

TUNING POROSITY, STACKING DENSITY AND MECHANICAL STRENGTH OF CARBON NANOFIBER CATALYST SUPPORT MATERIAL

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Introduction

Two important pre-requisites have to be fulfilled for a good catalyst support material: a high bulk density and a high porosity. High support densities result in a more efficient use of the reactor volume and are therefore economically favorable above low density supports. On the other hand, the porosity i.e., accessibility is important in order to avoid mass transport limitations.

Nowadays, new support materials, such as carbon nanofibers (CNF) are available. The properties of CNF potentially surpass those of conventional oxidic supports like a.o., silica and alumina [1,2]. Carbon nanofibers are chemically inert, pure and mechanically strong and thus suitable as catalytic support material. The CNF-bodies consist of entangled individual carbon nanofibers, which are formed during the catalytic growth via decomposition of CO and H₂ on Ni/SiO₂ growth catalysts.

In this contribution, we show that for CNF supports both macroscopic structural properties, i.e, stacking density and porosity can be tuned. The metal loading of the growth catalyst and the growth time of the CNF-bodies are key factors in that respect.

Experimental

Carbon nanofibers were grown via catalytic decomposition of CO in the presence of hydrogen on two Ni/SiO₂ growth catalysts (5 and 20wt% Ni). The Ni/SiO₂ catalysts were prepared via homogeneous deposition precipitation [3]. After deposition, a sieve fraction of 425-850 μm was calcined in static air at 600°C for 3 hours. Next, the Ni/SiO₂ was reduced in situ in 20 vol% H₂ in N₂ for 2 hours at 700°C. After cooling to 550°C, a gas mixture of 20 vol% CO and 7.5 vol% H₂ in N₂ was passed through the catalyst. After the growth, the reactor was cooled to room temperature and the resulting product was collected.

Silica was removed from the grown CNF-bodies by refluxing the product in 1M KOH. After subsequent washing with de-ionized water and drying overnight at 120°C the bulk density and BET pore volumes and surface areas were measured. To measure the bulk density, the mass of a fixed volume with stacked CNF-bodies were measured.

Results and Discussion

SEM results show that the grown CNF-bodies are enlarged replicates of the originating Ni/SiO₂ growth catalyst particles. The diameter of the final bodies is about twice or three times the diameter of the growth catalyst and leads thus at least a 10-fold enlargement of the body volume [4].

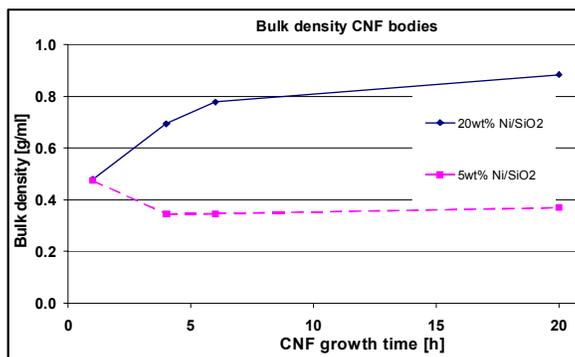


Figure 1. Relation between bulk density of CNF-bodies and growth time using 5 and 20wt% Ni/SiO₂ growth catalysts.

Figure 1 shows the relation between the bulk densities of the grown CNF-bodies with increasing growth time using the 5 and 20wt% nickel silica growth catalysts. It can be seen that the growth time and nickel loading of the catalyst are key factors, which govern the ultimate bulk density of CNF-bodies. The 20wt% Ni/SiO₂ catalysts yield strong CNF-bodies with a high bulk-density. In this highly loaded growth catalyst the nickel particles with a diameter of about 5 nm are close to each other leading to formation of a large number of fibers with a diameter of 25 nm. These fibers easily entangle due to their close proximity. The fibers on the external edge of a skein have a more open CNF structure due to more free space, see figure 2. The open structure of the fibers on the outside of the CNF-body and the densely packed fibers on the inner body is clearly shown. The thickness of this open structure on the outside of the bodies appears independent of the growth time. However, with increasing growth time the bulk density of the bodies increases significantly which is in accordance with formation of more carbon nanofibers per volume unit on the inside of the skein.

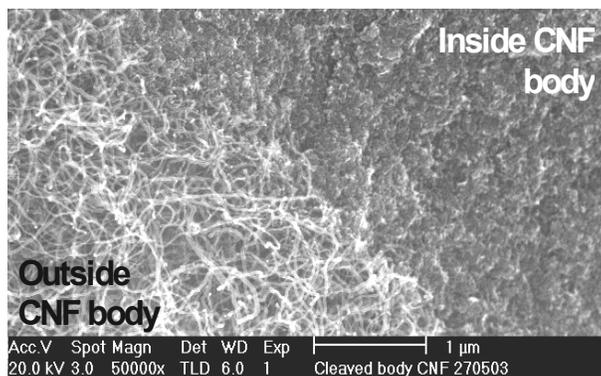


Figure 2. Sem images of a cleaved CNF-body grown from a 20wt% Ni/SiO₂ catalyst. The dense structure on the inside is responsible for the large bulk density.

Low loaded Ni/SiO₂ catalysts (5wt%) contain less nickel particles per unit of volume resulting in a lower density of the CNF skeins grown from this material. From this growth catalyst carbon nanofibers with diameters of about 12 nm were grown using exact the same growth procedure as was used for the 20wt% Ni/SiO₂. This change in diameter resulted in an increase of the external surface area, i.e. from about 120 to 220 m²/g.

The difference in CNF diameter (25 nm for the 20wt% Ni/SiO₂ versus 12 nm for 5wt% Ni/SiO₂) most likely is due to the fact that in the low loaded sample fewer Ni particles sinter together before the CNF growth starts. Besides the diameter of the fibers, also the number of fibers formed per volume is different using these two growth catalysts. For the highly loaded catalyst more and thicker fibers formed per unit of volume compared to the low loaded nickel catalyst. Therefore, low loaded Ni/SiO₂ resulted in a support with a lower density. This voluminous structure of the CNF-bodies coincides with the lower CNF-body strength.

Conclusions

The bulk density, porosity and mechanical strength of CNF bodies can be tuned during the catalytic growth of the fibers. The number per unit of volume and thickness of the fibers have a pronounced influence on those properties and can be tuned by the metal loading of the growth catalyst and the growth time.

References

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