

Structural Adsorption Studies on Water Molecules and Ions in Carbon Nanopores

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Abstract

Adsorption mechanism of water vapor on activated carbon fibers (ACFs) and single wall carbon nanohorns (SWCNHs) was studied with GCMC simulation and in situ small angle X-ray scattering (SAXS) in addition to water adsorption measurement. Water molecules can get a great stability in carbon nanopores through formation of hexamers and octomers even for almost surface functional group-free carbon pores with the aid of the total interaction potential calculation. The GCMC simulation showed the growth of water molecular clusters along the steep rising of the adsorption isotherm, which was evidenced by the fluctuation density profile determined by in situ SAXS. The fundamental distributions of water molecules in carbon nanopore spaces were classified into three-dimensional distribution of clusters, monolayer distribution, and uniform distribution of molecules. The adsorption hysteresis was interpreted by both of the cluster growth and change in the molecular distributions. In situ EXAFS study on aqueous “solution” of RbBr and CuCl₂ in carbon nanopores showed a remarkable dehydration around Rb⁺ and Cu²⁺ by more than 30 % compared with the bulk hydration number; the dehydrated water molecules form ordered water molecular structures in the carbon nanopore spaces.

Cluster growth mechanism of water vapor adsorption on nanoporous carbon

Water adsorption mechanism has been a great concern for carbon scientists. As water-water interaction is much more strongly attractive than water-carbon wall interaction, a general adsorption mechanism for fluid molecules cannot be applied to water. Ordinarily capillary condensation theory described by Kelvin equation or surface functional group-initiated cluster growth mechanism proposed by Dubinin et al has been used to understand the water adsorption on activated carbon (Mowla et al, 2003). However, the Kelvin equation cannot describe the rising pressure of water adsorption isotherm and even activated carbon of fewer amounts of surface functional groups can adsorb sufficiently water vapor. Consequently, we need a more experimentally evidenced mechanism. Although many mathematical expressions for description of the water adsorption isotherm on activated carbon have been proposed, these adsorption equations are not necessarily effective to get the structural understanding. Water molecules are confined in carbon nanopores and then ordinary surface analytical tools cannot be applied. However, molecular simulation should give a good insight to water structure in carbon nanopores.

Figure 1 shows representative water adsorption isotherms of pitch-based ACFs treated in Ar at 1300 K and H₂ at 1000 K. The shape of the isotherm does not depend on the surface treatment. We have tried to understand this behavior. We examined distribution of water molecules in nanopores of ACFs having average pore sizes of 0.7 and 1.1 nm by using in situ small angle X-ray scattering (SAXS) analysis, interaction potential calculation and grand canonical Monte Carlo (GCMC) simulation. Water interactions were calculated by using TIP-5P potential model for the interaction between water molecules and Steele potential for water-carbon interaction. The interaction potential calculation gave a reasonable agreement with experimental value of the heat of adsorption, showing that water molecules in the hydrophobic nanospace can get self-stabilization by cluster formation in the initial stage of adsorption.¹³ The GCMC simulated water adsorption isotherm briefly coincided with the experimental desorption branch, suggesting that adsorption is not in equilibrium, but desorption in equilibrium. We calculated the interaction potential to understand this hysteresis using the model elementary structures of the isolated clusters composed of 8 molecules, monolayers contacted with the pore walls, and uniformly dispersed molecules in the nanopore, as shown in Figure 2. Figure 2 shows the structure models of water adsorbed in carbon nanopore of 1.1 nm in width at fractional filling $\phi = 0.3$. The interaction potential change with the fractional filling for each elementary model was calculated. In the monolayer model, water molecules on a pore wall are positioned at regular intervals. We assumed that adsorbed water forms three and four-layers in the models of uniformly dispersed molecules in 0.7 and 1.1 nm pore sizes, respectively. Water molecules in a layer make square grid structure and are the middle of the grid in the neighbor layer. Water molecular orientation was arranged to form hydrogen bondings by

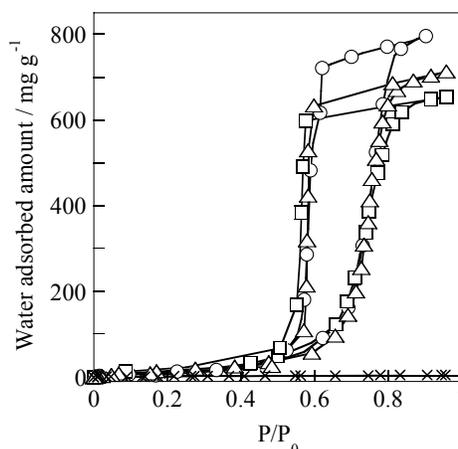


Figure 1. Water adsorption isotherms of ACFs at 303 K. ○ : ACF, △ : Treated in Ar, □ : Treated in H₂, × : Graphite

using Monte Carlo method. Canonical ensemble Monte Carlo simulation had been conducted for taking a stable structure at 303 K on a fixed molecular position before potential calculation. The water stability in the cluster model (a) of pore size = 1.1 nm was linearly increased with filling from 31 kJ mol⁻¹ at $\phi = 0$ to 37 kJ mol⁻¹ at $\phi = 0.5$. The water clusters cannot be distinguished from the uniform dispersion (c) above $\phi = 0.5$; the water clusters connect each other, giving the uniform distribution. The cluster model above $\phi = 0.6$ gives an unstable state due to the repulsion between these clusters. The water stability of the monolayer model exponentially increases below $\phi = 0.47$ and suddenly drops above $\phi = 0.6$ due to the repulsion between water molecules. In the uniform model, the water stability increases linearly from 5 to 36 kJ mol⁻¹. The above mentioned stability calculations suggest that adsorbed water molecules form clusters below $\phi = 0.4$ and uniform structure above $\phi = 0.6$.

In the ϕ range of 0.4 to 0.6, the monolayer formation gains an advantage. However, the stability difference of 2 kJ mol⁻¹ between the cluster and monolayer models cannot be the key factor, since a translational energy of a water molecule is the order of 4 kJ mol⁻¹ at 303 K. Accordingly, adsorbed water in the ϕ range of 0.4 to 0.5 should have a combination structure of the cluster and monolayer structure models (Figure 2 (c)). The present approach agreed well with the density fluctuation changes determined from in situ SAXS and gave a reasonable explanation for adsorption hysteresis (Ohba et al, 2004,2005,2007, Kimura et al, 2004. Honda et al, 2007). The similar model was applicable to water adsorption in smaller ACF nanopores of 0.7 nm in width and in nanopores of SWCNHs.

Less hydrated ions confined in carbon nanopore spaces

The chemistry of ionic solutions has contributed to a variety of fields; electrochemistry, biochemistry, catalysis, and synthetic chemistry are some examples. Ions are always hydrated in aqueous solution. Although there are many studies on adsorption of transition metal ions from solution on activated carbon, we do not understand the structure of ions in nanopores of activated carbon. The development of high performance electrical double layer capacitors requests an essential elucidation of ionic structures in nanopores of porous carbon. Then, we have determined the local structures around ions confined in carbon nanopores with the aid of the extended X-ray absorption fine structure (EXAFS). Pitch-based ACFs of 0.7 and 1.1 nm in width and SWCNHs were used as nanoporous carbons. We used RbBr and CuCl₂ as electrolytes, because the EXAFS technique is effective for determining the local structures around cation and anion of a large atomic number. The electrolyte solution of 0.1 and 1 mol dm⁻³ was introduced into the slit-nanospaces and dried by evacuation at 0.1 mPa and 383 K for 2 hour. After the deposition, water vapor was adsorbed to provide the corresponding solution only in the carbon nanopores. we denote the system of RbBr or CuCl₂ and adsorbed water in the nanospace as “nanosolution”. These ACF or SWCNH samples were installed in an EXAFS glass cell with windows of Lumirror film (350 μ m: Toray Ind. Inc.). The EXAFS measurements were performed on both Rb and Cu K-edges for the deposited and nanosolution-sealed ACF or SWCNH samples at the National Laboratory for High Energy Accelerator Research Organization (KEK) in Tsukuba. The EXAFS spectra of the corresponding solutions were measured for comparison. The radial structure functions (RSFs) for Rb and Cu were obtained from the EXAFS. In addition, the data were analyzed by an FEFF8 procedure with a Fourier-filtering method.

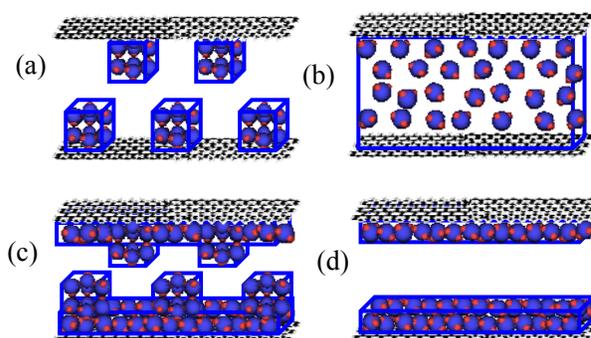


Figure 2. Structure models of adsorbed H₂O. (a) octamer cluster model, (b) uniform distribution model, (c) model of a combination of a small cluster and monolayer, (d) monolayer model.

Table 1. Local structural parameters of Rb ions confined in Nanopores of SWCNHs

Sample	Rb-O distance /nm	Hydration number	σ^2 10 ⁻⁵ nm ²
Rb-SWCNH	0.290	2.6	10.8
Rb-opSWCNH	0.293	2.6	15.3
Bulk Rb-1M	0.310	6.0	25.8

Rb-SWCNH: Rb ion solution in nanopores of SWCNH

Rb-opSWCNH: Rb ion solution in nanopores of open SWCNH

Bulk Rb-1M: Bulk Rb ion solution of 1M

The obtained RSFs were analyzed with FEFF8, providing a reliable coordination distance, coordination number, and Debye-Waller (DW) factor. The Rb-O distance of the RbBr nanosolution (0.28-0.27 nm) was smaller than that of the bulk RbBr solution (0.310 nm). The relative coordination numbers of water molecules around a Rb ion in the nanosolution were 3.8 and 5.3 for 0.1 M and 1 M nanosolutions, respectively. Here, the relative coordination number was obtained from the assumption that a Rb ion of the bulk 1 M RbBr solution is 6. Hence the hydration number around a Rb ion in the nanospace should be less than that in the bulk solution. As the DW factor is a scale of the mean-square fluctuation in the coordination distance for a Rb shell, a small DW factor (σ^2) suggests the presence of an ordered structure around the target ion. The DW factor around a Rb ion in the nanosolution is much smaller than that in the bulk solution. Therefore, there should be an ordered structure in the nanosolution compared with the bulk solution. This should stem from the highly ordered structured water confined in the nanospace observed by means of the preceding X-ray diffraction. Thus a remarkable dehydration around the Rb ion was observed (Ohkubo et al, 2002 and 2003).

The dehydration was more marked for Rb ions on SWCNH as shown in Table 1; the hydration number was only 2.6, indicating a quasi-one dimensional hydration in nanopores of SWCNH. Also the water-Rb ion distance and the DW-factor of confined Rb ion solution are smaller than those of the bulk solution. Consequently, the serious confinement of ionic solution leads to an intensive dehydration of Rb ions (Ohkubo et al, 2005). Thus, we have a possibility of realization of highly concentrated ionic solution compared with the bulk solution, which should be efficient for development of a higher capacitance in the case of the electrical double layer capacitance. Recently it was shown that SWCNH gave a considerably high capacitance (Yang et al, 2007).

Similar experiment on CuCl_2 was done for slit-shaped nanopores of ACFs. The hydration number of confined Cu ions becomes a half of the bulk ions. The Debye-Waller factor of confined Cu ion solution was much smaller than that of the bulk solution, indicating that dehydrated water molecules form a highly ordered structure around Cu ions. However, the Cu-water molecular distance became smaller slightly by the confinement, which was very different from Rb ion solution. This is because water molecules are strongly coordinated to the central Cu ion with the coordination bonding.

Thus, an evident dehydration occurs for even transition metal ions by intensive confinement in carbon nanopores. In future, adsorption of heavy metal ions in nanopores of activated carbon must be understood taking into account the dehydration of the confined ions.

Acknowledgements

The research was supported with Fundamental Research Fund S by JSPS

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