An Ordered Water Molecular Structure in Carbon Micropores

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Introduction

The adsorption isotherm of water on activated carbon is S-shaped in general and the mechanism of water adsorption by activated carbon has been studied. Dubinin and Serpinsky (DS) proposed a phenomenological mechanism for the S-shaped adsorption isotherm which presumes the cluster formation on the surface function groups [1]. Although adsorption result have supported the DS mechanism, there is no direct evidence on the cluster formation. We need a direct evidence on the cluster formation of water molecules on activated carbon. X-ray can penetrate activated carbon and the X-ray diffraction patterns of activated carbon are very diffuse. Consequently, it is possible to elucidate the structure of water molecules adsorbed in micropores of activated carbon by X-ray diffraction. Understanding the intermolecular structure of water molecules in the carbon micropore should be helpful to develop new properties of a water adsorbed carbon. This paper reports the X-ray diffraction study on water adsorbed in micropores of super-high surface area carbon.

Experimental

Superhigh surface area carbon ("Maxsorb", Kansai Coke and Chemicals) was used as the microporous carbon sample. The micropore structure was determined by N_2 adsorption at 77K. The water adsorption isotherm was gravimetrically determined at 303K after preheating at 383K and 1 mPa for 2 hrs. The in situ X-ray diffraction of water adsorbed in micropores of activated carbon at 303K was measured by the transmission method using an angle dispersive diffractometer. The monochromatic X-ray from MoKα radiation at 50 kV and 35 mA was used for the diffraction measurement and the observed range of the scattering parameter $s = 4\pi\sin\theta/\lambda$, was from 0.7 to 12 $Å^{-1}$.

Results and Discussion

The micropore structure of Maxsorb determined by N_2 adsorption isotherm measurement with using the high resolution α_s-plot [2] as follows: the surface area = 2300 $m^2 \cdot g^{-1}$, the micropore volume = 0.97 $ml \cdot g^{-1}$, and the average pore width = 1.30 nm (± 0.05 nm). **Fig 1** shows the water adsorption isotherm of Maxsorb at 303K. The water adsorption isotherm was of Type V. The water molecules are scarcely adsorbed below P/P_0=0.6, and then the uptake of water molecules steeply increases above P/P_0=0.6, which indicates that these micropores have typical hydrophobic nature.

X-ray diffraction patterns of water adsorbed in micropores as a function of the fractional filling ϕ and bulk liquid water were

measured. These X-ray diffraction patterns were determined after subtraction of the diffraction of carbon itself [3]. Although the whole feature of the broad diffraction pattern of adsorbed water was similar to that of bulk liquid water, but a significant low-angle shift of the peak was observed, which increases with the decrease in ϕ. The diffraction patterns were Fourier-transformed to the electron radial distribution functions [4]. **Fig.2** shows the electron radial distribution functions of adsorbed water of ϕ=1 and bulk liquid water. A distinct difference between adsorbed water and bulk liquid water is observed in the peak of 0.3-0.5 nm. A bulk water has the highest peak at 0.3 nm and another peak at 0.45 nm. On the other hand, the highest peak of adsorbed water is at 0.45 nm and adsorbed water has a shoulder around 0.3 nm. The peaks and shoulder at 0.3 and 0.45 nm should be attributed to nearest and second nearest neighbor molecules, respectively. The results explicitly suggests that water molecules in micropores form an ordered assembly structure. The structure of the adsorbed water is more ordered than bulk liquid water, considering that the shoulder at 0.3 nm is less than peak at 0.45 nm, which is similar to bulk ice.

Conclusion

The presence of ordered water molecular assembly in carbon micropores was explicitly shown. The water molecular assembly does not necessarily need presence of surface functional groups.

References

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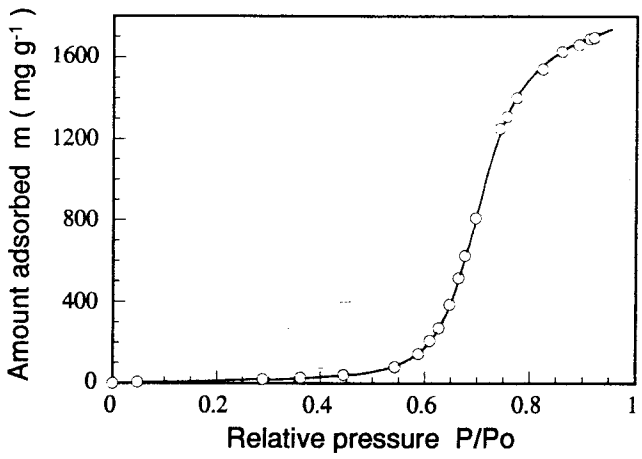

Fig.1 Water adsorption isotherm of Maxsorb at 303K

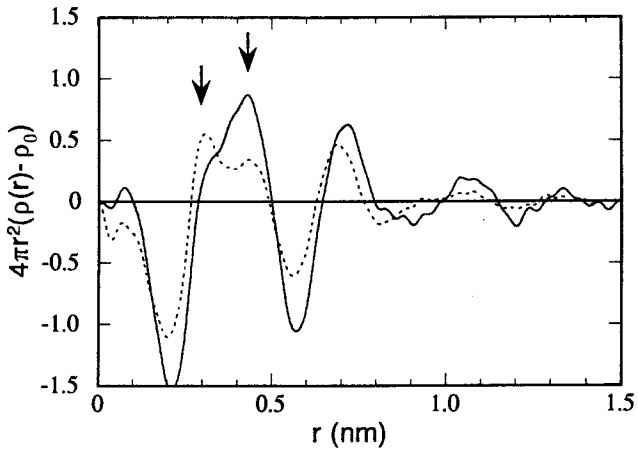

Fig.2 Electron radial distribution functions of adsorbed water at P/P_0=1 and bulk liquid water at 303K. Solid line: adsorbed water, Broken line: bulk liquid water.