OPTIMISATION OF CATALYTIC SYNTHESIS OF CARBON NANOTUBES. PURIFICATION AND MODIFICATION

PH.D. THESIS

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Introduction and objectives

The discovery of fullerenes and carbon nanotubes gave new life to carbon chemistry and the interest was further intensified by the various requirements of emerging nanotechnology. The synthesis of novel nanometer size materials is in the focus of material science research. Consequently, intense experimental and theoretical efforts are currently being devoted to preparation, characterisation and application of these nanostructures. Carbon nanostructures, particularly carbon nanotubes are of particular interest since they can be used for hydrogen storage, as polymer fillers, as nanosensors and nanowires (when the interior of the tube is filled with metal) in nanoelectrical devices, etc.

Several methods exist (electric arc-discharge, laser ablation, catalytic vapour deposition – CVD, etc.) for production of carbon nanotubes. Catalytic synthesis is operated under relatively mild condition and experimental apparatus is very simple. The CVD method is of great interest since it gives large quantity, good quality single- (SWMT) and/or multiwall (MWNT) carbon nanotubes. The purification and the modification are also indispensable requirements for the possible applications.

The investigations, I have discussed in my thesis, were performed on the following research fields:

1. developing new catalysts which are able to produce large quantity of MWNT while the formation of other carbon forms is suppressed,
2. *in situ* investigation of oxidation state of metal(s) on the support in order to understand the mechanism of the synthesis,
3. optimisation of the synthesis and investigation of effects of reaction parameters and reactants,
4. efficient purification of produced MWNT,
5. modification of MWNT.

Experimental methods

Catalysts, which consist of cobalt and/or iron deposited onto support surface, were prepared by impregnation, ion-adsorption precipitation and wet grinding methods. As catalyst support different oxide materials (MCM-41, Co-MCM-41, Si-MCM-48, Al-MCM-48, NaA-LTA, KL-LTL, NaY-FAU, 13X-FAU, SiO_2, $CaCO_3$, MgO, $Al2O_3$, $Al(OH)_3$) were used. Catalyst samples were tested for MWNT synthesis by decomposing acetylene (diluted with nitrogen) in a fixed bed flow reactor.

The characterisation of the crystallinity of the applied support was carried out by XRD.

The oxidation state of catalyst metal(s) on the support was investigated *in situ* by X-ray Photoelectron Spectroscopy (XPS).

The change of the quantity of the catalyst at the applied reaction temperatures was followed by thermal analysis.

The nature of produced carbon nanotubes was characterised by Transmission Electron Microscopy (TEM). TEM was used to assess the quantity of other carbon forms, the efficiency of the purification and to follow up the degree of cutting of MWNT.

The mechanical modification i.e. cutting of MWNT was carried out by vibration ball milling. After milling the adsorption isotherm of N_2 of the product was measured. From this information the surface area and the pore size distribution could be obtained.

New scientific results

1. We have studied Co and/or Fe catalysts supported on different materials in the synthesis of carbon nanotube. The crystallinity of the applied support does not have decisive effect on activity and selectivity of catalysts. The results on samples containing micro- and mesoporous materials point out that only metal clusters deposited on the outer surface of the support show selectivity in the synthesis and the porosity of the support has only minor effect on the morphology of carbon nanotubes.

On the basis of the activity of the catalysts and the quality of carbon nanotubes, NaY-FAU, 13X-FAU, SiO_2, Al_2O_3 and $Al(OH)_3$ proved to be effective supports.

2. Investigating the role of the metal we have shown that metals incorporated in the framework are not active in the synthesis of MWNT. We have pointed that after the reaction for the Fe/$Al(OH)_3$ sample iron-carbide formation is assumed under reductive conditions, while for Co/$Al(OH)_3$ photoemission peaks in the spectrum generated by *in situ* XPS method indicate the formation of metallic cobalt. For the Fe-Co bimetallic catalyst the XPS spectra suggest the formation of an Fe-Co alloy that is acting as an catalyst of significant activity and selectivity in the synthesis of MWNT. As it observed C(1s) peak attests that mainly graphitic carbon nanotubes containing negligible amount of amorphous carbon is producing.

3. Several reactants have been studied and the results have shown that under the applied temperature (600-800^{o}C) any compound containing carbon but methane is convenient reactant to produce MWNT with naturally different efficiency. Reactivity order can be listed from the activity and TEM pictures:

   acetylene > acetone > ethylene > n-pentane > propylene >> methanol = toluene >> methane.

   Acetylene is the most adequate carbon source for nanotubes formation and the acetone incidental to acetylene in dissu-gas results in MWNT with almost equal selectivity.

4. Studying the effects of acetylene and nitrogen flows, the quantity of the catalyst and the temperature we have observed that the catalytic activity and the carbon-yield are optimal under different parameter sets. We have shown that low linear rate of the reactant (5-30 ml/min) is favourable and the application of high flow of the carrier gas (20-320 ml/min) results in decrease of both activity and yield. It has been shown that decreasing the temperature below the generally applied 720^{o}C (620 and 670^{o}C) neither catalytic activity nor carbon-yield alters considerably while keeping the required selectivity. By increasing the quantity of the catalyst from 15 mg to 240 mg the carbon-yield increases which indicates that the reaction proceeds at catalytic centres of greater number.

5. Studying the first step of the purification of carbon nanotubes (removal of the metal catalyst and its support) we have shown that the catalyst containing $Al(OH)_3$ support could be removed in two steps with good efficiency (94 %) using concentrated NaOH solution. Applying autoclave the efficiency could not be increased further.

6. During the removal of the carbon-containing by-product from the nanotube sample no evident correlation has been found between oxidation reaction rate and electrochemical oxidation potential. Using $HClO_4$, H_2O_2 and O_3 under the experimental conditions the reaction was considerably slow. It has been shown that KMnO4 is the most effective reactant in the competitive oxidation respect of both yield and quality of the final product, although it has to be taken account that the number of purification steps increases owing to the formation of solid MnO_2.

7. It has been shown that using mechanical grinding cutting of nanotubes can be achieved and the final tube length depends on the milling time. Using 110 hours process about 120 nm long nanotube fragments can be produced in 10-50 grams quantities. It has been observed that after the process the surface area of the sample increases, the length/diameter ratio decreases and more intensive peaks is obtained in the measure of the pore size distribution.

8. Laser irradiation of vanadium sheets in air results in vanadium oxide microtubes that is not active per se in the synthesis of carbon nanotubes. Predominant formation of carbon nanotubes is found over the cobalt-impregnated samples. It has been suggested that according to the binary phase diagram of V-Co system V_3Co alloy is formed under reductive atmosphere and it is responsible for carbon nanotube formation.

Application of the results

According to our investigations several catalysts has proved to be effective for the synthesis of carbon nanotube. The Co,Fe/Al(OH)3 is the one of the most important catalyst from them due to its catalytic activity and selectivity. Applying this catalyst formation of negligible amount of amorphous carbon can be observed and the purification of the product is relatively simple. These facts qualify Co,Fe/$Al(OH)_3$ catalyst for producing large quantity carbon nanotube.

The mechanical grinding, which results in grams quantity of short fragments of carbon nanotube samples, is a promising process for such applications as hydrogen storage , fabrication of molecular sieves and polymer fillers.

Publications

Papers related to this thesis

1. **A. Siska**, K. Hernadi, I. Kiricsi, I. Rojik, J. B.Nagy: "The role of catalyst support in carbon nanotube synthesis", Electronic Properties of Novel Materials – Progress in Molecular Nanostructures, XIIth International Winterschool (Ed. H. Kuzmany), Woodbury, p:20-24, 1998.

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9. K. Hernadi, Z. Konya, **A. Siska**, J. Kiss, A. Oszko, J. B.Nagy, I. Kiricsi: ″The role of zeotype catalyst support in the synthesis of carbon nanotubes by CCVD″, *Stud. Surf. Sci. Catal.*, submitted.
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1. **A. Siska**, K. Hernádi, I. Kiricsi, I. Rojik, J. B.Nagy: "The role of catalyst support in carbon nanotube synthesis", XIIth International Winterschool on Electronic Propeties of Novel Materials, Kirchberg/Austria, 28.2-7.3.1998, poster.

2. **A. Siska,** K. Hernádi, I. Kiricsi, I. Rojik, J. B.Nagy: "Effect of catalyst support quality on carbon nanotube formation”, 4th Pannonian International Symposium on Catalysis, Smolenice, Slovakia, June 11-14, 1998, poster.

3. K. Hernádi, **A. Siska**, A. Fonseca, I. Kiricsi,, J. B.Nagy: “Catalytic synthesis of graphitic carbon nanotubes”, 4th Pannonian International Symposium on Catalysis, Smolenice, Slovakia, June 11-14, 1998, lecture.

4. **A. Siska**: ″Effect of catalyst support quality on carbon nanotube formation″, Ziele Academie Timisoara, Secion Chemie, Timisoara, 1998, lecture.

5. **Siska A.**: ″A katalizátorhordozó minőségének hatása a szén-nanocsövek katalitikus szintézisére″, XXI. Kémiai Előadói Napok, Szeged, 1998. október 26-28, lecture.

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7. **A. Siska,** Z. Kónya, A. Fonseca, J. B.Nagy, I. Kiricsi: ″Efficient purification of carbon nanotubes produced over Co,Fe-based catalyst supported on alumina″, NATO-ASI:

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12. **A. Siska**, K. Niesz, I. Vesselenyi, K. Hernadi, D. Mehn, Z. Konya, I. Kiricsi: ″Mechanical and chemical breaking of multiwalled carbon nanotubes″, EUROPACAT V., Limerck, Ireland, September 2-7, 2001, poster.

13. K. Hernadi, Z. Konya, **A. Siska**, J. Kiss, A. Oszko, J. B.Nagy, I. Kiricsi: ″The role of zeotype catalyst support in the synthesis of carbon nanotubes by CCVD″, 2nd FEZA, Taormina, Italy, September, 2002, oral.

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2. **Siska A.:** ″A katalizátorhordozó minőségének hatása a szén nanocsövek katalitikus szintézisére″, XXI. Kémiai Előadói Napok kiadványa, 44 (1998).

3. **Siska A.**: ″Szén nanocsövek katalitikus szintézise″, MTA Koordinációs Kémiai Munkabizottság ülése, Szeged, 2000. március 23.