CARBON 88 (2015) 133–138

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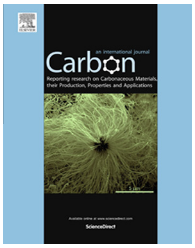

Evaluation of carbon nanopores using large molecular probes in grand canonical Monte Carlo simulations and experiments

Tomonori Ohba [a,*], *Shotaro Yamamoto* [a], *Atsushi Takase* [a], *Masako Yudasaka* [b], *Sumio Iijima* [b]

[a] *Graduate School of Science, Chiba University, 1-33 Yayoi, Inage, Chiba 263-8522, Japan*
[b] *Nanotube Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

ARTICLE INFO

Article history:
Received 15 January 2015
Accepted 27 February 2015
Available online 5 March 2015

ABSTRACT

Nanopores (pores between 1 and 5 nm) have been the object of a great deal of attention because they can selectively adsorb relatively large molecules such as macromolecules and polymer molecules. Conventional methods for analyzing porous structures—such as N_2 adsorption measurements at 77 K—can be used to investigate microporous and mesoporous structures, but there is a lack of investigation of nanopores or the boundary between micropores (<2 nm) and mesopores (2–50 nm). Here, we propose the evaluation method of nanopores using a large probe molecule, SF_6. Grand canonical Monte Carlo simulations for N_2 and SF_6 suggested that SF_6 was adsorbed in 1.5–5 nm nanopores, while there was N_2 adsorption for the wide range of pore sizes. The SF_6 adsorption could therefore be used to confirm existence of the nanopores. To test this, we used single-walled carbon nanohorns as porous carbons with widely distributed pore size. SF_6 was well adsorbed only in the nanopores at 195 K, whereas N_2 adsorption was observed in all micropores and mesopores. This structural analysis of nanopores using a large-molecule probing method complements structural analyses using N_2 adsorption, as well as other techniques.

1. Introduction

Adsorption techniques are widely used for the evaluation of solid surfaces and porous structures [1–5], and have become standard methods for the characterization of porous media with open pores. The characteristics of such structures are also evaluated using X-ray scattering, light scattering, and microscopic analyses [6–10]. Small angle X-ray scattering and transmission electron microscopy, which are techniques that have only relatively been used to evaluate porous structures, can be used to assess both open and closed pores [11–15]. Open pores are especially important, because molecules adsorbed in open pores show unique physical and chemical properties, and closed pores are not available for molecular adsorption. Typically, an N_2 adsorption isotherm measured at 77 K is used to assess the pore volume, pore size, and specific surface area in micropores and mesopores, which have pore diameters smaller than 2 nm, and from 2 to 50 nm, respectively [16–19]. Ar adsorption can be measured to evaluate porous structures [20,21]; this could also be true

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* *Corresponding author.*
E-mail address: ohba@chiba-u.jp (T. Ohba).

http://dx.doi.org/10.1016/j.carbon.2015.02.077
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for certain other adsorbed molecules, including Xe, CF_4, SF_6, and benzene [22–28].

Ultramicropores, which have a pore size of less than 0.7 nm, have stronger adsorption potential, and highly restricted spaces, even for light molecules. Such pores are therefore important for storage, separation, and catalytic reactions [29–31]. The evaluation of ultramicropores using the above-mentioned probe molecules is often unsuccessful. The adsorption of CO_2 and water under ambient conditions can be measured to evaluate ultramicropores, because the effective sizes of CO_2 and water at ambient temperatures are smaller than that of N_2 [32–37]. The measurement of He adsorption at extremely low temperatures has also been proposed as a method for the assessment of ultramicropores [38,39].

Mays proposed a new classification of pore sizes; nanopores, micropores, and millipores are 0.1–100 nm, 0.1–100 μm, and 0.1–100 mm, respectively [40]. Those definitions are suitable for the actual scales. However, pores narrower than 5 or 10 nm, have significantly attracted attention for their strong adsorption potential, and their practical utility for the adsorption of macromolecules and polymer molecules for drug delivery, and other applications [41–47]. Thus, pores between 1 and 5 nm were focused as nanopores in this article. The conventional methods used for the analysis of porous structures are less applicable for the evaluation of such nanopores, because of the boundary between micropores and mesopores. There is therefore a need for a new method for the evaluation of nanopores. In this article, we propose a novel method for the evaluation of nanopores using a large molecular probe (LMP). The efficiency of the LMP method was assessed using grand canonical Monte Carlo (GCMC) simulations of Ar, N_2, Kr, CH_4, Xe, SF_6, and CCl_4 adsorbed in carbon nanotubes (CNTs), and N_2 and SF_6 adsorption isotherms measured experimentally for single-walled carbon nanohorns (CNHs).

2. GCMC simulations and experiments

2.1. Simulation procedure

GCMC simulations were performed for molecules adsorbed in the internal nanopores of CNTs, where each simulation was performed at the boiling temperature of the adsorbed molecule. The boiling temperatures of Ar, N_2, Kr, CH_4, Xe, SF_6, and CCl_4 were set at 87, 77, 120, 111, 165, 209, and 350 K, respectively. The intermolecular interaction potential was calculated for both molecules, using one-centered Lennard-Jones potential models with the following potential parameters: $\sigma_{Ar} = 0.3405$ nm, $\varepsilon_{Ar}/k_B = 119.8$ K, $\sigma_{N_2} = 0.3632$ nm, $\varepsilon_{N_2}/k_B = 104.2$ K, $\sigma_{Kr} = 0.4047$ nm, $\varepsilon_{Kr}/k_B = 231.0$ K, $\sigma_{CH_4} = 0.3758$ nm, $\varepsilon_{CH_4}/k_B = 148.6$ K, $\sigma_{Xe} = 0.4047$ nm, $\varepsilon_{Xe}/k_B = 231.0$ K, $\sigma_{SF_6} = 0.5128$ nm, $\varepsilon_{SF_6}/k_B = 222.1$ K, $\sigma_{CCl_4} = 0.5947$ nm, and $\varepsilon_{CCl_4}/k_B = 322.7$ K [48–50]. The structure-less function proposed by Steele and Bojan [51] was used for the CNTs with diameters from 1.0 to 10.0 nm. The Lennard-Jones parameters of a C atom are $\sigma_C = 0.34$ nm and $\varepsilon_C/k_B = 28$ K. Here, the Lorentz–Berthelot mixing rules were simply adapted to the intermolecular interaction between a molecule and a C atom in a CNT. The unit cell size was 100.0 × 100.0 × 4.0 nm, and a three-dimensional periodic boundary condition was applied. The cutoff length was 2.0 nm. The calculation cycle comprised a number of steps equal to or more than 1×10^7 at each equilibrium point in the adsorption isotherm. The CNT pore volume V_{CNT} used for the calculation of the simulated filling factors was obtained from its relationship with the CNT diameter D, using the following equation:

$$V_{CNT} = \pi\left(\frac{D - \sigma_C}{2}\right)^2 \times 4 \tag{1}$$

here, the effective diameter of the adsorbed molecules was defined as $D - \sigma_C$. A filling factor was defined as adsorption density/liquid density. Here, the adsorption densities were obtained by dividing the number of adsorbed molecules by the pore volume.

2.2. Experimental procedure

Only the interstitial pores of CNHs are accessed by adsorbed molecules, whereas the internal pores are closed, as reported elsewhere [52,53]. The internal pores are accessible to molecules via partial oxidation, through nanosized gates known as nanogates or nanowindows; in other words, those pores can be changed into open pores [54–56]. Thus, molecules can be adsorbed in both the internal and interstitial pores. In this study, CNHs were oxidized at 673 K for 1 h in an O_2 atmosphere; these CNHs were named as open-CNHs. In a previous study, the oxidation conditions resulted in the formation of open gates that were large enough for both N_2 and SF_6 molecules and no blocking effect by N_2 and SF_6 molecules was seen for penetration through those gates and the corn parts of CNHs [55,56]. Adsorption isotherms were measured for N_2 at 77 K and SF_6 at 195 K, using a volumetric apparatus (Autosorb-1, Quantachrome Co.), after heating at 423 K at pressures of less than 10 mPa, for more than 2 h. Dubinin–Radushkevich (DR) analyses were conducted for the above adsorption isotherms to evaluate the pore volumes [16]. The total pore volumes were evaluated from the sum of the micropore and mesopore volumes, that is, the last point of the adsorption isotherm. The pore size distribution was evaluated using the Barrett–Joyner–Halenda (BJH) theory [17].

3. Results and discussion

The filling factors for various molecules in the cylindrical internal pores of CNTs were calculated using simulated adsorption isotherms, to ensure the validity of the nanopore evaluation performed using the LMP method (see Supplementary data). The pore condensation values for the small molecules Ar, N_2, Kr, CH_4 and Xe (molecular size = 0.35–0.40 nm) in the whole pores near $P/P_0 = 1.0$ were proof of the validity of the present pore structure analysis for both micropores and mesopores. The large molecules SF_6 and CCl_4 (molecular size = 0.51 and 0.59 nm, respectively) were relatively well-filled in the 1.5–5-nm CNTs and the 2–3.5-nm CNTs, respectively. The LMP method is therefore valid for the assessment of nanopores, especially using SF_6.

The CNH nanopores were evaluated using SF_6 adsorption at 195 K to assess the validity of the LMP method and to compare the LMP method with the conventional method using N_2