubbles of the same range as the channel size (Figure 33). Gas bubbles smaller than channel size pass through it without contacting the catalytic walls while gas bubbles larger than channel size coalesce at the bottom of the monolith without passing through it.

Figure 32. Bubble column with internal loop used for continuous catalytic ozonation experiments. Reprinted with permission of ¹⁷⁵.

Figure 33. Monolith composite working under Taylor flow in the liquid-phase ozonation of micropollutants process in wastewater stream.

After ozonation treatment in water treatment plants, a biological treatment is usually implemented. Therefore, it is very important that the intermediates produced after ozonation are not more toxic than the original pollutants. In the ozonation of the herbicide metolachlor,¹⁷⁷ CNF/monoliths were found to produce decomposition intermediates that are not more toxic than the original pollutants. In contrast, the toxicity values obtained at steady state using simple ozonation (Figure 34), i.e. without CNF/monolith catalyst, showed that the

produced compounds present higher toxicity for *Vibrio Fischeri* than the parent compound. Thus, the presence of the monolithic catalyst during the reaction reduced the toxicity values when compared to the non-catalytic ozonation experiment. Moreover, longer contact times with the catalyst produced further reduction in toxicity levels. On the other hand, placing the structured catalyst in order to operate under biphasic conditions was not as effective in the reduction of the toxicity when compared to the triphasic system.

Figure 34. Inhibition of luminescent activity of *Vibrio Fischeri* in the continuous ozonation experiments of metolachlor using CNF/monolith in biphasic and triphasic configuration. Reprinted with permission of ¹⁷⁷.

Ru or Pd supported on both CNF and N-CNF coated cordierite monoliths have been used for bromate reduction.¹⁷⁸ Bromate is consistently found in water treatment plants at concentrations that represent a significant cancer risk for lifetime exposures. The main origin of bromate is the ozonation of bromide during the water treatment process of advanced oxidation. After this treatment, bromate can be reduced to the innocuous bromide with H₂ using an hydrogenation catalyst. Detailed LCA study demonstrated that the catalyst based on carbon nanofibers on structured support (sintered metal fibre and carbon felt) has a substantially less harmful overall environmental impact than the conventional catalyst for water treatment application.¹⁷⁹ Several types of reactors were used for the experimental tests, namely conventional batch reactor, and continuous reactors such as CSTR (slurry), PFR (plug-flow reactor in packed bed) and monolithic reactor. In the monolithic reactor, a biphasic system is used, in which the water is saturated first with H₂ and afterwards the H₂-saturated water passes through the monolithic catalyst. This mode of operation was found to result in a suboptimal performance due to diffusional limitations. The operation using Taylor flow is expected to enhance the performance in bromate reduction.

Hydrodesulfurization (HDS) of naphtha¹⁸⁰ was conducted using CoMo supported on CNT coated monoliths. It was concluded that the activity of the CoMo catalyst over the CNT/monolithic was higher than that of the CoMo deposited onto the acid-treated monolith and CoMo/Al₂O₃ conventional catalyst. This is attributed to the high surface area and suitable pore size distribution (mesoporosity) of CNT/monolith. Ultimately, the HDS reaction over the CoMo/monolith material under optimized operating conditions reduced the sulfur content of naphtha from 2670 to 13 ppm.

4. Conclusion

In summary, the present review have highlighted the several advantages of using hierarchical structured reactors, combining nanoscopic coating layer for active phase dispersion (nanocarbons), or directly as metal-free catalysts, and macroscopic host matrix (structured reactor), for numerous relevant catalytic processes where mass and heat transfers can be significantly optimized leading to better catalytic performance and stability. The anchorage of the CNF and CNT, either pure or doped with heteroatoms such as N, S, onto a macroscopic and structured host matrix enables one to fully exploit a new class of catalyst support or metal-free catalysts, with higher effective surface area along with a short diffusion path, which significantly improve the performance of the catalytic process in both liquid- and gas-phase reactions. Indeed, these structured catalysts combine in an efficient manner the outstanding physical properties of the macroscopic host matrix with the nanoscopic dimension and strong metal anchorage sites of the CNF and CNT to provide a hybrid catalyst with improved catalytic performance both in gas- and liquid-phase processes. The possibility to finely tune the hydrophobicity/hydrophilicity of the carbon nanostructure on the composite also represents an elegant way to improve the catalytic performance and reduce secondary reactions. In liquid-phase reactions the combination of nanoscopic carbon, *i.e.* carbon nanotubes and nanofibers, and structured macroscopic host matrix, *i.e.* monolith and foam, leads to the development of structured catalyst with an easy catalyst recovery compared to traditional powdered catalysts. The improvement of the thermal conductivity of the catalyst through the use of carbon supports also allows one to prevent local hot spot formation which could be detrimental for the selectivity of the reaction and also for the safe operation of the plants.

5. Outlook

It is expected that structured catalytic reactors will face a relentless development in the future taken into account all the advantages discussed in the present review. The research field is not straightforward to be investigated as it combines on one side, nanostructured materials

which represent an enormous field of research, and, on the other, macroscopic host structures with different hydrodynamic properties. It was remarked that the detailed investigation of the hydrodynamic behavior within the nanocarbon structure is still scarcely investigated. This should be one of the promising directions for future study in order to get more understanding about the factors which influence the catalytic activity regarding the further optimization step. This should be investigated using new technique such as TEM tomography¹⁸¹⁻¹⁸² which allows one to get closer look about the carbon nanotubes or nanofibers arrangement within the structure and to correlate the structure and the catalytic performance during optimization process. It is expected that such data could help in the design of new hierarchical structure with improved catalytic performance as well directed selectivity. In addition, structure modeling is still missing on such hierarchical structured composites. Such modeling could be closely combined with advanced characterization techniques, *i.e.* dynamic TEM under ambient conditions,¹⁸³ allowing a dynamic imaging of the catalyst structure, at an atomic level, during the growth process could give rise to an in-depth understanding of the operated mechanism. It is expected that by combining innovative synthesis strategies, advanced characterization techniques, chemical engineering investigations and theoretical calculations, significant progress will be at hand for developing new catalytic systems with outstanding catalytic performance.

The detailed study regarding the influence of the doping on the catalyst performance, *i.e.* metal-free catalyst, and the ability to disperse metal/oxide nanoparticles, or to allow electron transfer, is another topic which needs to be investigated in regard to the catalytic performance improvement. Large effort has been made during the last decades on the surface modification of the nanocarbons through doping but additional research remains, especially in the understanding of the role and nature of doping on the active phase anchorage and also for performing catalytic reactions. It is expected that the combination between doped-carbon materials and hierarchical structured reactors for developing new catalytic processes will be one of the most important application field in the future.

Despite that the synthesis of the nanocarbon/structure reactors by CVD has reached a very development stage, the synthesis route should also be improved in order to take into account the problems of environmental concerns of the heavy toxic organic compounds generated during the CVD process. Preliminary work has been carried out using magnetic inductive coupling for the synthesis of CNTs/CNFs which hold several advantages such as short synthesis duration, rapid heating and quenching rate and the complete absence of secondary reactions leading to the formation of toxic organic compounds. The high quenching rate also significantly contributes to the reduction of residual amorphous carbon which was deposited on the carbon nanomaterials during the long cooling step. Another promising field of

research is the development of structured reactors by hierarchical autoassembling of carbon nanostructures using different structure directing agents and additive manufacturing of nanocarbon composites. The synthesis and application of monoliths based on graphene as structured reactors for chemical reactions is another new field that deserves further research. Graphene aerogels and monoliths have been synthesized in the literature but the applications are mainly limited to absorption and energy storage. Graphene has favorable properties for its use as structured catalytic support such as the high surface area, electric conductivity or possibility of doping. The composition of graphene is the same as for CNT but the basal graphitic plane is not curved and strained, lending some different properties to the deposited metal catalysts. Nanocarbon structured reactors will be also a perfect catalytic platform to perform organic reactions and bioreactions in flow substituting batch process and avoiding the separation of the dispersed catalyst. Because of all these reasons, it is anticipated a bright future for the nanocarbon/structured supports as catalytic reactor for the intensification of chemical processes.

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