Nanoingeneering the growth of a carbon nanofiber layer on micro-structured reactors

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Background

Microreactors share some common properties with other structured reactors, such as low pressure drop. Besides, its channel diameter (< 1mm) enhances mass and heat transport, enabling isothermal operation, improved selectivity and security [1]. To increase the catalytic surface area of microreactor, one option would be filling the microchannels with catalytic material. However, this will increase substantially the pressure drop. Thus, the best option is coating the microchannel walls by a well-adhered catalyst layer because it keeps a low fluidic resistance.

CNF and CNT hold many promises as catalyst support [2]. For instance, some gas-phase reactions benefit from the use of graphitic materials as catalyst support [3]. Furthermore, graphitic nanomaterials by themselves have outstanding performance in dehydrogenations reactions [4-5]. Unlike metal oxide support, CNF form aggregates with high surface areas, high mesopore volumes and low tortuosity. This is favourable for diffusion of liquids to catalytic sites, while keeping low pressure drop.

Nevertheless, CNFs in powder form have some drawbacks such high-pressure drop, plugging and flow maldistribution for fixed bed operation, and agglomeration and difficulty of filtration due to the formation of fines for slurry phase operation. The attachment of CNF to structured reactors would circumvent these drawbacks.

CNF coated microreactors must be endowed with good activity and durability to be competitive with conventional technology. To this end, catalytic coating must exhibit a good adhesion to substrate, open porosity (mesoporosity) to enhance the diffusion of reactants, uniform thickness of CNF layer, good mechanical strength and control over the microstructure of CNFs. The good mechanical stability of CNF inside microchannels is crucial to prevent channel blocking by loose CNFs.

In this work, we study the conditions for the growth of a well-adhered layer of carbon nanofibers (CNF) on microreactors via catalytic decomposition of hydrocarbon. The CNF coating properties have been optimised by studying different variables such as pretreatment of microreactor substrate, reaction temperature, hydrocarbon and addition of H_2. To our knowledge, it is reported the coating with carbon nanomaterials of silica microreactors [6-7], but there is no report of coating stainless steel microreactors. The catalytic microreactor is intended as e.g. for in-situ H_2 generation from NH_3 decomposition to feed a fuel cell in portable applications.

Experimental

We have coated stainless steel microreactor with a CNF layer by the following procedure. First, coating the stainless steel microreactor with a well-adhered alumina layer. Subsequently, Ni catalyst was impregnated via electrostatic interaction of alumina coating with a nickel solution at neutral pH. Finally, we have grown a CNF layer over microreactors via catalytic chemical vapour deposition (CCVD) of methane or ethane. The techniques used for characterization of CNF layer comprise SEM-EDX, XRD, Raman spectroscopy, TEM, Temperature programmed oxidation and N_2 adsorption.

Results

Figure 1 displays picture of the microreactor platelets after different preparation stages. Figure 1c shows the microchannels covered by a CNF layer (back colour). After CNF growth, the microreactor exhibited a complete coating with CNFs of uniform size (figure 2).
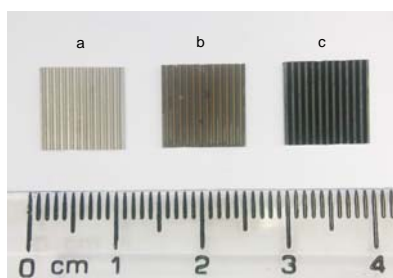
Figure 1. *microreactor platelets corresponding to several preparation steps. (a) as-received platelet, (b) platelet after thermal treatment and alumina coating, (c) platelet after CNF growth*
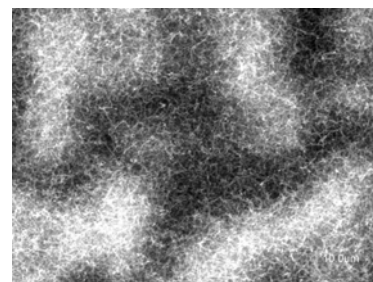
Figure 2. *Top view of a microreactor channel coated with the nanofibers*

The grown CNFs are of the fishbone type. This kind of nanofibers exposes numerous graphene edges. The presence of these edges has been reported to be beneficial for catalysis [8] because graphene edges can be functionalised to disperse catalyst particles. Figure 3 shows a representative Raman spectra. The D band is the disordered induced band. The presence of this band is an indication of CNF exposing graphene edges or defective graphitic structure. Depending on the growth conditions (hydrocarbon, the hydrocarbon:H_2 ratio, growth temperature), we obtained different CNF yields, CNF thicknesses and type of carbonaceous products in terms of graphiticity and morphology. When the growth temperature increases, the graphiticity increases accordingly, regardless the hydrocarbon. Additionally, increasing temperature also leads to less uniformity in the morphology of nanocarbons. At the highest temperatures metal dusting occurs These fragments of metals from microreactor walls catalyse the growth of different nanocarbon structures. This also leads to a non uniform growth, with some carbon protrusions plugging some microchannels.

For the optimised CNF coating, the weight loss after drop test was negligible (< 5 wt%). This good adhesion was confirmed by SEM characterisation. This technique revealed a complete coverage of the channels by CNFs. Figure 4 shows a detail of the CNF layer, which shows the tight contact between the CNF layer and the microchannel wall.
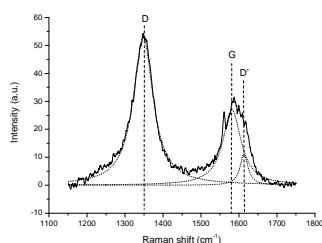
Figure 3. *Raman spectra of CNFs over microreactor*

Figure 4. *Edge of a microreactor channel coated with CNF layer*

Conclusions

Stainless steel microreactors have been coated by a uniform layer of entangled carbon nanofibers with satisfactory mechanical resistance. The CNFs have uniform size and microstructure. Thus, the CNF-microreactor has good perspectives as catalyst support or catalyst by itself.

References

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