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 microchannels [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

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 × 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 × 36 × 5 mm, typically ~12 g) is reduced for one hour with 20% H$_2$ in N$_2$. Growth is achieved at 600 °C under 100 mL/min flow of 20% C$_2$H$_4$ + 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 Micromeretics Tristar 3000. HR-SEM
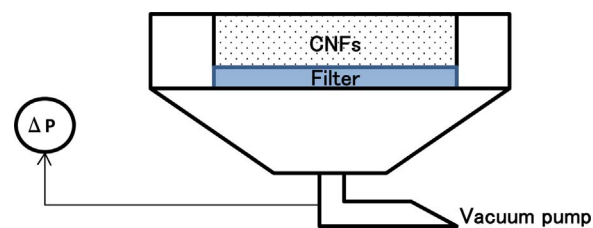
Fig. 2. Schematic representation of the filtration set-up for CNF layer formation.

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 ± 0.025 mm) from the thickness of the filter with the CNF layer (experimental variation ± 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
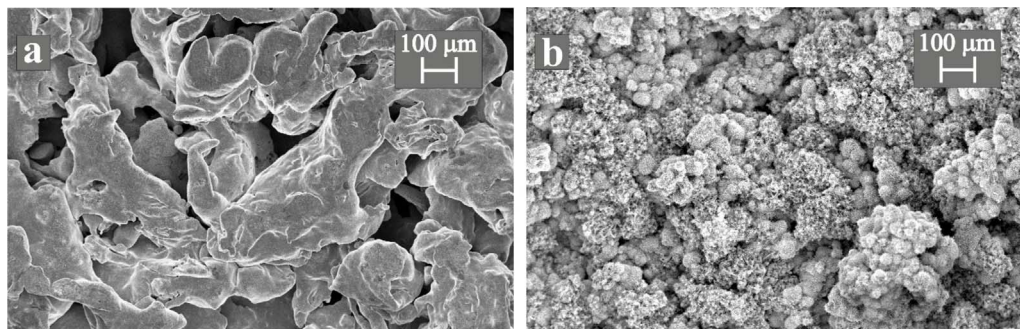

Fig. 1. Low magnification SEM pictures of a) as received stainless steel filter b) stainless steel filter covered with a grown carbon nanofibers layer.