Available online at www.sciencedirect.com
SCIENCE DIRECT
Chemical Physics Letters 421 (2006) 409–414
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Thermodynamic properties of benzene adsorbed in activated carbons and multi-walled carbon nanotubes

Piotr A. Gauden [a], Artur P. Terzyk [a,*], Gerhard Rychlicki [a], Piotr Kowalczyk [b], Katarzyna Lota [c], Encarnacion Raymundo-Pinero [d], Elzbieta Frackowiak [c], François Béguin [d]

[a] N. Copernicus University, Department of Chemistry, Physicochemistry of Carbon Materials Research Group, Gagarin St. 7, 87–100 Toruń, Poland
[b] Department III, Institute of Physical Chemistry, Polish Academy of Science, Kasprzaka Street 44/52, 01-224 Warsaw, Poland
[c] Institute of Chemistry and Technical Electrochemistry, Poznań University of Technology, Piotrowo 3, 60-965 Poznań, Poland
[d] CRMD, CNRS-University, 1b rue de la Férollerie, 45071 Orléans, Cedex 02, France

Received 21 December 2005; in final form 1 February 2006
Available online 24 February 2006

Abstract

The efficiency of multi-walled carbon nanotubes (MWNTs) and traditional activated carbons for benzene adsorption is studied. Benzene adsorption isotherms and the related values of the calorimetric adsorption enthalpy at 298 K are used to calculate the entropy and the state of the adsorbed molecules. The analysis of the experimental data leads to the conclusion that both thermodynamic functions are related to the kind of porosity present in the studied materials. Our results also show that in the case of MWNTs the adsorption between the tubes is a very important effect which determines the mechanism of this process.

1. Introduction

Lately, a great attention has been devoted to carbon nanotubes (CNTs) as potential adsorbents for various molecules. They can be applied in the separation of organic molecules with different sizes and shapes [1]. These properties depend not only on the canal diameter but also on the dispersion of diameters and on the functional groups at the edges. In order to understand the molecular sieving effects, the state of the adsorbate confined in the nanopores of various kinds of carbonaceous materials should be known.

Benzene adsorption measurements have been recommended by Dubinin et al. many years ago [2] as the standard test for determining the porosity parameters of activated carbons (ACs). Moreover, since the benzene ring is the major component of aromatic molecules, the latter are known to interact with graphite and with the graphitic walls of CNTs [1,3–12]. The weak intermolecular forces in a system composed of a closed-shell organic molecule immobilized on a CNT surface are π-stacking interactions. This kind of physisorption and non-covalent functionalization does not significantly perturb the atomic structure of CNTs, their electronic and transport properties, by contrast to their covalent counterpart [3]. The results presented by Tournus et al. [3] imply that the most favorable adsorption geometry must result from bridge to stack when increasing the nanotube diameter, with a cross-over at a given size which is found to depend on the CNTs chirality. Moreover, DFT calculations indicate that changing the substituents on benzene rings has a negligible effect on their interaction with a graphitic slit shape pore or a CNT, unless the group is bulky and can interact with a larger fraction of the interior of the nanopore [6]. Although the latter results show that there is a measurable adhesion between benzene-like molecules and graphite slit shape pores or CNTs, there is very little evidence of selectivity between different types of aromatic molecules.

* Corresponding author. Fax: +48 056 654 371.
E-mail address: aterzyk@chem.uni.torun.pl (A.P. Terzyk).

0009-2614/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2006.02.003

The problem of adsorption of organic compounds inside CNT type materials has been also discussed on the basis of theoretical [1,9] and experimental studies [6,10,13–19]. Bhide and Yashonath [9] investigated the structure and dynamic of C_6H_6 in the one-dimensional channels of narrow carbon nanotubes. They observed that the motion in this material occurs predominantly with the benzene plane perpendicular to the motion direction, and that the benzene plane orientation is strongly influenced by the channel diameter and the diameter modulation along the channel. In the case of single-wall carbon nanohorns (SWNHs), the adsorbed benzene molecules are stabilized mainly by weak self-interactions at the central regions of SWNHs, and they are quickly desorbed [5,18]. The tube tips, the walls, and the central regions of the hollow space were found to be the adsorption sites.

It is well-known that enthalpy measurements can provide valuable information on the adsorption mechanism, together with the energetic and structural heterogeneity of adsorbents, the adsorbate–adsorbent interactions, as well as the structure of the adsorbate confined in pores [20–22]. However, because of the time consuming experiments, the importance of this research is underestimated. Moreover, significant differences have been found between the isosteric (the bunches of isotherms are taken into account) and the differential (i.e., directly measured experimentally) enthalpy of adsorption [20,22]. We have widely discussed the necessity of using the data from calorimetric measurements (in comparison with those calculated from the Clausius–Clapeyron equation) for the description of adsorption processes [20,22].

In this Letter, we study the efficiency of multi-walled carbon nanotubes and traditional activated carbons for the removal of benzene. To our knowledge, it is the first time that the enthalpy of benzene adsorption is studied in CNTs.

2. Experimental

The porous carbon samples used in this work were a strictly microporous activated carbon film (Cox [23,24]),

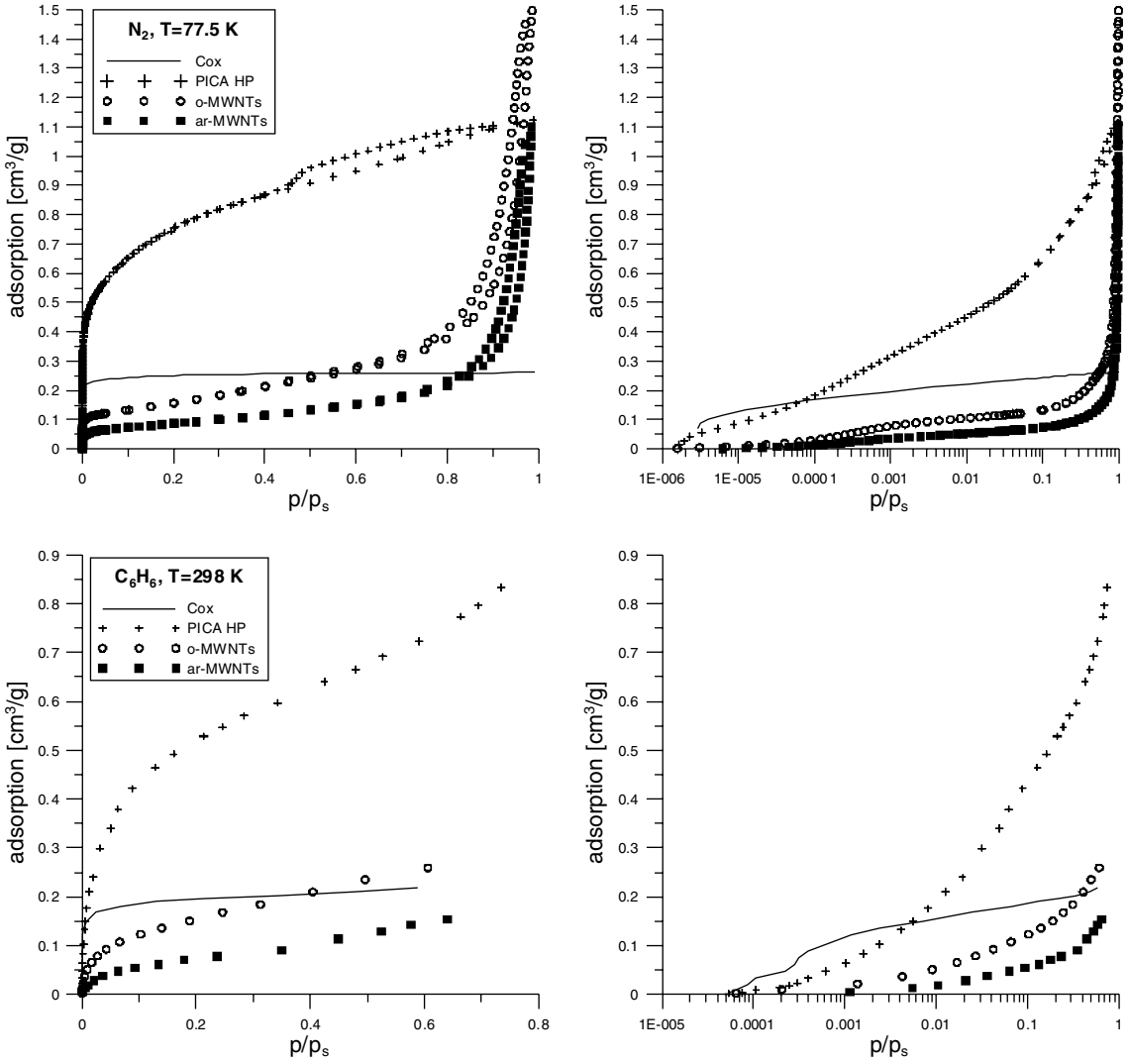

Fig. 1. Nitrogen and benzene adsorption isotherms for the studied carbonaceous adsorbents.