Rate-spectroscopic characterization of adsorption properties of carbon nanotubes

PH.D. THESIS

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Introduction

Nowadays carbon nanotubes can not be considered to as curiosity. The synthesis of nanotubes in a desired amount is routine work, such as their characterization.

The utilization of carbon nanotubes offers a number of potential applications. Their “popularity” is related to their specific structural properties. The nanotube, depending on its chirality can be conductor or semi conductor. Gas molecules can be adsorbed on the inner and outer surface of the tubes. Besides of their special electric and adsorption properties enhanced mechanical strength and thermal stability were also observed. Their adsorption properties related to the special nanostructure, initiated the research of applying the nanotubes as adsorbents for hydrogen storage. At present latter application seems to be quite unlikely, however the work on mentioned research field raised a number of questions to be answered.

Although the production of carbon nanotubes is relatively simple, the application of nanotubes as adsorbent requires materials of good quality, i.e., materials which are pure or contain contamination not influencing the adsorption properties adversely. The catalytic technique produces carbon nanotubes with considerable amount of contaminants such as residues of catalyst, metal particles and other carbonaceous formations. To obtain carbon nanotubes in pure form physical and/or chemical treatments are necessary, which often change the properties of nanotubes.

In adsorption-related applications the deep knowledge about the adsorption properties of the solid adsorbent (in this case the carbon nanotube) is often required. Sorption on faultless nanotubes can be described by theoretical methods. However, the value of the computed results can be judged, when they can be confronted with results of measurements. Nevertheless, only a few experimental studies have dealt with the dynamics of adsorption in carbon nanotubes.

Hydrogen storage is not the only option to apply carbon nanotubes as adsorbents. Therefore, the investigation of the adsorption properties of nanotubes is an important field of research. The frequency-response method has been shown to be useful for investigating the mass transfer kinetics of gases in various adsorbents. This technique can provide us with the possibility to investigate the dynamic adsorption properties of carbon nanotubes.

Aims of the work

The Department of Applied and Environmental Chemistry of the University of Szeged continues intensive research in the synthesis, characterization and application of carbon nanotubes. On the other hand, with the help of the frequency-response technique used in the Department of Micro and Mesoporous Materials successful work has been carried out to characterize the mass transport dynamics of sorption in various adsorbents. The present work concerns the research areas of both groups.

The properties of carbon nanotubes required by a specific application can be achieved by applying physical and/or chemical treatments. We examined the effect of various treatments on the adsorption properties.

The applied (mainly chemical) treatments can result in the formation of functional groups on the carbon nanotube surface. These groups are new adsorption sites. Our work showed the appearance of new sorption sites, and the affects of the sites on the adsorption properties.

The induced changes in the adsorption properties of carbon nanotubes can modify the mass transport dynamics of sorption. Our aim was to learn more about the nature of the rate-controlling step of the mass transport process in various carbon nanotube modifications.

The mass transport process can be influenced not only by the adsorbent but, also, by the properties of the adsorptive. The effect related to the structure of the adsorptive molecule was investigated on the dynamics of the mass transport processes in nanotube preparations.

Experimental:

Using the catalytic chemical vapor deposition (CCVD) technique single- and multiwalled carbon nanotube samples were obtained applying systematically varied synthesis conditions. Treating multiwalled carbon nanotubes with physical and/or chemical methods a series of nanotube samples was obtained.

The structural, physical and chemical properties (specific surface area, pore size distribution, chemical contents etc.) of the carbon nanotube samples were analysed with multitude of techniques such as transmission electron microscopy (TEM), nitrogen cryo-adsorption measurements, elemental analysis, infrared spectroscopy, frequency response (FR) method and temperature-programmed desorption (TPD) measurements.

New scientific results

The results obtained are summarized as follows:

1. The nitrogen adsorption isotherms related to the carbon content of the samples and the coincidence of the specific surface area values revealed that both the inner and the outer surface of the as-synthesized, the purified, the ball-milled and the ball-milled and oxidized samples are accessible for nitrogen and other molecules with similar size, in contrast to the suppositions reported in the literature.
2. During our work the frequency response rate spectroscopy, developed for studying the gas-solid interactions and mass transports, was successfully applied to experimentally examine the dynamic adsorption properties of mesoporous carbon nanotubes. With this technique we put an experimental method beside the theoretical treatments, ruling the literature to get the direct kinetic knowledge about the real materials.
3. The adsorption of gas molecules on the inner and the outer surface of the nanotubes, and the intra and intertubular mass transport processes could be distinguished with the frequency response technique.
4. We demonstrated that – irrespectively of the length of carbon nanotube and the catalyst content of the carbon nanotube sample – the adsorption-desorption step on the inner and the outer surface of the nanotubes is the rate-controlling step of the total mass transport process. This observation is valid between wide ranges of applied conditions, such as 77-373 K temperature range and various adsorptive gas molecules.
5. The shape of the frequency-response spectra demonstrated that the presence of oxygen-containing functional groups, generated by an oxidative treatment, resulted in the changing the mechanism of the rate-controlling step of the mass transport process. The examination of thermal combustion of these functional groups proved that the increased amount of these new sorption sites was responsible for the appearance of the intratubular diffusion as rate-controlling process step.
6. The dynamics of the mass transport process was found to be affected significantly by the size of carbon nanotube agglomerates. The self-assembly of

carbon nanotube fragments generated by the physical and chemical treatments resulted in the increase of the apparent density of the samples. The frequency response measurements showed that aggregation of carbon nanotubes resulted in the appearance of mesopores between the nanotubes, and the diffusion between the nanotubes could become the rate-controlling step of the transport process.

7. The examination of propane, isobutane and neopentane adsorption over carbon nanotubes showed that the dynamics of the mass transport process is hardly affected by the size and the structure of the adsorptive gas molecules, which could be explained with the one magnitude difference between the size of gas molecules and the inner diameter of the carbon nanotubes.
8. The examination of propane, propylene, propyne, allene and cyclopropane adsorption over carbon nanotubes showed that the dynamics of the mass transport process is hardly affected by the chemical properties of these gas molecules. On the other hand the correspondence between the chemical properties of the adsorptive and the coverage of the outer surface of the carbon nanotubes could be concluded.

Papers related to the thesis

1. Zs. Ötvös, Gy. Onyestyák, J. Valyon, I. Kiricsi
   Dynamics of nitrogen sorption on carbon nanotubes
   9^{TH} International Conference of Chemistry, Cluj,
   Proceedings of 9^{TH} International Conference of Chemistry, Cluj,
   Hungarian Technical Scientific Society of Transylvania, *150-153*
   IF: 0,

2. Zs. Ötvös, Gy. Onyestyák, J. Valyon, I. Kiricsi, L.V.C. Rees
   The Dynamics of H_2 and N_2 Sorption in Carbon Nanotubes
   Applied Surface Science *Vol*. 238, *Issues*: 1-4, (2004), *73-76*
   IF: 1,284

3. Gy. Onyestyák, Zs. Ötvös, J. Valyon, I. Kiricsi, L.V.C. Rees
   Acetylene sorption dynamics in carbon nanotubes
   Helvetica Chimica Acta *Vol*. 87, *Issues:* 6, (2004), *1508-1514*
   IF: 1,861

4. Zs Ötvös, Gy Onyestyák, J Valyon, I Kiricsi, LVC Rees
   The sorption of butanes over carbon nanotubes
   Studies in Surface Science and Catalysis *Vol.* 156, (2005), *617-624*
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5. Gy. Onyestyák, Zs. Ötvös, I. Kiricsi, L.V.C. Rees
   The sorption dynamics of C_3 hydrocarbons over carbon nanotubes
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   IF:

6. Zs. Ötvös, Gy. Onyestyák, A. Hancz, I. Kiricsi, L.V.C. Rees
   Surface oxygen complexes as governors of neopentane sorption in multiwalled carbon nanotubes
   Carbon *Vol.* 44 (2006) 1665-1672
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7. J. Valyon, Zs. Ötvös, Gy. Onyestyák, L.V.C. Rees
The sorption dynamics of propane, i-butane and neopentane in carbon nanotubes
Studies in Surface Science and Catalysis *Vol.* 160, (2006), *439-446*
IF: 0,489 (2004)

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Conference lectures and posters related to the thesis

1. Zsolt Ötvös:
   „Szénnanocsövek gáz-adszorpciós tulajdonságainak vizsgálata"
   „V. Doktori Kémiai Iskola" May 21-22 th., 2003., Tahi, (oral presentation)

2. Zs. Ötvös, Gy. Onyestyák, J. Valyon, I. Kiricsi, Z. Kónya, L. V. C. Rees:
   „The Dynamics of H_2 and N_2 Sorption in Carbon Nanotubes"
   "First International Meeting on Applied Physics", October 13-18th., 2003., Badajoz, Spain, (poster)

3. Zs. Ötvös, Gy. Onyestyák, J. Valyon, I. Kiricsi, Z. Kónya, L. V. C. Rees:
   „The Dynamics of H_2 and N_2 Sorption in Carbon Nanotubes"
   "1st Szeged International Workshop on Advances in Nanoscience", October 27-28 th., 2003., Szeged, (poster)

4. Zs. Ötvös, Gy. Onyestyák, J. Valyon, I. Kiricsi:
   „The Dynamics of Nitrogen Adsorption in Carbon Nanotubes"
   „9th International Conference on Chemistry", November 14-16 th., 2003., Cluj, Roumania, (oral presentation)

5. Ötvös Zsolt:
   „Szénnanocsövek adszorpciós tulajdonságai"
   "Kutatóközponti Tudományos Napok", June 2-3 rd., 2004., Budapest (oral presentation)

6. Zs. Ötvös:
   „Adsorption properties of carbon nanotubes"
   "MTA Kémiai Kutatóközpont Nemzetközi Tudományos Tanácsadó Testületének tudományos ülése", September 1-3 rd., 2004., Budapest, (oral presentation)

7, Zs. Ötvös, Gy. Onyestyák, J. Valyon, I. Kiricsi:
   „Adsorption Properties of Carbon Nanotubes"
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8. J. Valyon, Zs. Ötvös, Gy. Onyestyák, I. Kiricsi:
„Adsorption Properties of Carbon Nanotubes”
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9. J. Valyon, Zs. Ötvös, Gy. Onyestyák, L.V.C. Rees:
„The sorption dynamics of propane, i-butane and neopentane in carbon nanotubes”
“COPS-VII, 7th International Symposium on the Characterisation of Porous Solids”, May 25-28 th., 2005., Aix-en-Provence, France, (poster)

10. Zs. Ötvös, Gy. Onyestyák, J. Valyon, I. Kiricsi, L.V.C. Rees:
„The Sorption of Butanes over Carbon Nanotubes”
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11. Gy. Onyestyák, Zs. Ötvös, J. Valyon, I. Kiricsi, L.V.C. Rees,
“The Sorption Dynamics of C_3 Hydrocarbons over Carbon Nanotubes”
“Diffusion Fundamentals I., Basic Principles of Theory, Experiment and Application”, September 21-24 th., 2005., Leipzig, Germany, (poster)