Initial Filling Mechanism of Predominant Water Adsorption on Hydrophobic Slit-Shaped Carbon Nanopores

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Abstract. Predominant water adsorption in hydrophobic slit-shaped carbon nanopores begins at a threshold pressure of water vapor. Adsorption of water vapor was faster for pores of 0.7 nm in width than for pores of 1.1 nm in width. The formation of water dimers is the rate-determining step of the water adsorption from analysis of the adsorption kinetics. The adsorption amount from grand canonical Monte Carlo simulation oscillated with the calculation cycle up to an adsorption amount of 30 mg ml$^{-1}$ and then steadily increased to an equilibrium adsorption amount. The Gibbs free energy change with the cluster size of water molecules has a barrier for the cluster growth below the critical adsorption density. The snapshot analysis of the grand canonical Monte Carlo simulation showed that formation of nanoscale clusters of water molecules begins just at the critical density of 30 mg ml$^{-1}$. Then the nanoscale cluster formation should be essential to induce the predominant adsorption at the threshold pressure corresponding to the critical adsorption density.

Introduction

Water adsorption on nanoporous carbons has been actively studied for a long time [1-5]. As the water adsorption isotherm varies sensitively with the change of surface functional groups, the relationship between the water adsorption isotherm and surface functional groups has been studied using nanoporous carbons having different surface functional groups [6-10]. Water molecules are adsorbed on the surface functional groups with hydrogen bonding even below the relative pressure (P/P$_0$) of 0.05; these nanoporous carbons having surface functional groups are essentially hydrophilic. Phenomenologically, water adsorption on the nanoporous carbons of hydrophilicity can be briefly described by so-called Dubinin-Serpinsky equation [11]. Talu and Meunier introduced a structural view to the water adsorption mechanism [12]. However, nanoporous carbons of only slight amount of surface functional groups exhibit the water adsorption isotherm completely different from that of hydrophilic carbons; the water adsorption below P/P$_0$ = 0.3 is almost negligible and predominant adsorption begins above P/P$_0$ = 0.3 [13]. Hence, these nanoporous carbons should be originally hydrophobic. Pitch-based activated carbon fiber (P-ACF) and single wall carbon nanotubilities of high purity are representatives of hydrophobic nanoporous carbons. Even these hydrophobic nanoporous carbons have slight amount of surface functional groups which can be detected by X-ray photoelectron spectroscopy, the water adsorption isotherm does not change so much by reduction treatment of
surface functional groups with Ar or H₂ at high temperature [14]. Phenomenologically a clear hydrophobicity can be confirmed by formation of a hemispherical water droplet on these carbon pellets, as shown in Fig. 1. Accordingly, we can name these nanoporous carbons hydrophobic nanoporous carbons. In particular, P-ACF is a carbon sample fit for study on water adsorption on the hydrophobic nanoporous carbon according to authors’ systematic characterization using various techniques [15-19]. P-ACFs have considerably uniform slit-shaped nanopores of which pore width ranges from 0.6 to 1.4 nm. Then, the P-ACFs have been used for fundamental researches on confinement effect for molecules and ions.

Authors have shown that the structure of water and CCl₄ adsorbed in the nanopores depends on the pore width using in situ X-ray diffraction [20-22], and unique magnetism of O₂ adsorbed varies with the pore width [23-25]. In the case of water adsorption, the electron radial distribution function (ERDF) of water-adsorbed P-ACF (pore width w = 0.7 nm) at 303 K is almost similar to that at 170 K, whereas the ERDF of water-adsorbed P-ACF (w = 1.2 nm) depends sensitively on the measuring temperature; water in the 1.2 nm-pore at 303 K is still distinctly different from that of bulk liquid water, being rather close to a solid-like structure. The fact of solid-like structure of adsorbed water in carbon nanopores was ascertained with X-ray diffraction and neutron diffraction by Bellissent-Funel et al [26]. Thus, water molecules are predominantly adsorbed in hydrophobic nanopores of carbon, forming a highly stabilized solid-like structure. Then, there are fundamental questions why and how water molecules are adsorbed in the hydrophobic nanopores. As to the stabilization of adsorbed water, these authors showed that cluster formation of water molecules gave sufficient stabilization energy mainly stemming from hydrogen bonding among water molecules in the cluster [5]. Then, one of the above fundamental questions is resolved. However, still we wonder how water molecules are adsorbed above P/P₀ = 0.3. This article describes the study on this question. These are another essential question on water adsorption in hydrophobic carbon nanopores. The water adsorption isotherm has an explicit adsorption hysteresis. For example, Miyawaki et al. showed that the adsorption hysteresis loop depended on the pore width in the range of 0.7 to 1.4 nm; the adsorption hysteresis almost disappeared for the 0.7 nm-pores [27]. Similar results were often reported [28-30]. Iiyama et al. introduced in situ small angle X-ray scattering (SAXS) to obtain the density fluctuation in carbon nanopores having adsorbed water, although an exact correction of the water molecule-carbon wall scattering was difficult; they showed a clear difference of the density fluctuation for adsorption and desorption branches [31]. Ohba and Kaneko improved the in situ SAXS method to add the GCMC simulation; the GCMC-aided in situ SAXS suggested plausible distribution models of water molecules of water molecules and/or cluster in the carbon nanopores for adsorption and desorption branches [32,33]. Therefore, we can understand structurally both the adsorbed states of adsorption and desorption processes.

In this article, we describe the induction mechanism of the predominant water adsorption in the representative nanopores of p-ACFs at a critical pressure above P/P₀ = 0.3.

1. Simulation and Experimental Section

GCMC simulation was used to study on the water structure in the hydrophobic nanopores of w = 0.7 and 1.1 nm at 303 K, assuming a unit cell of 6x6xH nm³, which was the same method as that in our earlier publication [34]. Here H was the physical pore width defined as the distance between carbon-atomic centers across the nanopore. In each calculation cycle, random selection among three events of displacement, insertion, and removal was chosen such that there were equal probabilities of insertion and removal. The number of the calculation cycle was 10⁷ steps and the last 10⁴ steps were taken for the statistics collection in each adsorption point. The arrival at equilibrium was checked with number change of molecules within 1% for 3x10⁴ steps. The saturated vapor pressure P₀ was corrected by the pressure of bulk condensation in GCMC simulation. The calculation in canonical ensemble Monte Carlo simulation was done for 10⁷ steps to determine accurate water distribution from the water distributions after the calculation of GCMC simulation with 10⁴ steps in the calculation cycle.

The five-site transferable interaction potential (TIP5P) model of a water molecule was used for simulating water adsorption, which was combination of the Lennard-Jones interaction between oxygen
atoms and the electrostatic interaction between partial charges on the site of hydrogen atoms and lone pairs [35].

\[
\phi_{ij}(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right] + \sum_{i} \sum_{j} \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad (1)
\]

Here \(\varepsilon_{ij}\) and \(\sigma_{ij}\) are the water potential well depth (80.5 K) and the effective diameter (0.312 nm), respectively. The absolute value of the partial charge \(q_i\) is \(3.86 \times 10^{-20}\) C. The details of the model are given by Mahoney et al [31]. We assume that a carbon atom is neutral and then the interaction between water-graphitic carbon wall comes from the sum of the Lennard-Jones interaction. Thus, the interaction between a water molecule and graphitic carbon wall is represented by the potential function of the infinite carbon planes of graphite using Steele potential model [36],

\[
\phi_{sf}(z) = 2\pi\sigma_{sf}\varepsilon_{sf}\rho\Delta_c \left[ \frac{2}{5} \left( \frac{\sigma_{sf}}{z} \right)^{10} - \left( \frac{\sigma_{sf}}{z} \right)^{4} - \frac{\sigma_{sf}^4}{3\Delta_c (z + 0.61\Delta_c)^3} \right] \quad (2)
\]

where \(\sigma_{sf}\) and \(\varepsilon_{sf}\) are the water-carbon atomic distance and effective diameter, fitted by using Lorentz-Berthelot rule (\(\sigma_{sf} = 0.327\) nm and \(\varepsilon_{sf}/k_B = 49.3\) K). The symbols of \(\rho\), \(\Delta_c\), and \(z\) represent the carbon number density of graphite, the interlayer distance between graphite sheets, and the vertical distance of a water molecule from the atomic center of the carbon atom on surface, respectively. Then the water-carbon interaction in the nanopores is given by the sum of the interaction from both carbon walls [34].

\[
\phi_p = \phi_{sf}(z) + \phi_{sf}(H-z), \quad H = w_{\text{eff}} + 2z_0, \quad z_0 = 0.856\sigma_{sf} \quad (3)
\]

\(z_0\) is the contact distance between a water molecule and a graphite wall. We relate the physical pore width \(H\) to the effective pore width \(w_{\text{eff}}\), which is determined experimentally. Free energy change on cluster formation at an adsorbed amount was evaluated by the calculation of enthalpy and entropy terms using water cluster model in a unit cell. The enthalpy was determined by the adsorption energy obtained from the sum of the interaction potential. The entropy term was derived from the statistical state number calculated by simple site occupancy model for water clusters in a nanopore associated with degree of freedom in a cluster. We calculated site occupancy by associated molecules. Then the entropy was evaluated from the number of states from the site occupancy and freedom of associated molecules.

The pitch-based activated carbon fibers (P-ACFs) of average pore widths of 0.7nm (P-ACF0.7) and 1.1 nm (P-ACF1.1) were used as model slit pore systems for water adsorption at 303 K. Slight amount of surface oxygen was determined by X-ray photoelectron spectroscopy (XPS) (Mg K\(\alpha\), 10 kV, 10 mA); the surface oxygen/carbon ratio was determined from the peak intensities of O1s and C1s XPS. The adsorption isotherms of both P-ACFs were volumetrically measured at 303 K after preheating in a vacuum below 1 mPa at 383 K for 2 hours. The equilibrium adsorption amount was determined when the gas phase pressure change become less than 10 Pa for an hour. The change in the amount of water adsorbed on P-ACFs was observed every 0.1 sec for evaluation of adsorption kinetics, when the initial change in the adsorbed amounts is up to 150 mg ml\(^{-1}\), corresponding with the vapor pressure changes from vacuums to 1.9 kPa for P-ACF0.7 and 2.7 kPa for P-ACF1.1.

2. Results and Discussion
Figure 2 (a) shows the experimental water adsorption isotherms at 303 K on P-ACF0.7 and P-ACF1.1. A clear hysteresis loop is observed for P-ACF1.1, while P-ACF0.7 has almost no hysteresis loop, as previous reported [27, 37]. An adsorbed amount gradually increases with increasing pressure up to
adsorption below $P/P_0$ does not indicate the presence of highly concentrated surface oxygen groups. The predominant adsorption is also observed in simulated adsorption isotherms of both nanopores, as shown in Figure 2 (b); the abrupt increases of adsorbed amount for the 0.7 and 1.1 nm-nanopores are observed at $P/P_0 = 0.4$ and 0.6, respectively. These threshold pressures of the predominant adsorption roughly correspond to these of experimental adsorption isotherms, although the ascending pressure of the simulated adsorption isotherm for the 1.1 nm-nanopore is close to the descending pressure of the experimental desorption isotherm. Hence the adsorption branch for the 1.1 nm-nanopores should stem from a metastable adsorption process. As the kinetic data can provide information on the elementary adsorption process on both ACFs, experimental adsorption rates of water are obtained, as shown in Figure 3. Water adsorption almost reaches each equilibrium after 100 sec for P-ACF0.7 and 300 sec for P-ACF1.1. Thus, P-ACF of narrower pore width induces faster adsorption of water vapor. The chemical engineering analysis of the water adsorption process with an $n$-th order reaction model was used for determination of the elementary adsorption process. The best fitting curve for the adsorption rate is obtained, when $n$ is two. Here the second-order rate coefficients for P-ACF0.7 and P-ACF1.1 are $9.6 \times 10^{-4}$ and $3.5 \times 10^{-1}$ ml mg$^{-1}$ sec$^{-1}$, respectively. The best fitting to the second order reaction ($n=2$) indicates that the rate-determining step is water dimer formation. Then bigger water clusters should be immediately formed after the dimer formation. Thus, the dimer formation is a key for the initial cluster growth in the predominant adsorption of water in the hydrophobic nanopores. The dimers should be more stabilized in the narrower pores [5] and thereby adsorption of water starts gradually through the dimer formation even below $P/P_0 = 0.3$ only for P-ACF0.7. Still we have a question why adsorption begins just at the threshold pressure.

We simulated the adsorption amount changes as a function of a simulation step just above the threshold pressure ($P/P_0 = 0.4$ for the pore of $w = 0.7$ nm and $P/P_0 = 0.6$ for the pore of $w = 1.1$ nm), as shown in Figure 4 in order to figure out adsorption dynamics at the threshold pressures of adsorption from GCMC simulation. The simulated adsorption amount changes show the tendency similar to experimental adsorption kinetics. The increase of an adsorption amount is faster for the narrower nanopore; the beginning of the remarkable adsorption is observed around $2 \times 10^4$ simulation steps for the 0.7 nm-nanopore and $3 \times 10^5$ simulation steps for the 1.1 nm-nanopore. Then we can say that adsorption for the 0.7 nm-nanopore is faster than that for the 1.1 nm-nanopore. The simulation trend of the adsorption rate agrees with the above-mentioned experimental results. It is noteworthy that the simulated adsorption amounts with calculation cycle are scattered below 30 mg ml$^{-1}$ of the adsorption amount for both pore systems, giving a stationary increase above it. The amount of 30 mg ml$^{-1}$ should be a critical density for inducing the stationary adsorption of water in hydrophobic nanopores. We calculated the free energy change per a water molecule with the molecular association number to obtain the thermodynamic understanding, as shown in Fig. 5. The relationship between the free energy and molecular association number has a peak-top at dimer below 30 mg ml$^{-1}$ of the adsorbed density. Then, isolated water molecules have to go over an energy barrier of the peak-top at the dimer for successive cluster growth below 30 mg ml$^{-1}$ of the adsorbed density. The relationship having the peak-top transforms into the simple reduction of the free energy with the association number at 30 mg ml$^{-1}$ of the adsorbed density. This means that the cluster growth proceeds without an energy barrier above 30 mg ml$^{-1}$ of the adsorbed density. Then the water dimers spontaneously grow into nanoclusters such as pentamers and hexamers above 30 mg ml$^{-1}$ of the adsorbed density. Thus, the free energy changes provide the reason for the water dimer formation as the rate-determining step and presence of the critical density of 30 mg ml$^{-1}$.

The spontaneous growth of water clusters beyond the critical density was confirmed by GCMC simulation. Figure 6 depicts snapshots of water structure in the nanopores of the $w = 0.7$ and 1.1 nm.
The isolated water molecules appear at 15 mg ml$^{-1}$ of the adsorbed density. Small clusters such as dimers, trimers, and tetramers are formed at 30 mg ml$^{-1}$ of the adsorbed density. Water clusters gather mainly along carbon walls and merge together to form pentamers, hexamers, and larger clusters beyond 30 mg ml$^{-1}$ of the adsorbed density. Thus, water molecules form primary clusters of the necessary concentration at 30 mg ml$^{-1}$ of the critical density. The number distribution of associated molecules in a cluster is obtained from the snapshots, which explains well the above discussion, as shown in Figure 7. A maximum of the association number distribution of clusters shifts from zero to 5-7 with increasing the adsorbed density from 30 mg ml$^{-1}$ to 120 mg ml$^{-1}$. Thus, the adsorbed density of 30 mg ml$^{-1}$ is a critical factor for the successive growth of clusters. These results agree with the free energy change in Fig. 5. Then, water molecules in the nanopore remain mainly as monomers, dimers, and trimers below the critical density. The change in an averaged cluster diameter with the adsorbed density can be evaluated from the number distribution of association molecules in Figure 7 under the assumption of a spherical cluster shape, as shown in Fig. 8. For both nanopores, the mean cluster diameter steeply increases up to 0.5 nm until 60 mg ml$^{-1}$ of the adsorbed density, accompanying with an only slight increase. Thus, it is suggested the two-stage growth mechanism of clusters, that is, growth up to hexamer-order clusters below 60 mg ml$^{-1}$ of the adsorbed density and the number increase of the hexamer-order clusters. The experimentally observed size of unit clusters in the preceding SAXS experiment [32] coincides well with the above results.

The present study shows that water adsorption in hydrophobic nanopores of $w = 0.7$ and 1.1 nm suddenly start above the critical adsorbed density of 30 mg ml$^{-1}$. The critical density gives 1.0 nm of the average intermolecular distance of water, almost corresponding to tri-molecular size of the water molecule; this intermolecular distance should be associated with the percolation threshold. The primary clusters such as dimers and trimers merge each other to stable unit clusters of hexamer-order size beyond the critical adsorbed density.

Acknowledgments

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Figure 1. Image of a water droplet on a pellet of the P-ACF powder after reduction treatment in Ar atmosphere at high temperature at 0.1 seconds after contact of the water droplet with the pellet.

Figure 2. Water adsorption isotherms in experiment (a) and simulation (b). Circle: $w = 0.7$ nm and triangle: $w = 1.1$ nm. Closed symbol: Adsorption branch and opened symbol: Desorption branch.

Figure 3. Adsorption rates of water molecules on ACFs of $w=0.7$ (●) and $w=1.1$ nm (△). Inset shows the adsorption rate in the shorter time-period.
Figure 4. Simulated adsorption amount changes as function of calculation cycle for \( w = 0.7 \) (a) and 1.1 nm (b). The broken line indicates a critical adsorption amount.

Figure 5. Free energy against molecular association number in each cluster as a function of simulated adsorbed density of 5 (\( \times \)), 15 (\( * \)), 30 (\( \triangle \)), 60 (\( \square \)), and 120 mg ml\(^{-1}\) (\( ◇ \)). \( w = 0.7 \) (a) and 1.1 nm (b).
Figure 6. Snapshots of water molecules adsorbed in carbon nanopores of $w = 0.7$ (left) and 1.1 nm (right) at simulated amount of 15 (a), 30 (b), 60 (c), and 120 mg ml$^{-1}$ (d). A water molecule is expressed by a large blue sphere and two small red spheres. A carbon atom on a graphitic sheet is colored in black.

Figure 7. Association number distributions of water molecular clusters in pores of $w = 0.7$ (a) and 1.1 nm (b) at simulated amount of 30 (●), 60 (△), and 120 mg ml$^{-1}$ (□).
Figure 8. Adsorbed density dependence of mean cluster diameter.

*: $w = 0.7$ nm and $\triangle$: $w = 1.1$ nm.