

# Adsorption Properties of Porous Carbons: Influence of Preadsorbed Water on Gas Adsorption Behavior

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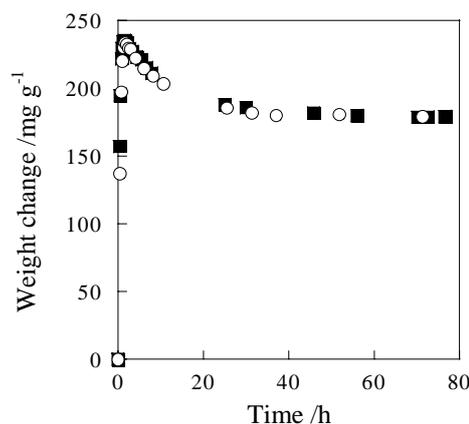
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Activated carbons fibers (ACFs) having considerably uniform slit-shaped micropores of great pore volume can adsorb various molecules in the micropores of the deep molecular potential well which stems from the overlapping of molecule-pore wall interactions from opposite pore walls. Thus, a substantial adsorption of vapor molecules begins at a very low-pressure region, giving rise to a monolayer adsorption and a further filling in residual spaces. However, only a limited amount of supercritical fluids are adsorbed even in micropores of ACFs at a subatmospheric pressure because of an insufficient fluid-surface interaction. Also, water vapor cannot be adsorbed in micropores of ACFs at a low relative pressure  $P/P_0$ . At high  $P/P_0$  region, however, even hydrophobic ACF can induce a predominant water adsorption, giving a remarkable adsorption hysteresis especially for wider micropore systems.

In practical application of porous carbons, surrounding atmosphere often contains humidity. Thus, it is important to estimate an influence of preadsorbed water on gas adsorption characteristics. We have found a noticeable uptake of adsorption amount upon the introduction of supercritical  $\text{CH}_4$  on water-preadsorbed ACFs and a super-high surface-area carbon (SAC) at 303 K [1]. Avraham *et al.* have also described a similar enhancement of adsorption for the water- $\text{N}_2$  system [2]. Here, a transient shift mechanism of an equilibrium pressure of water vapor induced by an introduction of the supercritical  $\text{CH}_4$  is proposed on the basis of the precise quantitative analyses of gas phase composition [3].

Four kinds of pitch-based ACFs (P5, P10, P15, and P20, Adol Co.) and a KOH-activated coal-based activated carbon (SAC31, Kansai Coke Co.) were used. Figure 1 shows the weight change of water-preadsorbed P20 after the introduction of the mixed gas of water and supercritical Ar or  $\text{CH}_4$  at 303 K. Here, the fractional filling  $\phi_w$  of micropores with preadsorbed water were 0.3 for Ar and 0.4 for  $\text{CH}_4$ . The adsorption increment showed a maximum 1-2 h after the introduction of the mixed gas, and reached a steady value after about 80 h. The weight changes must come from adsorption of water and/or  $\text{CH}_4$  (or Ar). If the weight increase comes from only the additional adsorption of water, the content of  $\text{CH}_4$  or Ar in the gas phase before and after the introduction of the mixed gas into the gravimetric cell containing water vapor of an equilibrium pressure must be unchanged. The precise quantitative analyses of gas phase components after and before the introduction of supercritical  $\text{CH}_4$  (or Ar) using the gas chromatograph showed no further adsorption of  $\text{CH}_4$  (or Ar), indicating that almost no supercritical gas adsorbed on the water-preadsorbed ACF.



**Figure 1.** Time dependence of whole adsorption on water-preadsorbed P20 at 303 K after the introduction of supercritical Ar or  $\text{CH}_4$ : (○) Ar at  $\phi_w = 0.3$ ; (■)  $\text{CH}_4$  at  $\phi_w = 0.4$ .

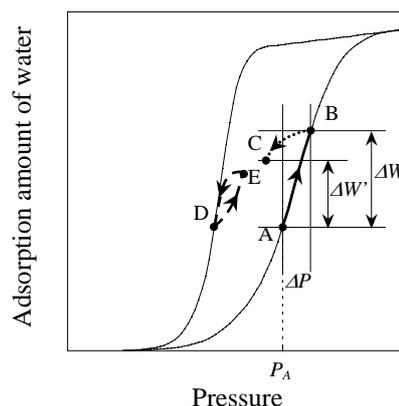
If the introduction of the mixed gas into the sample cell containing water vapor gives rise to the transient compression for the pure water vapor atmosphere, the effective partial pressure of water vapor around the sample must increase. An upward shift of the partial pressure of water vapor can induce a remarkable increase of the water adsorption near the rising pressure of the water adsorption isotherm. Figure 2 explains the above mechanism schematically. The pressure shift  $\Delta P$  increases the water adsorption by  $\Delta W$  (from point A to point B in Figure 2). 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  $\Delta P$  from  $\Delta W$  using

the pure water adsorption isotherm. For example,  $0.85 \pm 0.15$  Torr is obtained for  $\Delta P$  in the case of P20 at 303 K. The  $\Delta P$  values for  $\text{CH}_4$  and Ar 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 in Figure 1. As the compression by the introduction of the mixed gas is transient, the  $\Delta W$  must decrease with the relaxation of the temporary compression of water vapor. 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 2). 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,  $\Delta P$ . We assessed validity of our proposed mechanism from various points of view. For example, 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  $\text{CH}_4$ -water mixed gas on water-preadsorbed P20 at 303 K showed a sharp maximum about 1 h after the introduction, and went back to zero after the long time, as the above prediction. We also found a good relationship between the final adsorption uptake and area of water adsorption hysteresis loop or measurement temperature. All results supported our proposed mechanism.

In conclusion, the transient compression of the water vapor atmosphere gives rise to a remarkable additional adsorption of water that is associated with the adsorption hysteresis. This transient water adsorption has a long relaxation time due to the metastable state of adsorbed water. The proposed mechanism should be helpful to understand gas adsorption properties of practical activated carbon adsorbents, because activated carbon is often exposed to a humid atmosphere in practical applications. The mechanism recommends that the usage of activated carbon near 50% of relative humidity must be avoided.

## References

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**Figure 2.** Schematic illustration of the equilibrium pressure shift mechanism