Synthesis of carbon nanotubes in the pore system of mesoporous silicates

Ph. D. Thesis

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Introduction and aims

Carbon nanotubes are in the focus of materials science research since they are the newest member of carbon allotropes and have peculiar physical, chemical and mechanical properties; therefore, they represent a separate research field. Depending on their structures, carbon nanotubes can be conductive, semiconductive or isolating, which makes them promising materials for applications in nanoelectronics. Due to their remarkably high mechanical resistance they, might be one of the best potential strengthening materials in polymer chemistry. Several methods are used for the production of carbon nanotubes. The most frequently applied techniques differ either in the carbon source or the method to generate the high temperature at which the carbon precursor converts to carbon. The high temperature is can be produced either by electric discharge or laser ablation. For the catalytic syntheses (Catalytic Chemical Vapor Deposition, CCVD) lower temperature is required and carbon nanotubes can be produced in higher yield. Most applications require carbon nanotubes with uniform diameter. It is well known that zeolites and some ordered mesoporous materials such as MCM-41, MCM-48 or SBA-15 silicates have pores of molecular and/or macromolecular dimensions from 4 to 10 nm diameters, thus the pore structure of these materials could serve as „template" for the development of the graphitic structure of carbon nanotubes. In this work we examined the production possibilities of carbon nanotubes by applying various mesoporous silicates as host materials. Our aims were the following:

1. Synthesis and characterization of different mesoporous materials: (i) Si-MCM-41 (spherical and non-spherical), Si-MCM-48, and Si-SBA-15 materials possessing different morphology, pore structure and pore size, and (ii) MCM-41materials containing different substitute elements (isomorphously substituted Ti-, Al-, Fe-MCM-41 and Si-MCM-41 impregnated with iron (II) salt solution).
2. Synthesis of carbon nanotubes by two different methods: (i) catalytic decomposition of acetylene (CCVD) and (ii) graphitization (GAS) of the template molecules or polymerized divinylbenzene filling the pores of mesoporous silicates.
3. In case of graphitization we investigated: (i) the possibility of carbon nanotube production from the template of pure mesoporous silica or substituent element containing materials (carbon source with none or low oxygen content); (ii) the effect of the structure and dimension of pores on the quality of carbon nanostructures formed; (iii) the

possibility of producing carbon nanotubes from divinylbenzene polymer introduced into the pores after template removal; (iv) the influence of the substituent element in the mesoporous silicate on the quality and quantity of carbon nanotubes.

4. For CCVD reactions we investigated the influence of both the impregnation of the silicate by the catalytic component and isomorphous substitution on the formation of carbon nanotubes.

Experimental

Mesoporous silicates were synthesized using the liquid crystal template method as described in the literature. MCM-41 materials containing different substituent elements were produced by isomorphous substitution and in the case of Fe-MCM-41 by impregnation as well. The as-synthesized samples were characterized by different physical methods such as X-ray diffractometry, nitrogen adsorption measurements, TG measurements, NMR spectroscopy, infrared spectroscopy and transmission electron microscopy.

A part of the samples was heat-treated to remove the organic templates. The powders were placed in a quartz boat and put in a tubular oven. Under nitrogen flow, the temperature of the sample was slowly (2 ºC/min.) adjusted to 540 ºC, for SBA-15 to 450 ºC. At this temperature the nitrogen flow was switched for oxygen and the sample was treated for 5 h under this condition.

To fill the pores of MCM-41, MCM-48, and SBA-15 with polymers, the template-free samples were soaked in divinylbenzene solution (Aldrich, 80%, mixture of isomers). The polymerization was performed at 120 ºC for 24 h.

The production of carbon nanotubes was performed with two different methods. The first procedure was the heat treatment of the samples containing the template or polymerized divinylbenzene in inert atmosphere at high temperature (graphitization) while the second one was a typical CCVD method.

For graphitization, the samples were put in a quartz boat and placed at the cooler part of a horizontal tubular quartz reactor in which dry nitrogen was flowing at a rate of 50 ml/min. When the system was free of air and moisture, the temperature of the oven was increased to 800 ºC and the boat was drawn into the hottest zone of the reactor. The samples were held at this temperature for 5 and 30 min.

In the CCVD method 1 g of the catalyst was put in a quartz boat and placed into a horizontal tubular quartz reactor. The system was purified of air by introducing dry nitrogen into the reactor for 30 min at a rate of 300 ml/min. Then the reactor was slowly pushed into the oven and the temperature was increased to 700 ºC followed by mixing acetylene in the nitrogen stream with 30 ml/min rate. After one hour of reaction time, the acetylene flow was closed and the reactor was removed from the oven and cooled to room temperature under flowing nitrogen.

Samples were characterized with different physical methods such as X-ray diffractometry, nitrogen adsorption measurements, and transmission electron microscopy (TEM and HRTEM). For TEM analysis the silicate components were removed. This was carried out by dissolving the silicate in 38% hydrofluoric acid and 10 M sodium-hydroxide solution.

Results

1. We demonstrated that the carbon content of the template used for the synthesis of the some mesoporous silicate (MCM-41 and MCM-48) can be transformed into multiwall carbon nanotubes of rather uniform outer diameter. Neither catalytic components nor any external carbon source were required for the conversion.
   1.1. We obtained increasing pore size with increasing carbon chain length of the template of MCM-41 having a long alkyl chain and an ammonium ion head group, but no influence of template carbon chain length on the diameter of carbon nanotubes could be identified.
   1.2. For MCM-48, which has a cubic structure and part of its template contains oxygen atoms, the carbonization of the structure-directing organic matter in the pores results in well-shaped carbon nanotubes. However, no carbon nanotube formation was found for SBA-15 templated with Pluronic 123 block copolymer. This was attributed to the presence of oxygenated template and the larger pore size (5 nm) of the material.
   1.3. Carbonization of templates in mesitylene–expanded MCM-41 gave carbon nanotubes of top quality when we used a shorter autoclave treatment for the synthesis of MCM-41 (this yields a material with smaller pores). We believe that the pore size limits the production of carbon nanotubes and too large pores do not help the formation of carbon nanotubes. This hypothesis was confirmed for SBA-15 as well.

1.4. We could not produce any carbon nanotubes in spherical MCM-41 samples. This experimental evidence indicates that the morphology of mesoporous silicates influences heavily the production of carbon nanotubes in their pores by graphitization.

2. The production of carbon nanotubes was successful from divinylbenzene as well; no catalytic component was required. The synthesis of carbon nanotubes was successful after filling the pores of MCM-41 and MCM-48 with divinylbenzene and polymerizing it. However, HRTEM results revealed that the walls of these tubes are less graphitized than those of the tubes formed from the template of the host materials. For SBA-15, the synthesis of carbon nanotubes from divinylbenzene was unsuccessful confirming the influence of the pore diameter on the formation of carbon nanotubes.

3. We demonstrated that the interior of isomorphously substituted, non-spherical MCM-41materials can be used as a nanoreactor for the production of carbon nanotubes from template as well. The differing quantity and quality of carbon nanotubes in the presence or absence of substituted elements in the silicate walls indicates differing mechanisms of template decomposition in the channels. The acidic character of the silicate could have an important role in the formation of carbon nanotubes. This was proved using pyridine adsorption and KBr wafer IR technique.

4. For the CCVD method it was found that samples impregnated with iron (in this case only secondary bonds exist between the support and the metal precursors) were active catalysts in the production of carbon nanotubes, irrespective whether the support is hexagonal or spherical. It was proved that carbon nanotubes grow on the outer surface of the materials used as catalysts in the CCVD process.

5. For isomorphously substituted spherical MCM-41 samples, where the transition metal ions are embedded into the walls of the mesoporous silicate, formation of carbon nanotubes was found only on those samples having low Si/Fe ratio. The decrease of BET areas with increasing iron content of spherical silicate indicates that the silicate pores are less ordered. This was confirmed by XRD analysis as well. In these cases it seems likely that large amounts of iron are released from the silicate walls. The iron can form nanoclusters in the channels or on the outer surface of the silicate, which can catalyze the decomposition of acetylene towards carbon nanotubes.

Conclusions

The production of multiwall carbon nanotubes using mesoporous silicates as host materials represents a novel, interesting segment among the synthesis methods developed for carbon nanotubes production. However, this method is not competitive –at least in its present form– with the CCVD method for the large scale synthesis of carbon nanotubes. Further studies are necessary to develop this method into a large scale carbon nanotube synthesis technique.

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