COMPUTER SIMULATION APPROACH TO ADSORPTION OF CCl_4 ON ACTIVATED CARBONS

T.Suzuki, T.Iiyama, and K.Kaneko
Department of Chemistry, Faculty of Science, Chiba University,
1-33 Yayoi, Inage, Chiba 263 Japan

Introduction

There has been considerable interest in the assembly structure of molecules confined in a micropore. Recently we applied the in situ X-ray diffraction (XRD) technique to elucidate the structure of H_2O confined in carbon micropores [1]. Although in situ XRD experiments provide an indispensable information to study the molecular assembly in the micropore, it is not easy to understand the intermolecular interraction in the micropore. Grand Canonical Monte Carlo (GCMC) simulation provides a significant information on the fundamental mechanism of physical adsorption, especially micropore filling. We have studied the assembly structure of CCl_4 molecules confined in graphitic micropore and predicted the pore width-sensitive molecular packing structure using GCMC simulation [2] and obtained the experimental evidence by in situ X-ray diffraction [3]. In this work, we study the detailed assembly structure of CCl_4 confined in graphitic micropore with GCMC simulation.

Simulation

The micropore model of the space between two graphitic slabs was adopted and the CCl_4-graphite potential was calculated by use of Steele's 10-4-3 potential. The intermolecular potential was approximated by the Lennard-Jones interaction,

$$\phi_{ff} = 4\varepsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r}\right)^{12} - \left(\frac{\sigma_{ff}}{r}\right)^{6}\right]. \qquad (1)$$

Here $\varepsilon_{ff}/k = 325K$ and $\sigma_{ff} = 0.588nm$ for CCl_4 were used. We used an established technique of repetition of unit cell with size of $l \times l \times w$, where l is length, w is the width of unit cell. The rectangular box is replicated 2-dimensionally to form an infinite slit shaped micropore. The mean radial distribution function of the CCl_4 molecule was obtained by averaging whole molecules. The GCMC calculation was carried out for the graphite-slit model having the slit-width of 0.8, 1.0, 1.1, and 1.3nm. The average radial distribution of CCl_4 molecules adsorbed in the micropore at P/P_0=1.0 was calculated.

Results and Discussion

The simulated radial distributions (RDs) at P/P_0=1.0 for different pore widths are shown in figure 1. Almost all RDs other than the RD for 1.0nm are very close to each other and they are close to the RD of liquid phase CCl_4 [4]. These RDs have explicit peaks corresponding to the first-, second-, third-, and fourth-nearest neighbor molecules.

It is noteworthy that only the RD for the 1.0nm-width system is completely different from others. The characteristic RD for the 1.0nm pore is similar to that of the plastic crystal of CCl_4 observed at 253K in the bulk phase [4]. The results suggest that the plastic crystal structure is formed in the micropore of 1.0 nm in width even at 303K. Also the in situ X-ray diffraction experiments showed the presence of the plastic crystal-like structure of CCl_4 confined in micropores of

activated carbon fiber at 303K [3] as shown in figure 2.

The molecules confined in the micropore of w = 0.8nm form single layered structure with disordered hexagonal packing of CCl_4 molecules as shown in figure 3. In the wider pore width system, molecules form double layered structure as stacking of the basic plates. The two layers of hexagonal packing plate stack with parallel shift in w = 1.1nm system, as shown in figure 3 and comform the bcc structure with 101 face which is parallel to the pore wall. In the system of w = 1.3nm, the hexagonal packing plates stack in a turbostratic way. Consequently, these three systems of w = 0.8, 1.1, and 1.3nm are basically composed of hexagonal packing plates and provides similar RD. The molecules in the micropore of w = 1.0nm form the fcc structure which corresponds to the plastic crystal phase for bulk liquid of CCl_4 [4], as shown in figure 3. These structures are due to the geometrical requirement.

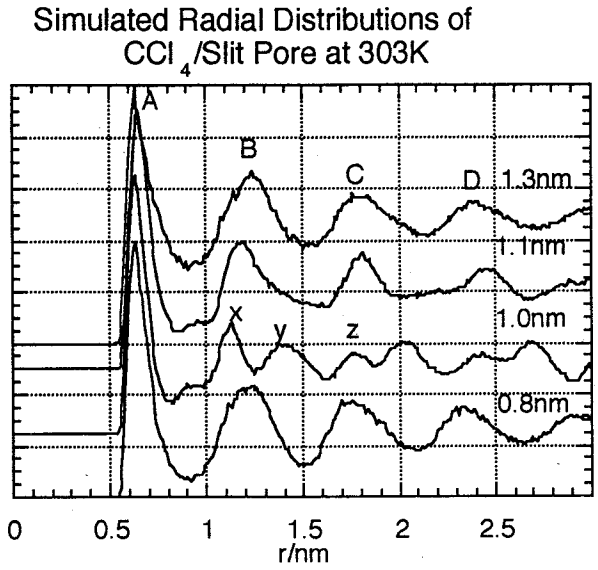

Fig.1

References

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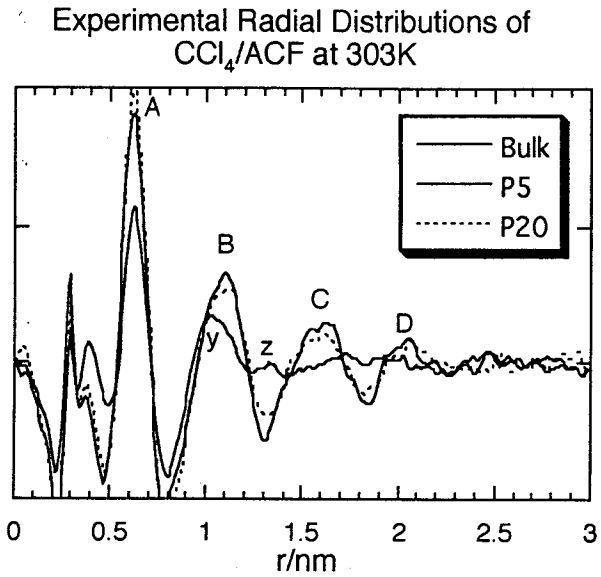

Fig.2

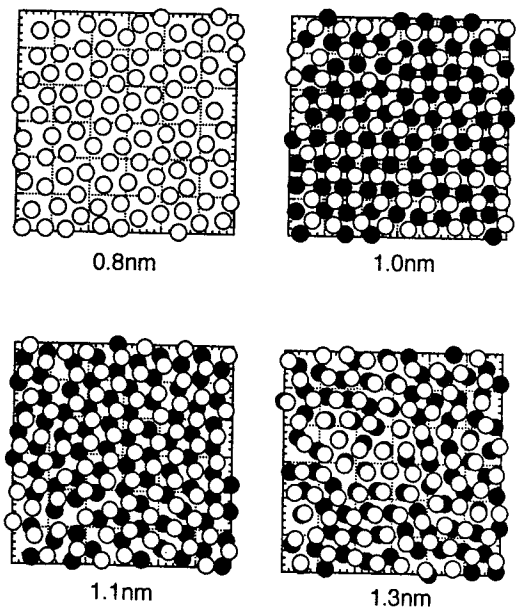

Fig. 3