Tuning the activity of nitrogen-containing carbon nanotubes by controlled nitrogen incorporation

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Introduction

Recently we have shown that nitrogen-containing carbon nanotubes (NCNT) grown from nitrogen containing hydrocarbons over metal based catalysts, can be used as heterogeneous basic catalysts [1]. The activity of these materials for the Knoevenagel condensation of benzaldehyde with ethyl-cyanoacetate was related to the concentration of the pyridinic nitrogen atoms in the NCNT. Thus to optimize the catalytic activity of these materials it is of crucial importance to understand the relation between the preparation parameters, growth gas, nature of the metal and temperature, on the amount and type of nitrogen incorporated in the NCNT. Some of these relations will be described in the current contribution.

Tubular nanostructured carbons are most effectively prepared over supported metal catalysts (Ni, Co, Fe) using a gaseous carbon source [2]. In a first step the hydrocarbon is decomposed on the metal surface. The adsorbed carbon atoms and nitrogen atoms, in case of a nitrogen containing hydrocarbon, diffuse through or over the metal particle to nucleate graphene sheets that are organized in CNT. Next the tube is growing from the decomposition of the carbides/nitrides. Clearly all these steps which are influenced by the temperature, growth gas and catalyst, might have a pronounced influence on the properties of the formed tubes. Therefore we have investigated the influence of temperature and growth gas (acetonitrile, pyridine and DMF) on the properties of the formed NCNT. Co/SiO_2 has been used as growth catalyst.

Materials and Methods

Co/SiO_2 (20 wt% Co) was prepare using Homogeneous Deposition Precipitation (HDP) [3].

For NCNT production 0.5 g of catalyst was loaded in a vertical quartz reactor and reduced at 973 K for two hours in a 20% H_2/He flow (total 100 $mLmin^{-1}$). Next, the reduced catalyst was kept at 880K (Tamman temperature) in a helium flow for one hour.

NCNT were grown from acetonitrile (ACN), pyridine (PYR) or N,N-dimethylformamide (DMF) between 823-1123 K by saturating a helium flow (50 $mLmin^{-1}$) with the desired precursor at 303 K. After 16-20 hours the growth reaction was terminated and the amount of NCNT determined.

The growth catalyst was removed by respectively refluxing in 1M KOH and 25% HCl solution. The NCNT were thoroughly washed with demiwater after each step. The amount of accessible basic sites was determined using acid/base titrations. The type of incorporated nitrogen was determined using XPS.

Results and Discussion

Figure 1 shows a typical TEM micrograph of the obtained NCNT. The contrast difference between the edges of the tube and the center points to hollow tubes. Table 1 shows some properties of the NCNT prepared over Co/SiO_2 at different temperatures and different growth gases. Both acetonitrile (ACN) and DMF are effective for preparing NCNT. ACN seems to be applicable over a wider temperature range and the yield of NCNT is higher compared to DMF. Pyridine (PYR) yielded carbonaceous material however, TEM, analysis showed that this was amorphous in nature. We relate these differences to the difference in stability of the precursors. DMF is too stable to be effectively converted while PYR is too reactive. Apparently ACN has the optimal stability/reactivity for forming NCNT over these catalysts. Please note that the particle size of Co, 12 nm in this study, is also of crucial importance. For larger particles (>40 nm) PYR is a suitable precursor (results not shown here).

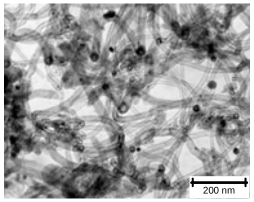

Figure 1: Typical example of NCNT

The temperature has a significant influence on the amount of nitrogen incorporated and the ratio of quaternary over pyridinic nitrogen (Np/Nq). With increasing temperature the amount of nitrogen decreased which can be explained by the higher stability of the carbides relative to the nitrides at these temperatures i.e., more carbides can be formed. Alternatively at these higher temperatures surface nitrogen atoms might easier combine to N_2 which can desorb. From literature it is also known that quaternary nitrogen is more stable at higher temperature which is in accordance with our observations that with increasing temperature the Np/Nq ratio is decreasing.

Table 1: yield and some properties of NCNT prepared over Co/SiO_2

	Temp (K)	Yield (g/gcat)	Amount of N	Np/Nq
ACN	823	10	7.4	2.2
	923	17	4.0	1.0
	1023	25	4.3	0.6
PYR*	923	8	7.5	2.0
	1023	6	7.4	1.5
	1123	5	5.6	0.9
DMF	823	4	1.8	0.8
	923	3	1.6	0.7
	1023	-	-	-

*Pyr resulted in amorphous carbon

Significance

NCNT widens the scope of heterogeneous reusable stable basic catalysts. To improve the understanding of the structure-activity relationship of these materials is crucial. Therefore well defined NCNT have to be prepared in which the amount, location and type of nitrogen needs to be controlled. With this research we contribute to determining and understanding the crucial parameters during the synthesis of NCNT.

References

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