CARBON NANOFIBERS FOR A HYBRID FILTRATION CONCEPT

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Introduction

Carbon nanofibers (CNFs) are widely studied because of their use as catalyst support materials, selective adsorption agents, energy storage, composite materials, nanoelectric devices, field emission devices, and as filter materials. CNFs also enable a hybrid filtration concept for respiratory protection: they can filter gasses by adsorption and they can filter airborne dust particles with their specific fiber shape and size. Up till now little has been published on this topic. Lorimier et al. (2005) addressed combined removal of particles and gas as well. They prepared materials that either had reasonably high particle filtration properties but low adsorption capacity, or low particle filtration properties with high adsorption capacities.

The small diameter of the fibers is inherently favorable for efficient aerosol filtration. Filtration of aerosols in combination with adsorption of hazardous gasses would yield a step forward in the field of respiratory protection. Its potential is assessed in the present study. Two production methods are applied and compared: a) CNFs were grown via a chemical vapor deposition method with a nickel catalyst; and b) CNFs are prepared via electrospinning and subsequent carbonization of polymers. The work on 'CNFs via electrospinning' is actually currently in progress. In order to determine the gas adsorption properties, the materials are characterized by nitrogen adsorption (BET) and toluene adsorption. In order to determine the aerosol filtration properties, the materials are characterized by particle-size dependent filter tests in a dedicated filter set-up.

Experimental

The production route of CNFs via a chemical vapor deposition method with a nickel catalyst is described in detail elsewhere (de Lathouder 2007, van Gulijk et al. 2006). Typically, a Ni gauze is used or a Ni catalyst is deposited on the support from an acidic $Ni(NO_3)_2$ solution in 0.5 M urea. The catalyst is then reduced (30 ml/min H_2, 120 ml/min N_2, 10 K/min) at 823 K for 2 h. CNFs are grown on the support in a tubular quartz reactor at 823 K for 4 h (10 ml/min H_2, 70 ml/min N_2, 120 ml/min CH_4). CNFs grown on Ni gauze, detach from the support by gently scratching the gauze. The gauze can be reused several times. To remove the metal catalyst from the fiber tips, the materials were optionally treated in 1 M HCl under reflux conditions for 2 h.

In addition to the preparation of unsupported CNF samples, carbon nanofibers were also grown on a supporting material. In this study a layer of C-TED cloth was used provided by MAST. The C-Tex range of activated carbon textiles are manufactured in the UK by MAST Carbon Advanced Products, building on the technology originally developed by the UK Ministry of Defence Laboratories at Porton Down. The technology utilizes viscose rayon textiles, treated with a proprietary Lewis acid system and a controlled atmosphere high temperature thermal treatment. The final product is an activated carbon having the same physical structure as the starting textile. BET surface areas for such carbon textiles are typically 1000 – 1600m2/g. In the case of C-TED a viscose rayon fake fur structure was impregnated with a Lewis acid solution and dried. The material was then heated in an oxidizing atmosphere to elevated temperatures (600 – 1000°C) and held at temperature until full conversion and activation had been achieved. CNFs were grown on the cloth as described above, the support was optionally pretreated before Ni addition by refluxing in 1 M HNO_3 for 2 h or by mild oxidation in air for 3 h (603 K 10% O_2 in N_2).

An alternative approach to obtain CNFs consists of two steps, i.e. the production of polymer (nano)fibers by electrospinning followed by carbonization and activation of the thus obtained material (Zussman et al. 2005, Kim et al. 2003). Electrospinning is a powerful technique that employs an electrostatically driven jet formation of a polymer solution from a syringe. During the traveling time of the jet to the grounded surface, the solvent evaporates and jet instability occurs, giving rise to the formation of fibers in the nanometer range 50 – 1200 nm). Polyacrylonitrile (PAN) is a suitable polymer for electrospinning of fibers, which can be carbonized when heated under anaerobic conditions. This work is currently in progress.

The unsupported fibers were characterized by nitrogen adsorption at 77 K to determine the BET surface area. The adsorption isotherm of toluene was measured to determine the potential of the unsupported fibers for organic vapor adsorption. The adsorption equilibrium isotherm was measured at 25°C using the 'Intelligent Gravimetric Analyser' (IGA), which is a gravimetric method.

A preliminary test of the aerosol filtration efficiency of the supported fibers was performed with ambient aerosol (particle size mainly well below 0.5 µm) at 1 cm/s air flow velocity with a condensation particle counter to determine concentrations before and behind the filter.

Results

Figure 1 shows the results of the nitrogen adsorption isotherm on the unsupported carbon nanofiber. The BET surface area derived from the isotherm is about 104 m^2/g. Commercially available activated carbons have a much higher surface area, typically in the range 1000-1500 m^2/g; for comparison Figure 1 shows the nitrogen isotherm on Kureha carbon, taken from Linders (1999). However, it should be noted that these carbon nanofibers were not activated.
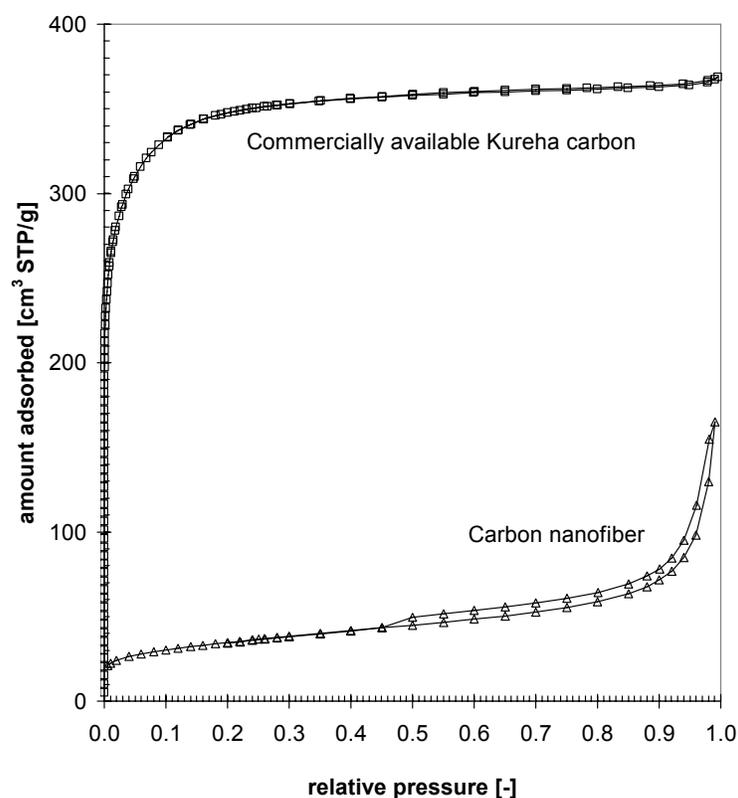

Figure 1. Nitrogen adsorption isotherms at 77 K on the unsupported carbon nanofibers compared with a commercially available Kureha carbon.

Figure 2 shows the results of the toluene adsorption isotherm on the unsupported carbon nanofibers; for comparison the toluene isotherm on Kureha carbon is shown, taken from Linders (1999). Clearly, the nanofibers have an adsorption capacity for organic vapors. Besides accessible for nitrogen, the pore structure is also accessible for larger organic molecules, even though these carbon nanofibers were not activated.
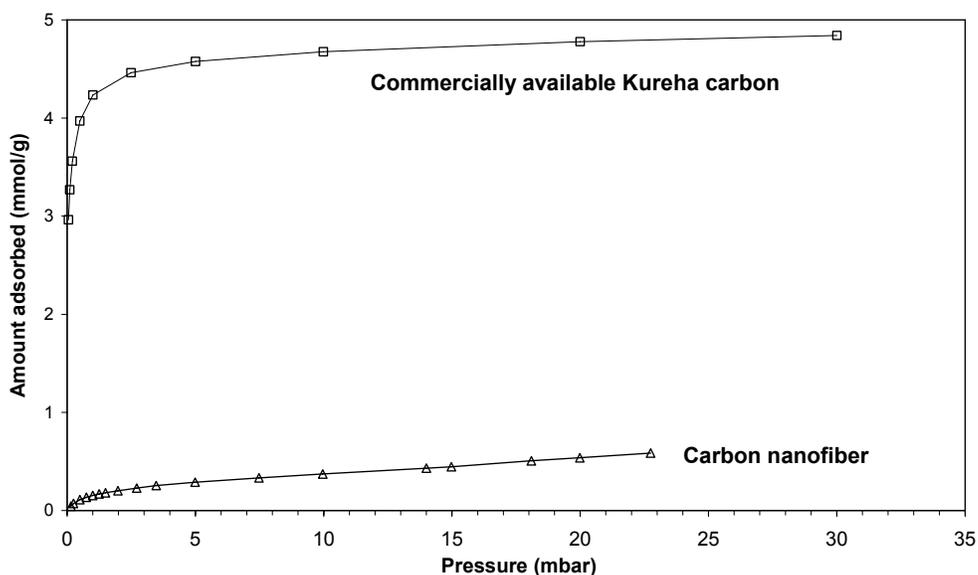
Figure 2. Toluene adsorption isotherm at 25°C on the unsupported carbon nanofibers compared with a commercially available Kureha carbon.

The aerosol filtration properties were determined with the supported fibers. This test showed a filter efficiency of >99.5%. More detailed filter properties at a higher flow velocity will be determined by measuring the size dependent penetration of a NaCl aerosol with a scanning mobility particle sizer (TSI model 3080 and condensation particle counter 3786).

Conclusions
Carbon nanofibers prepared via the chemical vapor deposition method with a nickel catalyst have shown a very promising filtration efficiency. Preliminary results show that airborne particles are filtered with an efficiency of at least 99.5% when fibers are deposited on C-TED cloth. The (unsupported) fibers exhibit a significant adsorption capacity, but this capacity cannot yet cope with traditional activated carbons. The capacity can be further optimized by activation of the fibers.
The second production route of fibers, electrospinning, has resulted in the formation of fibers in the nanometer range. Work is in progress to activate these fibers, and subsequently characterize the performance of the fibers on their adsorption capacity and filtration efficiency.

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