INVESTIGATION OF CATALYTIC SYNTHESIS OF MULTIWALL CARBON NANOTUBES AND THEIR GROWTH MECHANISM

PH.D. THESIS

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Introduction, goals

Carbon nanotubes are at the peak of their career in this decade. A very significant amount of theoretical and experimental research has been performed on the subject, resulting in numerous papers describing the synthesis methods, properties and application potential of carbon nanotubes. However, most of the envisioned applications are yet to be realized even on a pilot plant scale because of the lack of a cheap and productive synthesis method. Besides this practical application bottleneck, there are also some conceptually important problems to be solved in the field, some of which are related to the formation mechanism of carbon nanotubes. My thesis is related to these problems as well.

The details of the CCVD (Catalytic Chemical Vapor Deposition) synthesis technology are being extensively studied both at Szeged and at Namur. I have joined this research by studying the nanotube production activity of several modified supported metal catalysts, especially with respect to the relationship between the pore structure of the support and the quality and quantity of the obtained multi-wall carbon nanotubes. Additionally, we studied the chemical state of the metallic catalyst components *in situ* under reaction conditions in the case of bimetallic catalysts in order to gain insight into the formation mechanism of carbon nanotubes.

One advantage of the CCVD method is that practically any gaseous or vaporized hydrocarbon can be used as carbon source. It was on this basis that we studied the possibility of converting various plastic wastes into nanotubes.

One of the most widespread analytical methods in nanotechnology is Transmission Electron Microscopy (TEM). Even now, most of the TEM micrographs measured are analyzed by human eye only. We studied the possibility of a computer-based analysis capable of evaluating the shape and size of particles visible in a TEM image. Our goal here was the development of a shape recognition and particle counting software.

Experimental

Our experimental work was focused on the CCVD synthesis of multi-wall carbon nanotubes to a large extent. These experiments were performed in a horizontal reactor using various catalysts and carbon sources. The system consisted of a horizontal quartz tube mounted in a high temperature tube furnace, a quartz boat for holding the catalyst bed and flow controllers for the inlet gases. A

small modification to the reactor allowed us to let liquids and vapors of solid materials in as well. The reactor temperature was controllable between 300–1400 K.
The synthesized catalyst samples were characterized by physico–chemical methods. We determined their specific surface area using an automated nitrogen adsorption instrument and recorded their infrared spectra both before and after carbon nanotube synthesis using a Mattson Genesis 1 FT-IR instrument. X-ray diffraction was utilized to study the structural changes taking place in the catalyst and to identify the graphitic and amorphous carbon species formed on the catalysts. The thermal stability of the catalysts and the carbonaceous species formed was assessed by TG-DTG.

We applied *in situ* XPS and Mössbauer spectroscopy to study the formation mechanism of carbon nanotubes.
The carbon nanotubes were studied by TEM after removing the catalyst particles and the support. The TEM images were analyzed by a home-developed PC program.

New scientific results

1. We studied the effect of the support and of the metallic catalyst particles on the quality and quantity of carbon nanotubes formed using the CCVD method. We also investigated the applicability of plastics as carbon sources in CCVD.

1.1 We were able to confirm an earlier finding concerning the extraordinary catalytic activity – and consequently, the superior carbon nanotube production ability– of iron and cobalt supported aluminum oxide.

1.2 We have shown that the catalytic activity of bimetallic catalysts containing both iron and cobalt exceeds the activity of single-metallic ones containing either metal.

1.3 We have shown for the first time in literature that nickel and vanadium supported ZSM-5 is an inferior CCVD catalyst as it can not produce carbon nanotubes of adequate quality and quantity. On the other hand, a catalyst containing the combination of the two metals was able to convert acetylene into multi-wall carbon nanotubes of good quality in large amounts.

1.4 We proved that the type of the pore structure of catalyst supports has an influence on the quality of the carbon nanotubes formed. However, this effect is not commeasurable with that of the metallic component.

1.5 We have shown that PE, PP, PE/PP, PS and PET plastic wastes can be converted into multi-wall carbon nanotubes of good quality on supported cobalt catalyst. A later optimization of the process –with an emphasis on controlling the thermal decomposition of the plastics– could render it suitable for carbon nanotube production.

2. Bimetallic catalysts performed very well in the CCVD synthesis of multi-wall carbon nanotubes with respect to both quality and quantity. Therefore, we have undertaken a detailed analytical study (using BET measurement, XRD, XPS and Mössbauer spectroscopy) in order to understand their working mechanism.

2.1 We have proved using Mössbauer spectroscopy that under CCVD conditions, the two metallic components present in the bimetallic 50-50 atomic% Fe-Co catalyst form nanometer sized alloy particles. This result confirms the findings of our previous *in situ* XPS studies about the formation of an alloy phase.

2.2 We have proved by *in situ* XPS measurements that no alloy phase is formed in bimetallic nickel–vanadium catalysts. The two components are present as separate metallic particles on the support.

2.3 We have shown that under CCVD reaction conditions vanadium is partially incorporated into the zeolite crystal as a framework ion. The interpretation of the corresponding XPS results was confirmed by the fact that zeolites isomorphously substituted with vanadium are well-known is zeolite chemistry.

3. We have developed our own software for the analysis of TEM images. The program is capable of recognizing particles of tubular, fibrillar and other morphologies and can determine the numerical ratio of these particles in a selected image segment.

Practical applicability of the achieved results

Carbon nanotubes appear to be at the peak of their career nowadays. Although several of their properties are known already, the thorough understanding of these is still lacking in many cases. The goal of the present thesis was to investigate some of these properties as well as to understand the details of a selected carbon nanotube synthesis method. The practical importance of these studies is in the selection of the right CCVD catalyst. Using catalysts of high activity and good product quality may lead to the up-scaling of carbon nanotube production, which in turn is a prerequisite for their industrial application. Potential mass markets for multi-wall carbon nanotubes include the plastic industry (filler) and battery production (capacity enhancer). I believe the results outlined in the present thesis may contribute to the development of these fields.

List of publications

Papers related directly to the thesis

1. Production of carbon nanotubes on different metal supported catalysts
   I. Vesselényi, K. Niesz, A. Siska, Z. Kónya, K. Hernádi, J. B.Nagy, I. Kiricsi
   Reaction Kinetics and Catalysis Letters, 2001, **74**(2), 329-336.
   Impact factor: 0.475 Number of citations: 1

2. Modification of multiwalled carbon nanotubes by different breaking processes
   I. Vesselényi, A. Siska, D. Méhn, K. Niesz, Z. Kónya, J. B.Nagy, I. Kiricsi
   Journal de Physique IV, 2002, **12**, 107-112.
   Impact factor: 0.291 Number of citations: 1

3. Large scale production of short functionalized carbon nanotubes
   Z. Kónya, **I. Vesselényi**, K. Niesz, A. Kukovecz, A. Demortier, A. Fonseca, J. Delhalle, Z. Mekhalif, J. B.Nagy, A.A. Koos, Z. Osvath, A. Kocsonya, L.P. Biró, I. Kiricsi
   Chemical Physics Letters, 2002, **360**(5,6), 429-435.
   Impact factor: 2.526 Number of citations: 7

4. Comparative study of catalysts containing transition metals in production of carbon nanotubes
   I. Vesselényi, K. Niesz, Z. Kónya, J. B.Nagy, I. Kiricsi
   AIP Conference Proceedings, 2002, **633**, 190-193
   Impact factor: 0.000 Number of citations: 0

5. Comparison of Fe/Al_2O_3 and $Fe,Co/Al_2O_3$ catalysts used for production of carbon nanotubes from acetylene by CCVD
   Z. Kónya, **I. Vesselenyi**, K. Lazar, J. Kiss, I. Kiricsi
   IEEE Transactions on Nanotechnology, 2004. 3(1), 73-79.
   Impact factor: 2.088 Number of citations: 3

6. XPS study of multiwall carbon nanotube synthesis on Ni-, V-, and Ni,V-ZSM-5 catalysts
   Z. Kónya, **I. Vesselényi**, J. Kiss, A. Farkas, A. Oszkó, I. Kiricsi
   Applied Catalysis, A: General, 2004, **260**(1), 55-61.
   Impact factor: 2.378 Number of citations: 5

Summary:

Impact factor: 7.758 Number of citations: 17

Posters and talks related directly to the thesis

1. Comparison of Fe/Al_2O_3 and $Fe,Co/Al_2O_3$ catalysts used for production of carbon nanotubes from acetylene by CCVD
   Z. Kónya, **I. Vesselényi**, K. Lázár, J. Kiss, I. Kiricsi
   Proceedings of SPIE-The International Society for Optical Engineering, 2003, **5118**(Nanotechnology), 296-304.

2. Study of $Co,Fe/Al_2O_3$ catalyst in the production of carbon nanotubes
   1st NANOCOMP meeting, Kirchberg, 05-06/03/2001, előadás

3. In situ XPS study of $Co,Fe/Al_2O_3$ catalyst in the production of multiwalled carbon nanotubes
   2nd NANOCOMP meeting, Zaragoza, 10-12/09/2001, előadás

4. Comparison of different metal supported catalysts in the production of carbon nanotubes
   3rd NANOCOMP meeting, Namur, 27/02-01/03/2002, előadás

5. Mösbbauer study of $Co,Fe/Al_2O_3$ catalyst in the production of multiwalled carbon nanotubes
   4th NANOCOMP meeting, Nice, 09-11/10/2002, előadás

6. In situ XPS study of Ni-, V-, and Ni,V-ZSM-5 catalyst in the production of carbon nanotubes
   5th NANOCOMP meeting, Szeged, 05-07/03/2003, előadás

Other papers and conference proceedings

1. Functional groups generated by mechanical and chemical breaking of multiwalled carbon naotubes
   K. Niesz, J. B.Nagy, A. Fonseca, I. Willems, Z. Kónya, **I. Vesselényi**, G. Bister, I. Kiricsi
   AIP Conference Proceedings, 2001, **591**, 345-348.
   Impact factor: 0.000 Number of citations: 0

2. Mechanical cut of carbon nanotubes
   K. Niesz, Z. Kónya, **I. Vesselényi**, A. Fonseca, J. B.Nagy, I. Kiricsi
   AIP Conference Proceedings 633, 100-102 (2002)
   Impact factor: 0.000 Number of citations: 0

3. Mechano-chemical functionalization of carbon nanotubes
   K. Niesz, Z. Kónya, **I. Vesselényi**, A. Fonseca, J. B.Nagy, I. Kiricsi
   AIP Conference Proceedings 633, 82-85 (2002)
   Impact factor: 0.000 Number of citations: 1

4. Mechanical and chemical breaking of multiwalled carbon nanotubes
   K. Niesz, A. Siska, **I. Vesselényi**, K. Hernádi, D. Méhn, G. Galbács, Z. Kónya, I. Kiricsi
   Catalysis Today, 2002, **76**, 3-10.
   Impact factor: 2.146 Number of citations: 4

5. Carbon nanotubes - on the eve of success?
   K. Niesz, I. Vesselenyi, D. Mehn, Z. Konya, I. Kiricsi
   Materials Science Forum, 2005, **473-474**, 141-146.
   Impact factor: 0.498 Number of citations: 0