

DIMER-MEDIATED MICROPORE FILLING OF Xe IN A CARBON NANOSPACE

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Introduction

Vapors are adsorbed in carbonaceous micropores by micropore filling mechanism. The molecule-surface interaction is enhanced due to overlapping of interactions from opposite pore-walls in the carbonaceous micropore. Therefore, activated carbon has an excellent adsorptivity for vapors. Even activated carbon cannot adsorb sufficiently supercritical gas. Recently authors stressed the importance of the role of the intermolecular interaction in micropore filling. Supercritical NO molecules are dimerized with the aid of a weak chemisorptive effect at the micropore entrance to be abundantly adsorbed in the carbon micropores[1]. High pressure adsorption of N₂ in activated carbon indicated highly concentrated dimer formation in the micropore[2]. Therefore, the dimer formation can assist micropore filling of supercritical gas. Hence it is important to elucidate the dimer mediated micropore filling of supercritical gas.

Molecular simulation has been helpful to understand the mechanism of micropore filling in activated carbons using a graphite slit pore model[3,4]. The authors also applied the molecular simulation to understand the intermolecular structure of molecules confined in the micropore using the radial distribution function. On the other hand, Xe is a spherical molecule and the intermolecular interaction is considerably strong. It is known that Xe molecules tend to form the dimer in the gas phase even at an ambient temperature (0.06% at 300K)[5]. Hence molecular simulation of Xe in a graphitic slit pore should give a clear insight on the dimer

mediated micropore filling mechanism.

Simulation and Experimental

We calculated the adsorption isotherm of Xe in the graphite-slit pore having different pore widths w at 196 K and 300K using GCMC method using the parameters of $\epsilon_{ff}/k_B = 273$ K and $\sigma_{ff} = 0.396$ nm[6]. The average radial distribution function of a Xe molecule was calculated as an average intermolecular distance from the snapshot at an equilibrium state.

The adsorption isotherm of Xe on activated carbon fiber (ACF) having an average pore width = 1.2 nm, which was evaluated by N₂ adsorption at 77 K, was measured gravimetrically at 196 K.

Results and Discussion

Figure 1 shows the simulated and observed adsorption isotherms of Xe at 196 K. The observed adsorption isotherm on ACF has no steep jump, while simulated isotherms of $w = 1.1, 1.2,$ and 1.3 nm have a steep adsorption jump at the low pressure region. The jumping pressure increases with the increase of w . Although the average pore width of ACF is 1.2 nm, the simulated isotherm of $w = 1.3$ nm is the closest to the observed isotherm. However, their difference can be explained by the contribution of the simulated adsorption of smaller pores. As ACF should have slight pore size distribution, this agreement is reasonable.

The radial distribution analysis was applied to adsorption process near the jump at the low pressure region. Figure 2 shows radial distribution function at 196 K as a function of the pressure. There are two distinct peaks in all radial distribution functions. The first A and the section B peaks can be associated with the contact distance of two Xe molecules and the nearest distance between Xe molecules on opposite pore-walls. Further, the radial distribution function of 7.0 Torr just before the adsorption jump has a hump C at 0.8nm which agrees with the nearest second neighbor distance of the closed packing of Xe molecules. Hence, probably Xe molecules form the dimer at 5.2 Torr and they produce the cluster just before the adsorption jump. The cluster formation should be indispensable to induce a marked adsorption. Even at 300 K the radial distribution has a similar to that at 196 K, if the pressure is raised, as shown in Figure 3.

References

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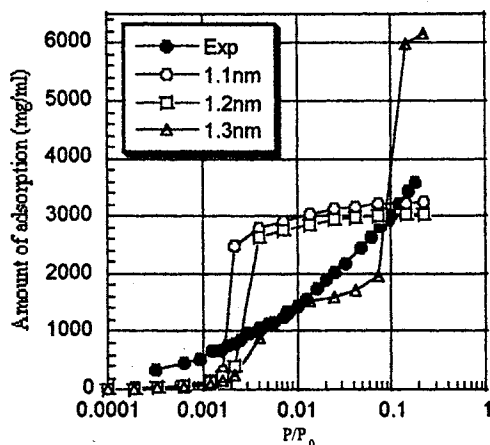


Figure 1. The observed adsorption isotherm of Xe on ACF of the average porewidth=1.2nm and simulated Xe adsorption isotherms.

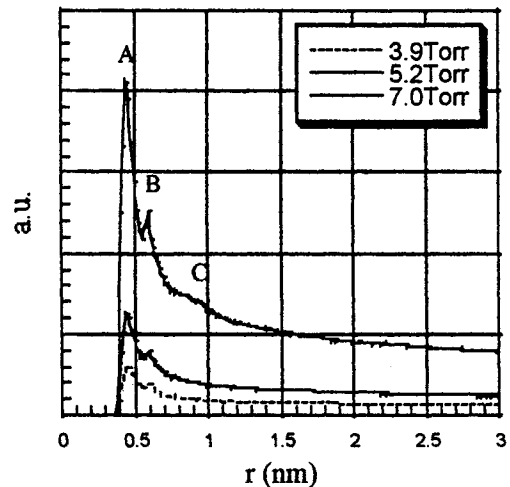


Figure 2. Radial distribution function of Xe in the micropore of $w=1.0\text{nm}$ at 196K.

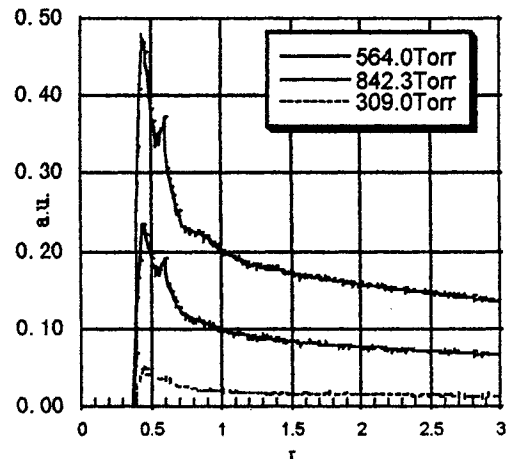


Figure 3. Radial distribution function of Xe in the micropore of $w=1.0\text{nm}$ at 300K

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