

Preferential π interaction of Cyclic Organic Molecules with Graphitic Nanoporous Carbon

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Introduction

There has been an increase in the use of activated carbons in the construction of environmentally friendly technologies with sufficient safety. Activated carbon has basically slit-shaped micropores, which provide much better accessibility for most molecules than the cylindrical pores of zeolites [1,2]. With the exception of the surface functional groups involved in the adsorption of polar molecules, the specific interaction involved in the gas adsorbability of activated carbons has not been studied sufficiently.

Smith et al. [3] conducted the first study on the comparison between benzene and cyclohexane adsorptions on graphite; in this study, stronger cyclohexane adsorption was observed than benzene adsorption. On the other hand, the strong π -electron interaction of benzene with nanopore surfaces was observed by Dosseh et al. [4]. Moreover, comparison studies on adsorbed molecules of sp^2 and sp^3 carbons have been conducted for benzene and cyclohexane and for ethane and ethylene [5-7]. Radovic et al. used molecular orbital calculations to emphasise the essential importance of the conjugated π -electron nature of the basal plane of the graphite in the adsorption of organic molecules [8]. The characteristic interaction, the π - π interaction of the sp^2 carbons in an adsorbed molecule with graphite, is caused by the electron cloud delocalization between the sp^2 carbons in the molecule and graphite. We still need to understand the difference between the adsorbed structures of the sp^2 and sp^3 carbon atoms of the adsorbate molecules upon adsorption on graphitic pores.

The cyclohexene molecule has two sp^2 carbon atoms in addition to four sp^3 carbon atoms, making it an appropriate probe molecule for research on the comparison of the adsorptions of sp^2 and sp^3 carbon atoms. To understand the difference between the adsorbed structures of the sp^2 and sp^3 carbon atoms, we adopted grand canonical Monte Carlo (GCMC) simulation for studying cyclohexene adsorption on activated carbon. In addition, this study could serve as a guide in the development of better adsorption media for separating cyclohexene from commercial natural gas.

Simulation Procedure

The cyclohexene molecule has a distorted plane structure that consists of five single bonds (C-C) and one double bond (C=C). The sp^3 and sp^2 carbon atoms must be distinguished using interaction potential calculation and GCMC simulation. A 16-centre model for the rigid cyclohexene structure in this study was adopted for the calculation ($\epsilon / k_B = 31.9$ K for H,

35.6 K for sp^3 -carbon and 35.6 K for sp^2 -carbon; $\sigma = 0.252$ nm for H, 0.311 nm for sp^3 -carbon and 0.321 nm for sp^2 -carbon) [9,10]. The Lennard-Jones potential $\phi_{AB}(r_{ij})$ is given by eq.1.

$$\phi_{AB} = 4 \sum_i \sum_j \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

Here r_{ij} is the distance between the i -th atom in molecule A and a j -th atom in molecule B . The Lorentz-Berthelot rules were applied to obtain the interaction energy and size parameters for the hetero-atomic interaction. Here each component atom in the molecule was assumed to be electrically neutral; the equilibrium molecular geometry was used for calculation. The slit-shaped pore was modeled using the interface between two semi-infinite graphite slabs; the molecule-carbon wall interaction was approximated by the 10-4-3 Steele potential model.

The electrically neutral cyclohexene atoms assumed here nominally give no electrostatic contribution to the interaction between the cyclohexene and the pore wall. However, the electrostatic interaction is roughly included in the Lennard-Jones parameters obtained from the ab initio calculation by Faller et al. [11]. Grand canonical Monte Carlo simulations of the cyclohexene were performed using 3×10^6 steps at 298 K, with three equivalent trials for the creation, deletion, and movement of the molecules. The pressure was calculated from the bulk molecular density in the unit cell of $6 \times 6 \times 6$ nm³ by using the van der Waals equation after more than 1×10^8 calculation steps and the accumulation of 9×10^7 steps. A unit cell size of $6 \times 6 \times w$ nm³ and a periodic boundary condition were used in this calculation.

Results and Discussion

Fig. 1 shows the adsorption isotherms of cyclohexene in

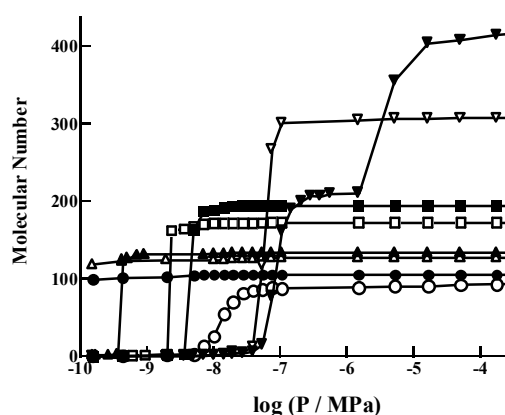


Fig. 1 – Adsorption isotherms of cyclohexene at 298 K. \circ : $w = 0.5$ nm, \bullet : $w = 0.6$ nm, \triangle : $w = 0.7$ nm, \blacktriangle : $w = 0.8$ nm, \square : $w = 0.9$ nm, \blacksquare : $w = 1.0$ nm, ∇ : $w = 1.5$ nm, and \blacktriangledown : $w = 2.0$ nm.

pores with $w = 0.5\text{--}2.0$ nm at 298 K. The ordinate represents the number of cyclohexene molecules adsorbed in the pore, with wider pores resulting in larger numbers of molecules above 10^{-5} MPa. As the pore with $w = 0.5$ nm is too narrow to accommodate cyclohexene molecules easily, adsorption begins above 10^{-8} MPa. On the other hand, the pore with $w = 0.6$ nm, which has the deepest potential minimum (-8000 K) for the in-plane arrangement, exhibits a quite intensive adsorption for cyclohexene; this adsorption begins even below 10^{-10} MPa. As the pore with $w = 1.0$ nm has double minima, which are in the range from -4000 to -4500 K, adsorption begins at 5×10^{-9} MPa. The adsorption for $w > 1.0$ nm begins above 5×10^{-9} MPa. The cyclohexene molecule has a distorted ring structure, making dense packing in a smaller slit pore space very difficult. The adsorbed density markedly varied with the pore width, being much smaller than the bulk liquid density in a smaller pore. This can be understood from the following snapshot analysis.

Fig. 2 shows the snapshots at 10^{-3} MPa for $w = 0.6, 0.7, 0.8,$ and 1.0 nm. Cyclohexene molecules form a single adsorbed layer that is inherent to the pore width for $w = 0.6\text{--}0.8$ nm, as shown in Fig. 4. In the pore with $w = 0.6$ nm, the cyclohexene molecules basically exhibit the in-plane arrangement. Strictly speaking, the cyclohexene molecules are tilted against the pore wall due to the stronger sp^2 carbon-pore wall interaction. The tilt angle will be shown later. Single adsorbed layers having the side-on and head-on arrangements are observed in the pores with $w = 0.7$ and 0.8 nm, respectively, which is expected from the results shown in Fig. 4. Two adsorbed layers of cyclohexene molecules are formed in the pore with $w = 1.0$ nm. In the case of the pores with $w = 1.5$ and 2.0 nm, molecules at the monolayer position orientate along the pore walls; molecules in the central space of the pore have almost a perpendicular configuration against the pore wall with less molecular orientation.

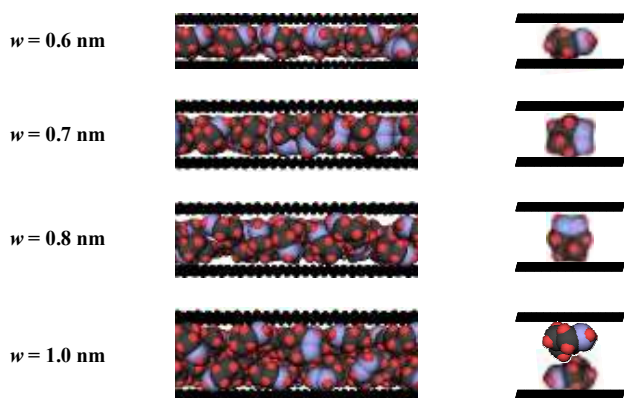


Fig. 2 – Snapshots of adsorbed cyclohexene in the nanopores with $w = 0.6, 0.7, 0.8,$ and 1.0 nm at $P = 10^{-3}$ MPa. Right side: Schematic model of typical structure of adsorbed cyclohexene. Blue, grey, and red spheres depict sp^2 -carbon, sp^3 -carbon, and hydrogen, respectively. Graphitic carbon walls are represented by the loose lines composed of black spheres.

Conclusions

The sp^2 carbon atoms can interact preferentially with the graphite walls in comparison with the interaction of the sp^3 carbon atoms for the specific pore widths. The hydrogen atoms bound to the sp^2 carbons are also distributed on the pore walls, whereas those bound to the sp^3 carbons are orderly distributed in the pores. In comparison to the carbon atoms, there exist nearer hydrogen atoms to the pore walls. The preferential conformations of the sp^2 carbon and hydrogen atoms interacted with sp^2 carbon on the pore walls induces a slight tilting of the cyclohexene against the graphite walls.

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