HYSTERESIS-ASSOCIATED PRESSURE-SHIFT-INDUCED WATER ADSORPTION IN MICROPORES OF ACTIVATED CARBON FIBERS

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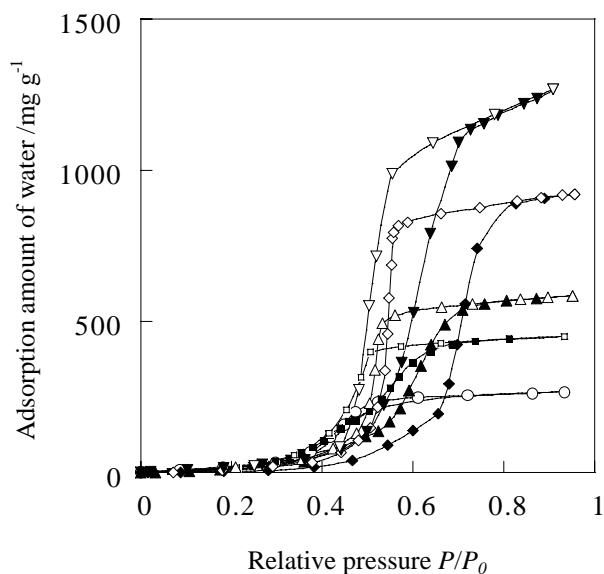*401 Academic Activities Building, University Park, PA 16802-2308*
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Introduction

Activated carbons fibers (ACFs) possess considerably uniform slit-shaped micropores of great pore volume. Molecules are strongly adsorbed in the micropores of the deep molecular potential well which stems from the overlapping of the molecule-pore wall interaction from opposite pore walls. Thus, a substantial adsorption of vapor begins at a very low-pressure region, giving rise to a monolayer adsorption and a further filling in residual spaces.

However, the interaction of a water molecule with the hydrophobic system such as ACF is too weak to induce a predominant adsorption at a low relative pressure P/P_0. Even hydrophobic ACF can induce a predominant water adsorption at high P/P_0 region, giving a remarkable adsorption hysteresis for wider micropore systems, as shown in Figure 1. Recently, Ohba et al. reported that the presence of preadsorbed molecules changes the effective potential well determining a further adsorption [1]. Thus, the potential curves for adsorption and desorption must be different from each other even at the same pressure, and this difference may cause the adsorption hysteresis. Iiyama et al. showed that the adsorbed state of water in micropores of ACF upon adsorption and desorption are different from each other for the system having an adsorption hysteresis with in situ SAXS method [2]. Here, the adsorption hysteresis must provide important information on adsorption.

On the other hand, it is well-known that water molecules can produce a host structure of the hydrogen-bonded network, in which includes a guest molecule. Methane, which has gathered much attention from the energy and environmental aspects, forms the clathrate compound with water, so called methane hydrate. The methane hydrate is formed at low temperature and/or at high pressure; e.g. above 80 MPa at 303 K [3]. The storage of the methane hydrate at ambient conditions has been requested. We can

Figure 1. Adsorption and desorption isotherms of water on microporous carbons at 303 K. The solid and open symbols denote adsorption and desorption isotherms, respectively.
(,) P5; (,) P10; (,) P15; (,) P20; (,) SAC31.

expect that the organized water form a stable structure with methane in the micropores of the ACF.

Recently, we reported a noticeable uptake of adsorption upon the introduction of the supercritical methane on water-preadsorbed ACFs and a super-high surface-area carbon (SAC) at an ambient temperature [4]. In our previous paper, we suggested a possibility of formation of a special compound of water and methane. In this article, a transient shift mechanism of an equilibrium pressure of water vapor induced by an introduction of the supercritical methane is proposed on the basis of the precise quantitative analysis of gas phase composition [5].

Experimental

Four kinds of pitch-based ACFs (P5, P10, P15, and P20, Adol Co.) and KOH-activated coal-based activated carbon (SAC31, Kansai Coke Co.) were used. The micropore parameters determined with the aid of subtracting pore-effect method (SPE) using high-resolution α_S plots of the nitrogen adsorption isotherms at 77 K is shown in Table 1. The adsorption isotherms of argon and methane on P20 measured gravimetrically at 303 K. The adsorption amount of supercritical argon or methane was 10 mg g^{-1} at best at 101 kPa in both case. The carbon samples were pretreated at 383 K and 1 mPa for 2 h prior to the adsorption measurements. The effect of the introduction of argon (T_C = 150.7 K) or methane (T_C = 190.6 K) on water adsorption was measured at 303 K after equilibrium of water adsorption with the aid of a gas chromatograph (GC-8AIT, Shimadzu Co.) as reported elsewhere [5].
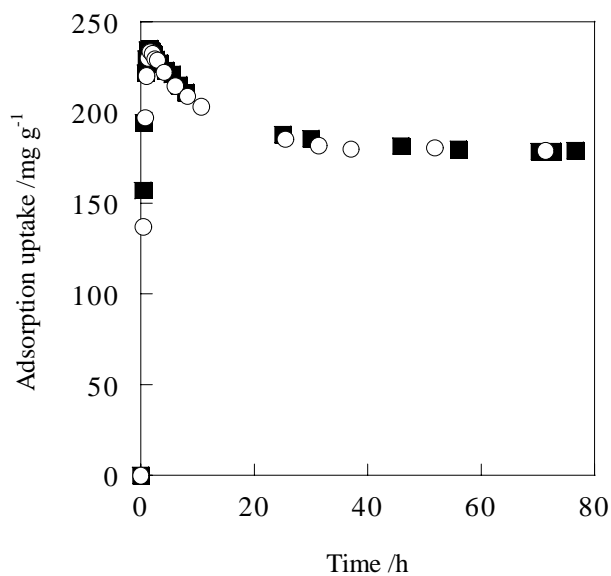
Results and Discussion

Effect of Introduction of a Supercritical Gas on Water Adsorption. Figure 2 shows the weight change of water-preadsorbed P20 after the introduction of argon or methane at 303 K. Here, the fractional filling ϕ_W of micropores with preadsorbed water are 0.3 for argon and 0.4 for methane. As mentioned in our previous paper [4], the adsorption increment shows a maximum 1-2 h after the introduction of the mixed gas, and reaches a steady value after about 80 h. The weight changes must come from adsorption of water and/or methane (or argon).

If the weight increase comes from only the additional adsorption of water, the content of methane or argon in the gas phase before and after the introduction of the mixed gas of water and methane or argon into the gravimetric cell having water vapor of an equilibrium pressure must be unchanged. The precise quantitative analysis of gas phase components after and before the introduction of supercritical methane using the gas chromatograph indicates no further adsorption of methane. In case of the mixed gas of argon and water, the same result is also obtained. Therefore, almost no amount of supercritical gas adsorbs on the water-preadsorbed ACF.

Equilibrium Pressure Shift Mechanism through Adsorption Hysteresis. If the introduction of the mixed gas into the sample cell containing water vapor gives rise to the transient compression for the pure water vapor atmosphere, the effective partial pressure of water vapor around the sample must increase. An upward shift of the partial pressure of water vapor can induce a remarkable increase of the water adsorption near the rising pressure of the water adsorption isotherm. Figure 3 explains the above
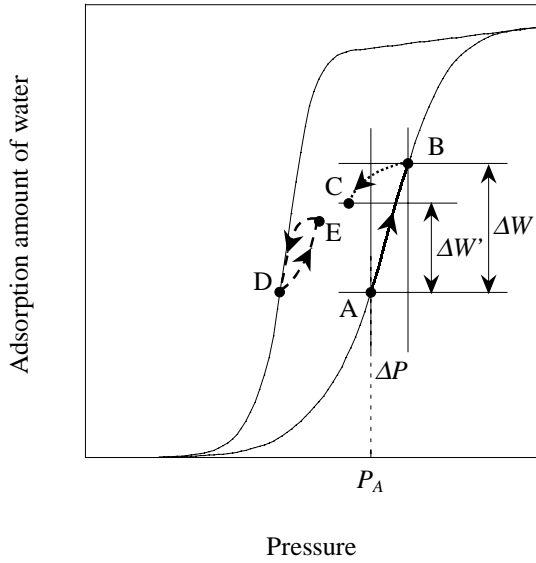
Table 1. The micropore structural parameters

	a_S (m^2 g^{-1})	W_0 (cm^3 g^{-1})	w (nm)
P5	884	0.294	0.67
P10	958	0.407	0.86
P15	1310	0.599	0.94
P20	1800	0.946	1.1
SAC31	2290	1.33	1.2

Figure 2. Time dependence of whole adsorption on water-preadsorbed P20 at 303 K after the introduction of supercritical argon or methane: (   ) argon for ϕ_W = 0.3; (   ) methane for ϕ_W = 0.4.

mechanism schematically. The pressure shift ΔP increases the water adsorption by ΔW (from point A to point B in Figure 3). On the assumption that the characteristic weight change is only due to the additional adsorption of water even at a maximum of the time dependence, we can estimate ΔP from ΔW using the pure water adsorption isotherm. For example, 0.85 ± 0.15 Torr is obtained for ΔP in the case of P20 at 303 K. The error of the ΔP determination comes from the difference of ϕ_W and/or the introduction speed of the mixed gas. The ΔP values for methane and argon agreed with each other, suggesting that the observed adsorption uptake is mainly ascribed to water adsorption even at the maximum of the characteristic time dependence. As the compression by the introduction of the mixed gas is transient, the ΔW must decrease with the relaxation of the temporary compression of water vapor.
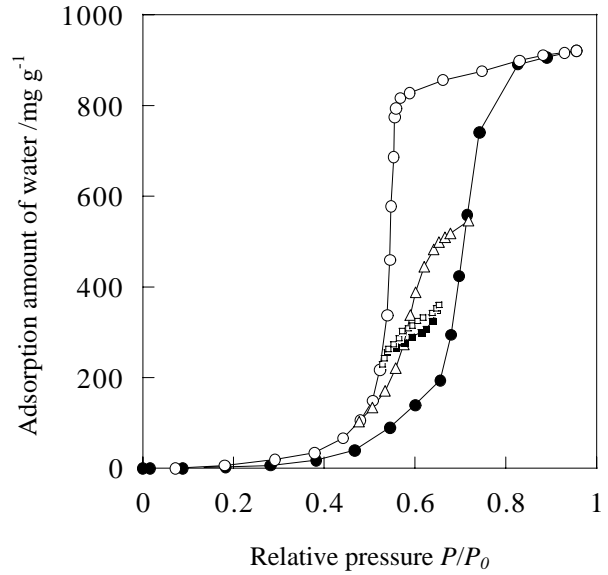
Figure 3. Schematic illustration of the equilibrium pressure shift mechanism.

Figure 4. Adsorption and desorption scanning curves of water on P20 at 303 K: ( ) desorption scanning curve from the adsorption branch; (,) adsorption and desorption scanning curves from the desorption branch; (,) adsorption and desorption isotherms. The solid and open symbols denote adsorption and desorption isotherms, respectively.

The change of the adsorption amount of water must follow the desorption scanning curve, which starts from point B on the adsorption branch (the dotted line from point B to point C in Figure 3). Here, the equilibrium water pressure at point C must be lower than the initial water vapor pressure before the introduction of the mixed gas because of the additional adsorption of water by the mixed gas introduction. As point C is in the metastable state, the final enhancement of adsorption $\Delta W'$ depends on the degree of the compression of the water vapor atmosphere, that is, ΔP.

Figure 4 shows the actual desorption scanning curve of pure water adsorption on P20 at 303 K in the adsorption and desorption isotherms. The starting point of the desorption scanning curve is adjusted to the point at which the adsorption amount is almost similar to the maximum amount of mixed gas adsorption, that is, $\phi_W + \Delta W$ (point B in Figure 3). The pressure at this starting point is exactly the same as $P_A + \Delta P$; here, P_A indicates the pressure at point A. Moreover, the pressure at the point that the adsorption amount equals $\phi_W + \Delta W'$ (point C) using this desorption scanning curve agrees with that for the mixed gas adsorption, supporting our mechanism.
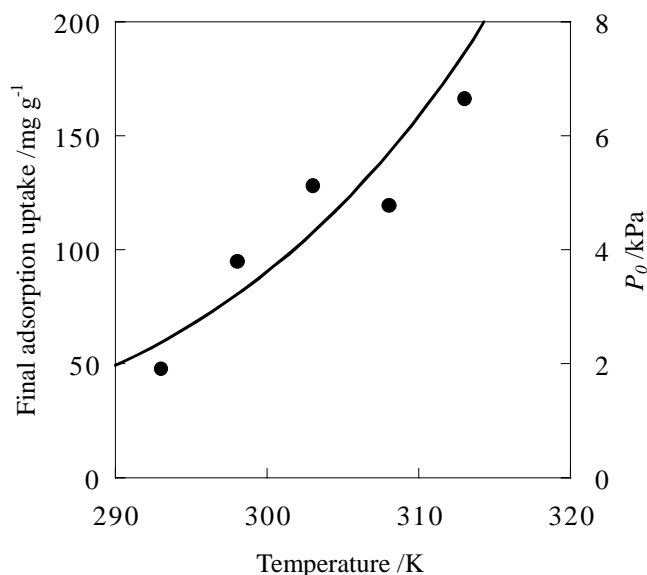
This mechanism is supported by the following result on the desorption branch of the isotherm of water. As shown in Figure 4, the desorption from the point on the adsorption scanning curve from the desorption isotherm of water goes back to the initial point of the adsorption scanning curve. If we introduce the mixed gas into the sample cell containing water vapor controlled by desorption (point D in Figure 3), the adsorption may occur according to the adsorption

scanning curve, but it must return to the initial point D in the course of time. The time dependence of the adsorption uptake on the introduction of the methane-water mixed gas on water-preadsorbed P20 at 303 K shows a sharp maximum about 1 h after the introduction, and goes back to zero after the long time, as the above prediction.

Temperature and Hysteresis Loop Area Dependences of Adsorption Uptake. As mentioned in our previous paper [4], the adsorption uptake strongly depends on temperature or the micropore structure parameters, although the shapes of the time dependence after the introduction of the mixed gas are similar to each other. These tendencies can be interpreted by our mechanism. The adsorption isotherms at different temperature almost coincide with each other, using the relative pressure P/P_0. At the same ϕ_W, therefore, the P/P_0 value must be agree with each other even at the different temperature. As the P_0 of bulk water vapor changes with temperature exponentially, the absolute water pressure P at the same P/P_0 must change in a similar way to P_0, that is, the molecular number density of water in the gas-phase at the given P/P_0 increases with increasing the temperature. Therefore, the compression effect against the water vapor by the introduction of the mixed gas should be strengthened as increasing the temperature, causing a more remarkable adsorption uptake. Figure 5 shows the

Figure 5. Temperature dependences of the final adsorption uptake on water-preadsorbed P20 and the saturated pressure P_0 of water vapor in the bulk phase. The circle symbol and the solid line indicate the final adsorption uptake and P_0, respectively.

Figure 6. Relationship between the area of water adsorption hysteresis loop and the final adsorption uptake on the water-adsorbed microporous carbons at 303 K.

temperature dependences of P_0 of the water vapor and the final adsorption uptake, that is, $\Delta W'$ in Figure 3 on water-preadsorbed P20. Apparently, the final adsorption uptake shows a good relation with P_0, as expected by our mechanism.

Figure 6 shows the relationship between the area of hysteresis loop and the final adsorption uptake for the water-preadsorbed ACFs and SAC31 at 303 K. Here, the area of the hysteresis loop is obtained from the difference of integrated values for adsorption and desorption curves over the whole P/P_0 range. According to our mechanism, the final adsorption uptake must apparently correlate with the difference between the adsorption branch and the desorption scanning curve of the water adsorption, that is, the area of the water adsorption hysteresis loop. The larger the loop area the more the final adsorption uptake, indicating a validity of our mechanism.

Conclusion

The hysteresis-associated pressure-shift-induced water adsorption mechanism is presented for the adsorption of the mixed gas of water and supercritical gas on the water-preadsorbed microporous carbon. This mechanism should be helpful to understand the gas adsorption properties of practical activated carbon adsorbents, because activated carbon is often exposed to a humid atmosphere in common applications. This mechanism recommends that the usage of activated carbon near 50 % of relative humidity must be avoided upon the introduction of another gas.

References

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