



Immobilization of carbon nanofibers (CNFs) on a stainless steel filter as a catalyst support layer



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ABSTRACT

A layer of carbon nanofiber (CNF) agglomerates is used to produce a catalyst support layer that can be immobilized on a stainless steel filter and that can be removed when desired. For immobilization a filtration procedure is developed that produces a stable CNF layer at relatively low shear force flows (< 0.18 m/s). Under these conditions the device can be used as a chemical reactor. Increasing the shear force flow rate enables removal of the CNF layer. The interaction between the CNF agglomerates within the immobilized layer is stronger than the attachment of the entire layer to the surface of the stainless steel filter. The weaker interaction between the layer of CNF agglomerates and the filter surface therefore determines the stability of the layer. High surface roughness of the filter on micro-scale as well as deep penetration of CNF agglomerates in the pore mouths of the stainless steel filter both enhance stability of the CNF layer.

1. Introduction

The majority of commercially applied chemical processes uses heterogeneous reactions, where one important reaction-type is three-phase gas-liquid-solid reactions (G-L-S). Typical reactors used for these are trickle bed reactors or slurry phase reactors, with respective pros and cons. The main drawback of packed bed trickle phase reactors is internal diffusion limitations whereas separation of catalyst and product is much more facile compared to slurry phase operation [1,2]. Structured reactors [2–5] are an alternative for slurry and trickle-bed reactors, which has been an active research field for many years. In structured reactors good external mass transfer, short diffusion distances and good temperature control can be achieved in combination with low pressure drop. Disadvantages, compared to trickle bed or slurry phase reactors, are the moderate catalyst loading, higher catalyst (immobilization) costs and challenging liquid distribution [1].

In structured reactors the surface area, needed to support highly dispersed active particles, is usually provided by using a wash coat, as structured packings like monoliths [6,7], foams, filters [8] usually provide insufficient surface area. This wash coat layer needs to be thin (10–100 μm) to minimize diffusion limitations, however this is a trade-off with the higher available surface area that would result from a thicker layer. Washcoats need maximal porosity and minimal tortuosity. Another important drawback of washcoats on structured packings is catalyst recycling and replacement. Replacement of the catalyst neces-

sitates removal of the entire structured packing from the reactor, increasing costs significantly.

A layer consisting of carbon nanofibers has been proposed as an alternative to washcoat layers. These carbon nanofibers constitute a much more open structure than the conventional washcoat layer, the structure mimicking the inverse structure of the washcoat [9]. Carbon nanofibers can be produced e.g. through arc discharge, catalytic chemical vapour deposition [10,11] and plasma enhanced chemical vapour deposition [10]. For catalytic chemical vapour deposition a carbon containing gas (e.g. ethylene [12], ethyn [10], methane [12], acetylene [8], syngas, CO) is flowed over transitions metal particles (e.g. Ni [10,13], Fe [14], Co [14]) at elevated temperature. The carbon containing gas decomposes at the surface on one side of the metal particle and carbon diffuses through or over the metal particle. The carbon then segregates at another side of the metal particle, producing a carbon nanofiber.

Previous work in our group reported on preparation procedures and catalytic applications of thin layers of CNFs on monoliths [15], foam structures [11,13], metal foils [14], thin layers [16] and in micro-channels [17]. The goal of this study is to explore the possibility to prepare a removable support layer on a structured packing using CNFs. This idea is inspired on the observation that particles consisting of entangled CNFs tend to stick together after filtration, so that re-dispersion is sometimes difficult to achieve. It is speculated that this effect is caused by interaction between CNFs sticking out of the

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individual agglomerates, causing a mechanical interaction similar to the well-known Velcro tape [18]. We explore how attachment between CNF agglomerates, as well as CNF agglomerates with the surface of the structured packing, can be used to achieve reversible immobilization on the surface of the structured packing. In this way, it would be possible to replace only the catalyst in case of deactivation, leaving the structured packing in the reactor. It is proposed that an immobilized CNF layer can combine the advantages of a highly porous catalyst support with the option to load and de-load exclusively the carbon nanofiber supported catalyst. In this study we will be using sintered metal filters as a model for a structured packing in order to explore the concept. Once the concept is successfully produced, this model support will be used in nitrite hydrogenation on future work.

2. Experimental

2.1. Materials

The stainless steel filter used for this study is a Sika R50, a 1.4404 (316L) steel from GKN Sinter Metals [19], consisting of 65 wt% Fe, 19 wt% Cr, 12 wt% Ni, traces of Mo and Si. This filter has average pores of 50 μm and a BET surface area of 0.14 m^2/g (Fig. 1a). From the as-received, 5 mm thick stainless steel sheet, rectangles of 16 \times 36 mm are cut, using electrical discharge machining.

Two different types of carbon nanofibers are used in this study. CNF agglomerates (MF-C150, commercially available from Carbon Nanotube & Fibers 21) are used, containing individual fibers of 80–150 nm in diameter and a purity of > 80%, with < 20% amorphous carbon and < 2% Ni/Fe. These CNFs agglomerates as received have an average size of 110 μm . This type CNF-aggregates was selected, despite the relatively low surface area, because of the observation that homogeneous CNF layers were obtained after deposition, in contrast to other types of CNF-aggregates.

The second type of carbon nanofibers is produced in house by growing carbon nanofibers directly on the surface of the stainless steel filter, using ethylene (99.95%, Praxair), hydrogen (99.999%, Linde) and nitrogen (99.999%, Linde). CNFs are grown in a home-designed vertical quartz reactor. The stainless steel filter (16 \times 36 \times 5 mm, typically \sim 12 g) is reduced for one hour with 20% H_2 in N_2 . Growth is achieved at 600 $^\circ\text{C}$ under 100 mL/min flow of 20% C_2H_4 + 20% H_2 in N_2 for 2 h. This procedure is inspired on previous growth procedures conducted on stainless steel foils in our group [14].

Milli-Q water (Synergy Millipore machine) is used for pressure drop and compressibility testing.

2.2. Characterization

The average agglomerate size of CNFs is measured by laser light diffraction in a Mastersizer 2000 from Malvern Instruments. BET surface areas of these CNF agglomerates have been calculated from N_2 adsorption measured with a Micromeritics Tristar 3000. HR-SEM

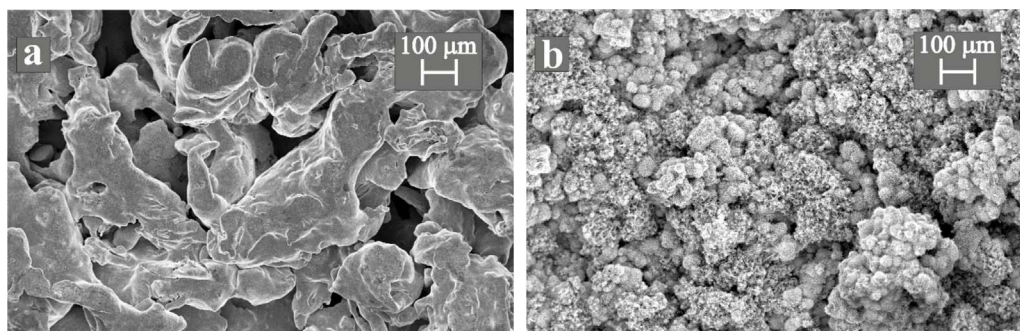


Fig. 1. Low magnification SEM pictures of a) as received stainless steel filter b) stainless steel filter covered with a grown carbon nanofibers layer.

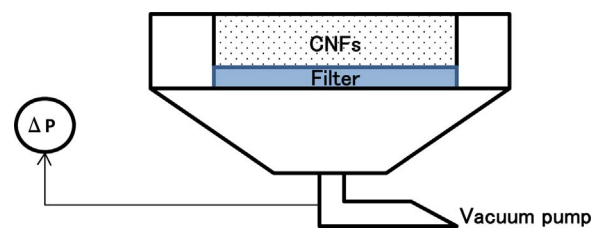


Fig. 2. Schematic representation of the filtration set-up for CNF layer formation.

pictures were obtained in a Zeiss Merlin Scanning Electron Microscope equipped with an EDX detector. Stability of the grown CNF layer is tested by sonicating the layer in an ethanol solution in a VWR USC300TH sonication bath.

2.3. Preparation immobilized CNF layers

The CNF agglomerates are separated into three size by dispersing the as-received CNFs in ethanol and using three sieve mesh sizes (80, 150 and 250 μm) for wet sieving.

Formation of layers of immobilized CNF agglomerates is achieved in a home-designed set-up shown in Fig. 2. The CNF agglomerates for deposition are suspended in 15 mL ethanol, using 12.5, 25 or 50 mg CNFs. A layer of the CNF agglomerates is formed by filtration, *i.e.* removal of the ethanol through the stainless steel filter (Fig. 2) and therefore this equipment is named “filtration set-up”.

The CNF suspension is poured onto the stainless steel filter, while the pump is off, and immediately the pump (capacity 1.7 m^3/h) is started. This pump capacity results in a pressure difference over the empty stainless steel filter smaller than 200 mbar, the lower limit of the pressure indicator. Within typically five seconds the ethanol is removed by filtration with a pressure drop varying between 300 and 700 mbar. As soon as the ethanol has passed through the filter the pressure drop reverts to less than 200 mbar. When the ethanol is completely removed the pump is turned off.

During the filtration, the CNF layer is compressed by a combination of both the force that is exerted by the pressure drop over the CNF layer, as well as by shear forces of ethanol flowing along the CNF agglomerates. These mechanical forces cause the agglomerates to be pushed together, and/or are pushed against the surface of the filter, with or without a grown CNF layer.

Layer thicknesses of immobilized CNF layers were determined with an analogue thickness meter, with a round plunger with a diameter of 5 mm and an accuracy of 0.01 mm. The CNF layer thickness was calculated by subtracting the thickness of the empty stainless steel filter (experimental variation \pm 0.025 mm) from the thickness of the filter with the CNF layer (experimental variation \pm 0.1 mm), each in two spots per individual sample. To determine the layer thickness and its error margin, 3 samples were measured per data point.

A qualitative measure for the density of the immobilized CNF layer is obtained by measuring the permeability to water, by measuring the

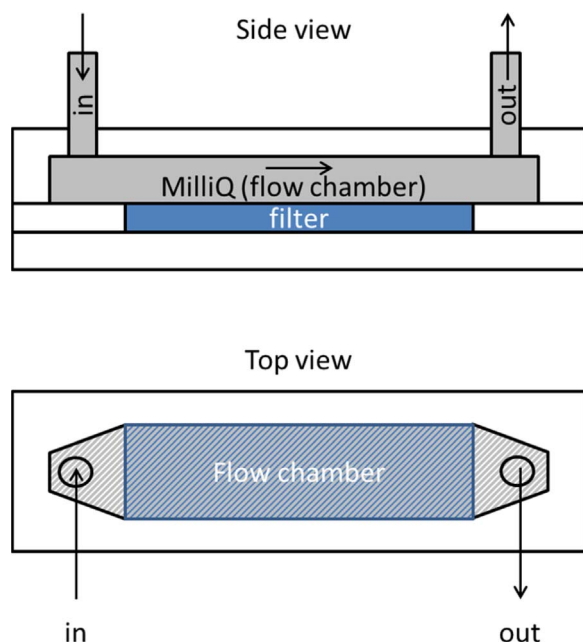


Fig. 3. Schematic side- and top view of home designed set-up for CNF layer stability testing.

flow rate of water through the substrate at a fixed pressure drop of ~ 90 mbar. This experiment is named the “pressure drop test”. The same procedure was also used to try to densify the CNF layer, by repetitively applying the 90 mbar pressure drop and using the accumulative time to show the effects of longer exposure times. The immobilized CNF layer is subjected to typically five subsequent tests; in between tests the flow was paused to measure the amount of MilliQ water flowed through.

2.4. Stability of immobilized CNF layers

Stability of the prepared CNF layer is tested in a home-designed set-up, shown in Fig. 3. This set-up consists of a holder for the rectangular stainless steel filter with on top a flow chamber, with a height of 11 mm. To minimize mechanical damage during handling, the same holder as used in the filtration set-up is used here, which is transferred from the filtration equipment to the stability testing equipment.

The CNF layer stability is tested by flowing MilliQ water over the immobilized CNF layer, with flow rates up to 0.6 m/s for typically 10 min. The stability of the layer is determined by measuring the amount of CNFs that is removed on basis of weight change of the sample, after thorough drying in a vacuum oven overnight. The top part of the stability testing set-up is made of transparent poly(methyl methacrylate) (PMMA) allowing recording of an *in-situ* movie during CNF removal.

3. Results

3.1. CNF agglomerates

The CNF agglomerates, as received, exhibit a (volume) particle size distribution ranging from 7 to 1000 μm (Fig. 4), measured in an ethanol suspension with laser light diffraction, with an average size of 110 μm . The as-received CNFs have a BET surface area of 32 m^2/g .

Fig. 4 shows the CNF particle size of the as received CNF agglomerates and the three size fractions separated by wet sieving, resulting in a fraction of smaller particles (average particle size 95 μm), a medium fraction (average particle size 150 μm) and a large fraction (average particle size 400 μm).

As can be seen in Fig. 5a, the CNFs agglomerate into apparently

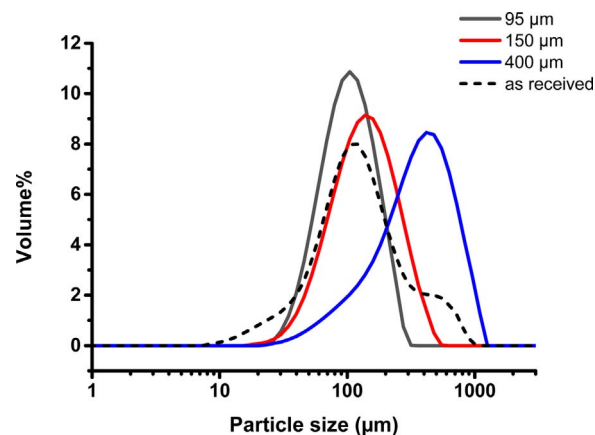


Fig. 4. Volume averaged particle size distributions of as received CNF agglomerates and the three selected size fractions, according to laser light diffraction.

dense particles with a smooth surface, at low magnification. Intermediate magnification (Fig. 5b) shows however the rough nature of the external surface with some individual CNFs sticking out. The high magnification in Fig. 5c however clearly confirms the highly open morphology, generated by entangled CNFs with a typical diameter of 100 nm.

3.2. CNF layer synthesis

A CNF layer is grown directly on the stainless steel filter under the conditions described in the experimental section, attempting to generate a binder layer between the CNF agglomerates and the stainless steel. This results in a typical average ethylene conversion of 20% over 2 h of CNF growth. This CNF layer completely covers the surface of the filter (Fig. 1b) with a typical thickness of a few μm , measured in a SEM-picture (shown in SI, Fig. A1a). The diameter of the CNFs ranges from 5 to 250 nm (SEM-picture, shown in SI, Fig. A1b). According to N_2 adsorption this results in a typical BET area of $\sim 290 \text{ m}^2/\text{g}_{\text{carbon}}$, which corresponds to a CNF diameter of 6.2 nm. This indicates that the smaller CNF diameters are dominant. The grown layer is well attached to the stainless steel, as sonication in ethanol for 15 min removes only 1 wt% of the CNFs and shear force testing (10 min, 0.36 m/s) results in negligible removal of CNFs. Strong attachment of CNFs grown directly on metal substrates was also reported previously [13,14]. It has been proposed that a thin, microporous carbon layer is formed that closely follows the surface roughness of the metal surface and CNFs are rooted in that layer, explaining the observed mechanical stability [13,14]. The growth catalyst particles were identified as Fe particles based on EDX analysis.

3.3. CNF agglomerates immobilization

The CNF agglomerates are pushed together, which results in a CNF layer in which the individual agglomerates are not distinguishable anymore in SEM (Fig. 5d), indicating significant interaction between CNF agglomerates. The filtrate is collected and no CNFs could be detected (with a detection limit of 0.01 mg)

Fig. 6 shows the effects of particle size and amounts of CNFs on the resulting layer thickness of the immobilized CNF layer. Fig. 6 shows a small effect of particles size, where smaller particles show slightly thinner layers, as would be expected. The increase in layer thickness compared to the amount of CNFs applied is slightly less than proportional, which suggests that thicker layers are slightly more compressed.

A CNF layer of 12.5 mg of CNFs results in a layer thickness of 200–350 μm thickness; when considering the particle size (95, 150 and 400 μm), it is clear that the layer is only 1–3 particles thick, causing partial coverage of the surface of the filter, as visually observed. CNF

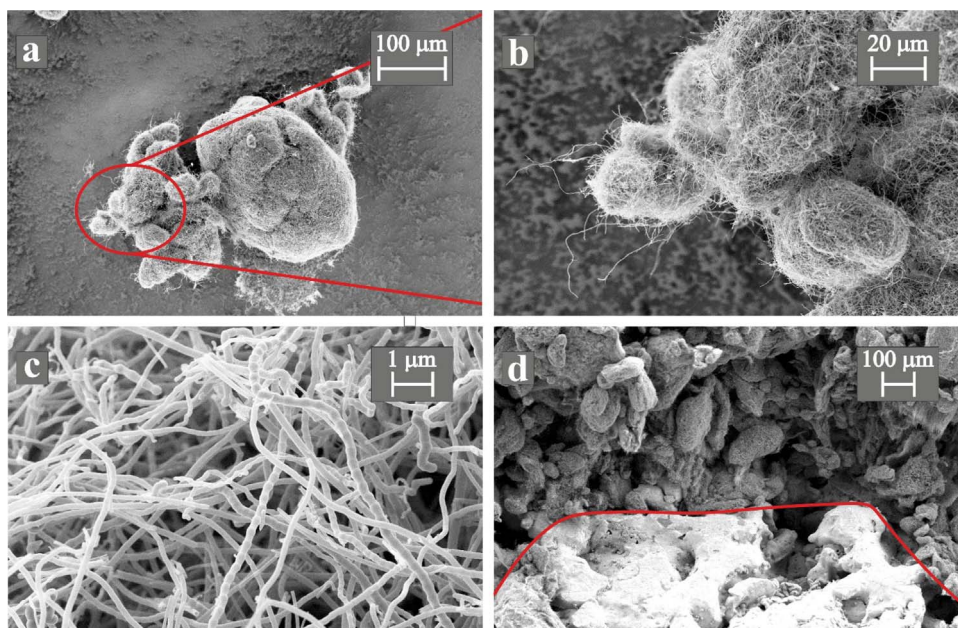


Fig. 5. SEM pictures of as received carbon nanofibers a) at low magnification, b) intermediate magnification and c) high magnification, d) cross-section of a deposited CNF layer (top), making a 90° angle at the line with the bare stainless steel filter below (bottom).

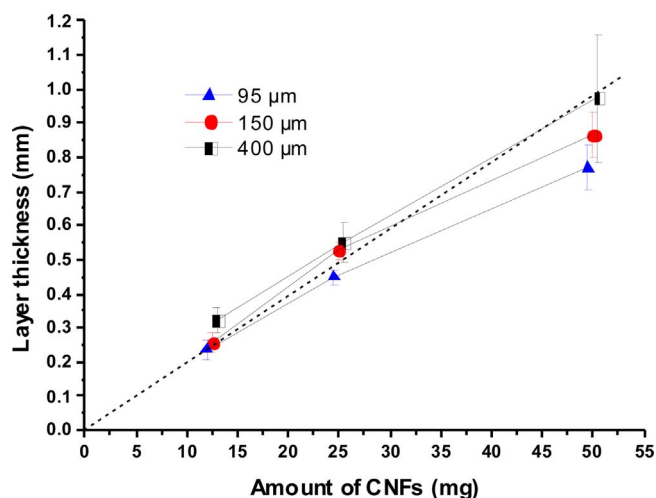


Fig. 6. Influence of the particles size and amount of CNFs on the resulting thickness of the CNF layer after immobilization with 400 mbar pressure drop; data points shifted slightly for visualization, dotted guide line to show proportionality related to 95 μm, 12.5 mg layer.

layers of 25 and 50 mg of CNFs result in fully covering, homogeneous layers, although the 50 mg layer resulted in larger variations in the observed layer thickness.

The pressure drop during filtration for all experiments in Fig. 6 is strongly influenced by the amount of CNFs used for preparation of the immobilized CNF layer, as expected; however, the effect of particle size appears insignificant.

Fig. 6 shows reasonably reproducible data for 90 μm particles and with 150 μm particles, in contrast to 400 μm particles showing larger scatter. This is probably caused by poor homogeneity resulting from the fact that the layers thicknesses (300–1200 μm) are typically 1–3 times the average particles size of 400 μm. Wet sieving results in much higher yields for 150 μm particles than for 95 μm particles, therefore the 150 μm particles are selected for further testing.

3.4. Densification of the CNF agglomerates layer

The rates of flow through the CNF layers of the three particle size fractions were measured with water at 90 mbar pressure-drop for respectively 240, 120 and 90 s. These CNF layers were immobilized beforehand with 300–400 mbar pressure drop during filtration. On average the 95 μm fraction results in a flow through of 0.04 L/min, 150 μm results in 0.11 L/min and 400 μm results in 0.26 L/min. This shows that the smaller the particles, the higher the resistance of the CNF layer, indicating that the layer becomes denser, as expected.

Repetitive exposure to 90 mbar water pressure results in decreasing flow rates (Fig. 7), demonstrating that the forces exerted by the water pressure on the CNF layer cause densification of the CNF layer.

3.5. Stability of the CNF agglomerates layer

The deposited layers were exposed to water flowing along the surface during 10 min for testing the stability of the CNF layers consisting of 25 mg CNFs agglomerates sized 150 μm. Fig. 8 shows the influence of the flow rate on the stability of these CNF layers, immobilized with a pressure drop of 400 mbar and resulting in 0.5 mm thick layers, as described above.

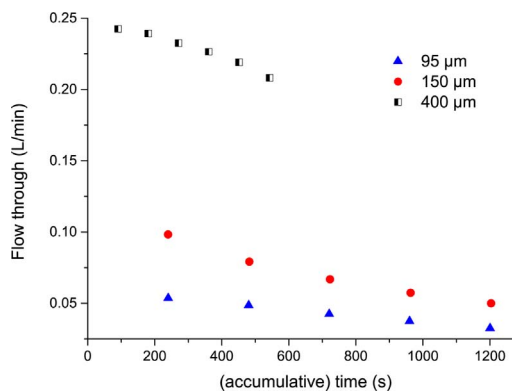


Fig. 7. Effect of accumulative time on flow rate of water through a 25 mg CNF layer (90 mbar pressure drop) supported on the stainless steel filter, immobilized with 300–350 mbar.

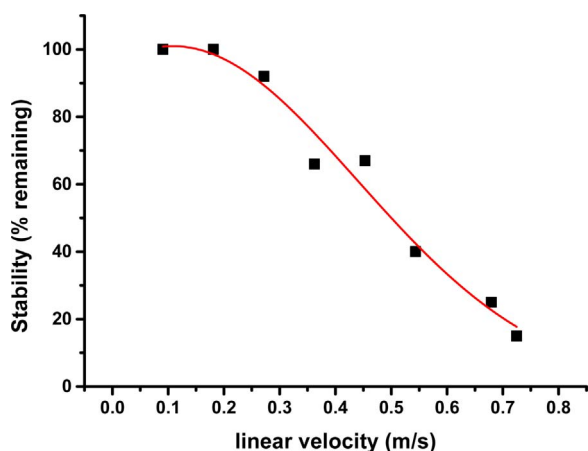


Fig. 8. Effect of linear flow velocity in shear force testing on the CNF layer stability for an immobilized CNF agglomerates layer consisting of 25 mg CNFs of the 150 μm fraction, immobilized with 400 mbar pressure drop.

The removal of CNFs, if any, happens mostly in the first few minutes. For all linear velocities causing removal, removal is observed to occur in pieces starting close to the entrance of the water flow, removing the entire layer locally and thus exposing clean external surface of the metal filter. The relatively sharp boundary between clean and CNF-covered filter moves slowly downstream. Fig. 9 shows snapshots from an *in-situ* movie of the removal of CNFs when flowing water with a velocity of 0.45 m/s

3.6. Effect of pressure drop during immobilization

Fig. 10 shows the effect of the pressure drop, used during the filtration when immobilizing the CNF agglomerates, on the stability of the CNF layer. For these tests CNF layers (25 mg, 150 μm fraction) were subjected to 0.36 m/s for 10 min.

From Fig. 10(■) it can be clearly seen that the stability of the immobilized CNF layer increases with increasing pressure drop during filtration. In contrast, densification of the layers after filtration by flowing water at 90 mbar, as shown in Fig. 7, showed no significant effect on stability of the CNF layer (not shown).

3.7. CNF binder layer

Fig. 10(●) also shows the stability of the immobilized CNF agglomerates layer when it is immobilized on a CNF layer grown on the surface of the filter. The stability tests are conducted as described above. Surprisingly the resulting stability appears inferior compared to the CNF agglomerates layer on the empty filter. Furthermore, it seems independent of the pressure drop applied during deposition of the agglomerates, as can be seen in Fig. 10(●).

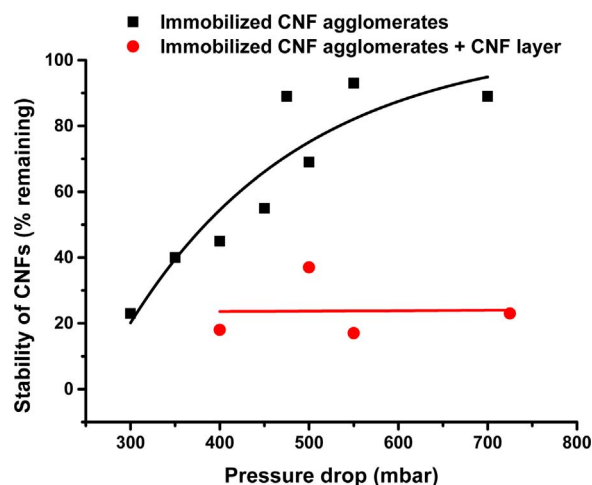


Fig. 10. Effect of pressure drop during filtration on the stability of the immobilized CNF agglomerates on CNF-covered filter (●) and on the empty filter (■), tested at 0,36 m/s linear velocity for 10 min, on an immobilized CNF layer consisting of 25 mg CNFs sized 150 μm.

4. Discussion

Immobilization of CNF agglomerates is achieved by filtration. The most reproducible procedure was found to be immobilization of 25 mg of CNFs of the 150 μm fraction, by using a pressure drop of 400 mbar during filtration. The immobilized CNF layer was shown to be stable when flowing water over the layer with linear velocity up to 0.18 m/s, whereas removal of CNFs is observed at higher velocities (Fig. 8). Also, it can be seen that at high flow rates (> 0.7 m/s) almost the entire CNF layer is removed and complete removal is anticipated at even higher flowrates or via back-flushing.

In short, the immobilized CNF layer is stable at intermediate flow rates (till 0.18 m/s) allowing in principle operation as a catalytic reactor. Importantly, the layer can be removed from the structured packing by simply increasing the flow rate, without the need of removing the packing itself from the reactor.

Fig. 7 shows that CNF layers with large particles are more permeable for water to flow through the layer, as expected. Fig. 7 also shows a decrease in flow rate as a result of repetitive exposure to the pressure drop (90 mbar) when flowing water through the layer. This suggests that the density of the CNF layer increases by pushing the CNF aggregates more into each other.

Fig. 10 clearly shows that presence of the grown CNF binder layer decreases the stability of the layer of CNF agglomerates, apparently weakening the interaction between the CNF agglomerates and the stainless steel filter. The lower stability with a CNF binder layer is attributed to the decreasing surface roughness when growing CNFs. This surface roughness decrease is visualised in both SEM pictures in Fig. 1 as well as by confocal microscopy shown in SI Fig. A2. Both show decreasing micro roughness of the stainless steel surface when growing

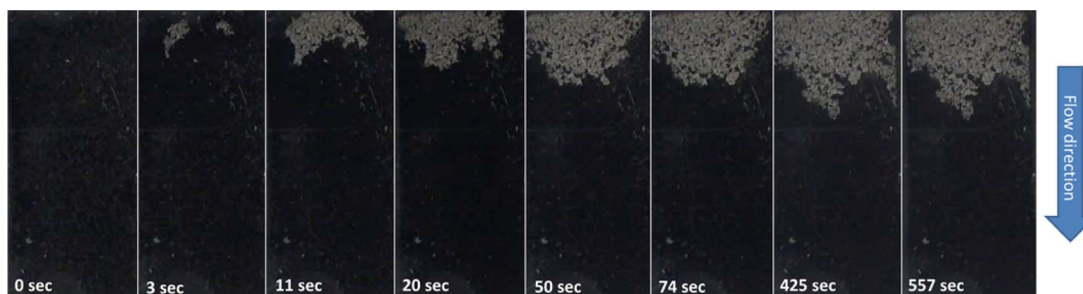


Fig. 9. Removal of CNF particles for a layer of 25 mg CNFs (150 μm fraction) during flow over testing, 0.45 m/s linear velocity (flow direction top to bottom), top view of the sample showing the CNF layer (black) with stainless steel filter underneath (grey).

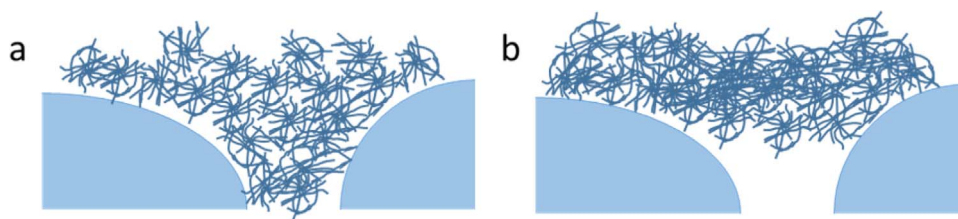


Fig. 11. Schematic representation of interaction of the CNF agglomerates with the surface micro-roughness of the stainless steel filter a) CNF agglomerates penetrate into the pore mouth by applying high pressure drop during immobilization via filtration, b) densification, by prolonged exposure to pressure drop, of the layer without pore mouth penetration due to low pressure drop during immobilization via filtration.

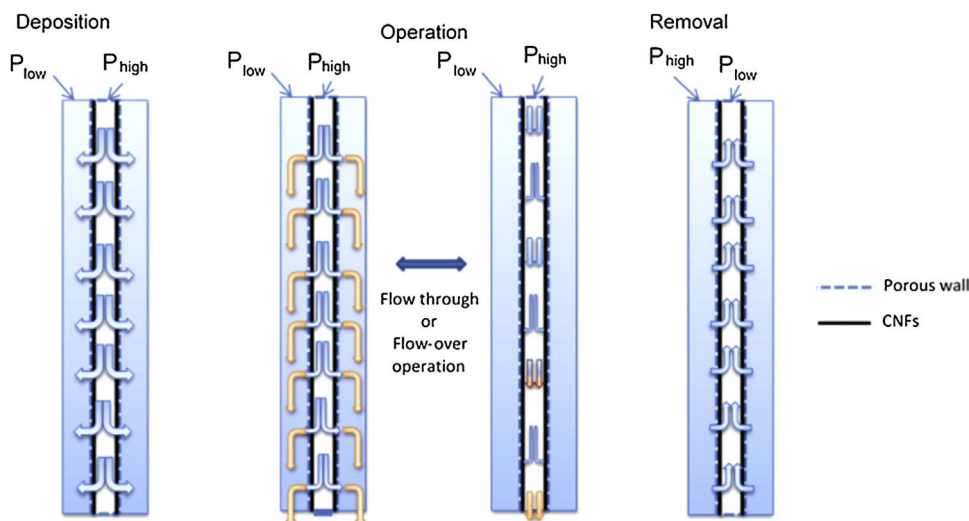


Fig. 12. Schematic representation of a possible reactor design using the porous catalyst support structure as developed in this article.

a CNF layer. On the other hand, the roughness in nanometer scale clearly increased when CNFs are present. Roughness on micro-meter scale is apparently important for creating stable layers.

The results in Fig. 9 show that pieces of the entire layer are removed from the filter, indicating that the interaction between the layer of CNF agglomerates and the filter surface is weaker than the interaction between the CNF agglomerates within the layer. In other words, the interaction between the layer and the filter surface determines the stability of the layer. The stability of the layer of CNF agglomerates on the bare stainless steel filter increases with increasing pressure drop during immobilization (Fig. 10). This is attributed to deeper penetration of the CNF agglomerates into the pore-mouths of the filter, therefore making better use of the surface micro-roughness, as schematically presented in Fig. 11a.

This proposal can also explain the results of the prolonged pressure drop tests. The observed densification (Fig. 7) of the CNF layer increases the interaction between the CNF agglomerates within the layer, but does not influence the stability of the layer. Apparently, the CNF agglomerates are so well attached that the pressure drop provided is not able to push the agglomerates deeper into the pore-mouths (Fig. 11b). In contrast higher pressure drop during immobilization via filtration increases the stability, as shown in Fig. 10. During build-up of the CNF layer, the agglomerates are initially not connected and the first agglomerates can penetrate deeper into the pore-mouths (Fig. 11a), resulting in deeper penetration and better attachment of the entire layer to the surface of the filter.

In this work, metallic filters were used for relatively easy immobilization of CNF agglomerates. However, it is shown that the stability of the CNF layer is mainly determined by the macro-roughness of the filter. The additional CNF-layer grown on and attached to the metal filter, aiming at a binder layer, displayed an adverse effect on the CNF layer stability. Therefore, in future also alternative filter materials that do not allow direct CNF growth, such as ceramics or carbon based

filters, should be explored. Clearly, additional work would be needed to develop this concept further to enable implementation in practical catalytic reactors. A practical reactor is envisaged consisting of concentric tubes where the inner tube is the porous wall that is considered in this study, as shown in Fig. 12. Immobilization of the CNF layer can be done by flowing through the wall from inside to the shell, depositing the CNFs as a filter cake at the inner-surface of the porous tube. The reactor can then be operated either in flow-through mode in which the shell acts as reactor outlet, or in flow-over mode by operating the inner-tube as both inlet and outlet. Removal of deactivated catalyst is then easily achieved by back-flush operation.

The catalytic performance of these CNF layers as catalyst support loaded with Pd have been tested for nitrite hydrogenation for water cleaning, which will be reported in detail in a future paper.

5. Conclusion

In this study a CNF layer is synthesized as a stable catalyst support layer for operational conditions. This layer is shown to be stable up to 0.18 m/s flow over the layer. This CNF layer can be removed by increasing shear force flow rate.

A CNF agglomerates layer immobilized directly on the stainless steel filter is more stable than the same layer deposited on a stainless steel filter with a grown CNF layer. It is proposed that the grown CNF layer decreases the micro roughness of the stainless steel filter, causing the decrease in stability.

The fact that the layer is removed in pieces of the entire layer during flow tests, leaving behind a bare filter surface, shows that the CNFs layer stability is determined by the interaction of the CNFs layer with the stainless steel filter surface. This is confirmed by the increased stability of the CNFs layer when increasing the pressure drop during immobilization via filtration, increasing the bonding between the surface of the filter and the CNF layer via deep penetration in the pore

mouths of the filter.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cattod.2017.05.031>.

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