

# Study of Water Adsorption on Activated Carbon with Different Surface Oxygen Complexes

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## ABSTRACT

An investigation was made to correlate between amount of oxygen complex present on activated carbon and its water adsorption behavior. Activated carbon was oxidized with  $\text{HNO}_3$  at 340 K for 30 hours, followed by a subsequent pre-heat treatment under argon atmosphere for 8 hours at various temperatures in order to remove oxygen complexes progressively on the oxidized activated carbon. The types and amounts of oxygen complexes were estimated by temperature programmed desorption (TPD). Characteristics of pore structure, represented as BET specific surface area, on the carbons were determined by nitrogen adsorption at 77 K. The water adsorption isotherms on the carbons with different amount of oxygen complexes were also obtained at 298 K. The water isotherms were affected by both of surface oxygen complexes and carbon pore characteristics; therefore, the data acquisition was made, in this study, solely to study the effect of surface oxygen complexes. The amounts of adsorbed water were related to those of oxygen complexes present on the carbon surfaces, especially to the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  producing complexes that attracted water molecules at a low vapor pressure range, rather than CO producing complexes did.

## INTRODUCTION

Activated carbon possesses powerful adsorption properties, and has been most widely used as an industrial adsorbent for removing pollutants and purifying water [1-3]. In cases where activated carbon is used in air, their performance is greatly affected by the presence of moisture or water molecule. It is known that oxygen complex act as primary site and water molecules are adsorbed strongly on the primary site via hydrogen bonding. The small amount of water adsorbed on the oxygen complex, therefore, reduces adsorption capacity and selectivity of activated carbon [4-6].

It is also known surface carbon-oxygen complexes (carboxylic, carbonyls, phenols and lactones) are produced by treating carbons with oxidizing agents, either in the gas phase such as air and  $\text{O}_2$  or in the solution such as  $\text{HNO}_3$ ,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{H}_2\text{O}_2$  [7]. Issa I. Salame et al. [8] studied the process of water adsorption on oxidized activated carbons oxidized by different agents, and showed that water adsorption at very low surface coverage is dependent on density of surface oxygen complexes. D. D. Do et al. [9] carried out molecular simulation to understand the mechanism of water adsorption on activated carbon. They proposed a model, which water molecules form clusters around functional groups, for isotherms of water on different carbons by using computer simulation. In their model water molecules penetrate into a micropore, forming a cluster of five water

molecules. Their model gave a very good description for a given water adsorption isotherms.

In this paper, an investigation is made to correlate between amount of oxygen complex present on activated carbon and that of water adsorbed by excluding the water adsorbing on the carbon surfaces.

## EXPERIMENTAL

Commercially available granular activated carbon (CAL; Calgon Mitsubishi chemical corporate, Japan) derived from coal was used in this study. The CAL was sieved to 0.85-1.18 mm in particle size, demineralized with 6N HCl solution at 333 K for 24 hours, and then washed with distilled water until silver chloride precipitation did not appear by addition of silver nitrate. In order to form oxygen complexes on the carbon surfaces, the CAL sample thus demineralized was further oxidized in 12N-HNO<sub>3</sub> solution at 340 K for 30 hours and then washed with distilled water until the pH of supernatant solution reached constant. The sample thus prepared was symbolized as HNO<sub>3</sub> CAL. The HNO<sub>3</sub> CAL was further heat-treated under a flowing Ar atmosphere for 8 hours at designated various temperatures in order to progressively remove oxygen complexes. The heat-treated activated carbons were represented by adding heat treatment temperature to HNO<sub>3</sub> CAL, for example, as 773K HNO<sub>3</sub> CAL. Those samples were stored in capped bottles until they were used.

Temperature programmed desorption (TPD) experiments were performed in a horizontal furnace equipped with a quartz tube. About 0.1 g of the carbon samples was dried in the furnace under Ar atmosphere and heated at 5 K/min up to 1273 K. The concentrations of five gases (CO<sub>2</sub>, H<sub>2</sub>O, CO, CH<sub>4</sub> and H<sub>2</sub>) evolving during TPD were measured by a gas chromatograph. Nitrogen adsorption isotherms at 77 K were obtained using a gas adsorption apparatus (BELSORP18-PLUS, BEL, JAPAN), and BET surface area ( $S_{\text{BET}}$ ) was calculated from the isotherms. Water vapor adsorption isotherms on the activated carbons with different amount of oxygen complexes were also obtained at 298 K by the BELSORP18-PLUS.

## RESULT AND DISCUSSION

Heat treatment of HNO<sub>3</sub> oxidized carbons in inert gas results in evolution of gases, such as CO<sub>2</sub>, H<sub>2</sub>O and CO, which are originated from thermal decomposition of surface oxygen complexes present on the carbon surfaces [10,11]. Oxygen complexes present on carbon surface can be estimated from the amount of gases evolved during TPD [10]. Fig.1 presents gas evolution profiles from HNO<sub>3</sub> CAL, showing that CO<sub>2</sub>, H<sub>2</sub>O and CO were the main gases evolved during TPD runs. It is also noted that H<sub>2</sub> started to evolve above the temperature of 1200K and CH<sub>4</sub> was not detected.

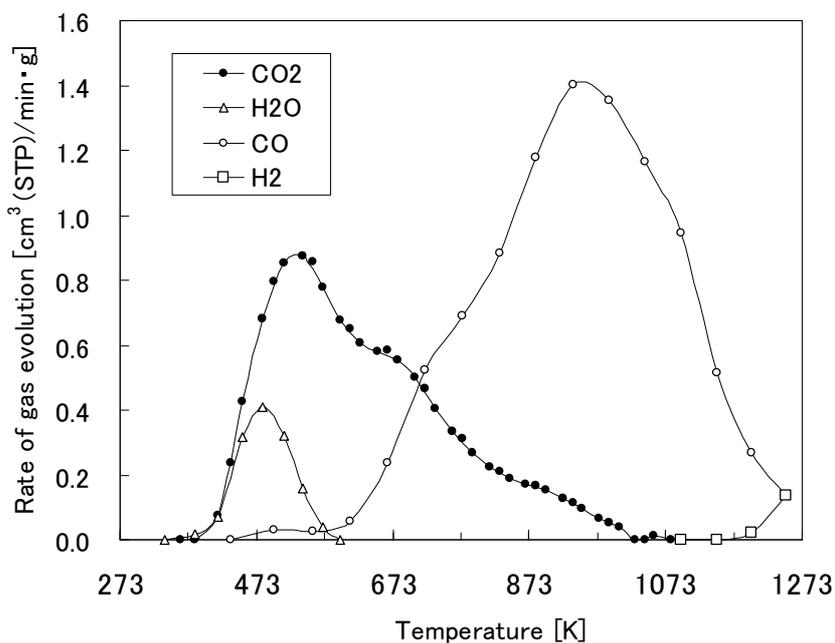


Fig.1. TPD profiles (CO<sub>2</sub>, H<sub>2</sub>O, CO and H<sub>2</sub>) of HNO<sub>3</sub> CAL (12N-HNO<sub>3</sub> oxidation at 340 K for 30 h). TPD measurement was performed at 5 K/min up to 1273 K in Ar.

The amount of surface oxygen complexes was removed progressively by heat treatment of HNO<sub>3</sub> CAL at designated temperatures for 8h in Ar gas. The total amounts of oxygen containing gases evolved up to 1273 K from a set of the HNO<sub>3</sub> CAL samples are listed in Table 1, which shows that the amounts of CO<sub>2</sub>, H<sub>2</sub>O and CO decreased with increasing heat treatment temperatures. A small amount of surface oxygen complexes still existed on the sample of 1273K HNO<sub>3</sub>CAL. These surface oxygen complexes may be produced when heat-treated samples were stored in atmospheric air after the heat treatment. In order to obtain the carbon sample from which oxygen complexes were completely removed, the HNO<sub>3</sub> CAL sample was heat-treated at 1273 K for 8 h and then TPD measurement was performed on this cleaned carbon without exposing in air. This

sample is donated as 1273K(vac) HNO<sub>3</sub> CAL and also listed in Table 1. The 1273K(vac) HNO<sub>3</sub> CAL evolved considerably small amount of CO, suggesting that almost all the surface oxygen complexes were eventually removed by heat treatment at 1273 K and surface oxygen complexes present on the 1273K HNO<sub>3</sub> CAL were produced by slow reaction of carbon with oxygen in atmospheric air.

Table 1 Results of TPD and N<sub>2</sub> adsorption on HNO<sub>3</sub> CAL and heat-treated HNO<sub>3</sub> CALs

Sample	Gases evolved [mmol/g]			Total oxygen atoms *	S <sub>BET</sub>
	CO <sub>2</sub>	H <sub>2</sub> O	CO	[mmol/g]	[m <sup>2</sup> /g]
HNO <sub>3</sub> CAL	2.18	0.37	4.42	9.15	758
473K HNO <sub>3</sub> CAL	1.81	0.20	4.40	8.22	n.d.
573K HNO <sub>3</sub> CAL	n.d.	n.d.	n.d.	n.d.	771
673K HNO <sub>3</sub> CAL	0.83	0.13	4.12	5.90	n.d.
773K HNO <sub>3</sub> CAL	0.51	0.10	3.57	4.69	n.d.
873K HNO <sub>3</sub> CAL	n.d.	n.d.	n.d.	n.d.	843
923K HNO <sub>3</sub> CAL	0.12	0.04	2.37	2.65	885
1023K HNO <sub>3</sub> CAL	0.14	0.06	0.96	1.30	893
1123K HNO <sub>3</sub> CAL	0.07	0.03	0.36	0.53	901
1273K HNO <sub>3</sub> CAL	0.14	0.07	0.59	0.95	883
1273K(vac) HNO <sub>3</sub> CAL	0.00	0.00	0.03	0.03	932

n.d. : not determined

\* : calculated from amounts of CO<sub>2</sub>, H<sub>2</sub>O and CO evolved up to 1273 K.

A set of the HNO<sub>3</sub> CALs with and without heat treatments was subjected to N<sub>2</sub> adsorption measurements at 77 K and the values of BET surface area (S<sub>BET</sub>) were calculated from N<sub>2</sub> adsorption isotherms and also listed in Table 1. The values of S<sub>BET</sub> tend to increase with heat treatment temperatures. This observation suggests that N<sub>2</sub> molecules became accessible to the pore surfaces of carbons by the decomposition of oxygen surface groups upon heat treatment.

The H<sub>2</sub>O adsorption isotherms at 298K were obtained for a set of the HNO<sub>3</sub> CAL samples. Fig.2 shows the H<sub>2</sub>O isotherms for HNO<sub>3</sub> CAL, 923K HNO<sub>3</sub> CAL and 1273K(vac) HNO<sub>3</sub> CAL, as an example.

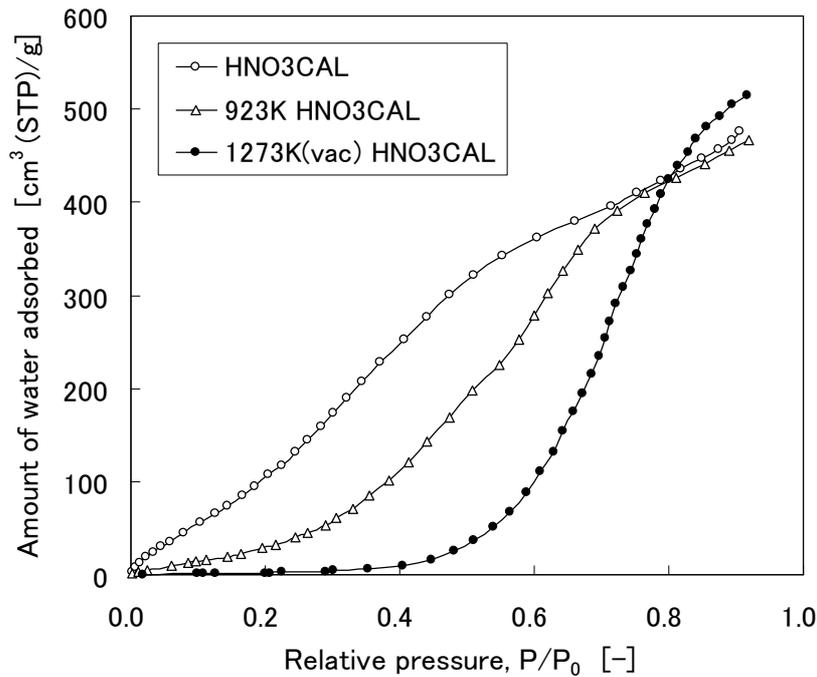


Fig.2. Adsorption isotherms of water vapor at 298K for HNO<sub>3</sub> CALs. (HNO<sub>3</sub> CAL, 923K HNO<sub>3</sub> CAL, and 1273K(vac) HNO<sub>3</sub> CAL)

Water adsorption on surface containing no oxygen complexes is different from oxygen complexes present. There seems three regions for the adsorption isotherm of 1273K(vac) HNO<sub>3</sub> CAL; eventually no H<sub>2</sub>O was adsorbed up to a relative pressure ( $P/P_0$ ) of 0.3 and then the carbon started to gradually adsorb H<sub>2</sub>O molecules in a relative pressure range of 0.3-0.5 and H<sub>2</sub>O was adsorbed abruptly above a relative pressure of 0.5. It is clearly seen that addition of oxygen groups on the carbon surfaces increases up take of H<sub>2</sub>O, whereas their removal reduces H<sub>2</sub>O adsorption capability. It is clearly seen that HNO<sub>3</sub> CAL containing a larger amount of surface oxygen complexes adsorbed larger amount of water at a lower relative pressure range. D. D. Do et al. [9] reported that water molecules are adsorbed on surface oxygen complexes preferentially and formed cluster around oxygen complex. At a higher range of relative pressure, however, 1273K(vac) HNO<sub>3</sub> CAL showed higher water adsorption capacity, which seems to be caused by difference of pore volume, as a result of carbon atoms removed from the carbon surfaces as CO<sub>2</sub> and CO.

In order to observe further the correlation between surface oxygen complex and water adsorption, the amount of H<sub>2</sub>O adsorbed on surface oxygen complexes, for a given relative pressure ( $P/P_0$ ), was calculated by subtracting adsorption data on the carbon with no surface oxygen groups, 1273K(vac) HNO<sub>3</sub> CAL, from those of oxygen containing HNO<sub>3</sub> CAL samples. The amount of water adsorbed on surface oxygen complexes is plotted in Fig.3 against that of oxygen surface complexes as a function of relative pressures. The axis of abscissas in this figure is expressed as total amount of oxygen atoms, as already

shown in Table 1. When H<sub>2</sub>O adsorption occurs at a low P/P<sub>0</sub>, say P/P<sub>0</sub> = 0.1, the amount of water adsorbed on oxygen complexes increases with extent of oxygen atoms present on the carbon surface. However, there is a region where the amounts of water adsorbed are poorly related to the amounts of oxygen atoms; that is, in a range of 1 to 5 mmol/g. This observation suggests that types of oxygen functional groups are important for H<sub>2</sub>O adsorption rather than total oxygen atoms. As an extreme case, when H<sub>2</sub>O adsorption occurs at a high relative pressure P/P<sub>0</sub> = 0.7, adsorption of H<sub>2</sub>O becomes independent of the oxygen contents. Surface oxygen complexes are the sites for the H<sub>2</sub>O adsorption at an initial stage of water adsorption and the amounts of H<sub>2</sub>O adsorbed are related to both of types and amounts of oxygen functional groups on the carbon surfaces. As H<sub>2</sub>O adsorption proceeds with increasing P/P<sub>0</sub> value, H<sub>2</sub>O molecules form a cluster around an oxygen complex. Under these circumstances, oxygen complexes are no longer directly effective to H<sub>2</sub>O adsorption.

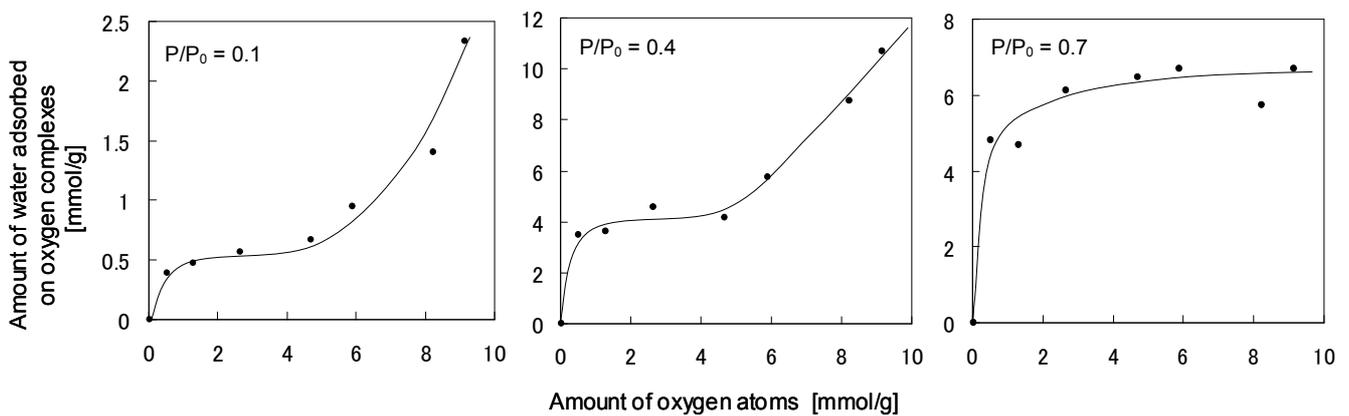


Fig.3. Relationship between amounts of oxygen atoms present on HNO<sub>3</sub> CALs and those of water adsorbed on oxygen complexes.

A question arises which type of surface oxygen complexes is closely related to H<sub>2</sub>O adsorption. Fig.4 shows the amount of H<sub>2</sub>O adsorbed at P/P<sub>0</sub> of 0.1 against amount of CO<sub>2</sub>, H<sub>2</sub>O and CO evolved as a result of thermal decomposition of oxygen complexes. The amounts of water adsorbed on surface oxygen complexes are somewhat related to those of CO<sub>2</sub> and H<sub>2</sub>O evolved from the carbon surfaces. It is suggested, therefore, that the complexes decomposing as CO<sub>2</sub> and H<sub>2</sub>O by heat treatment seem to be related to water adsorption.

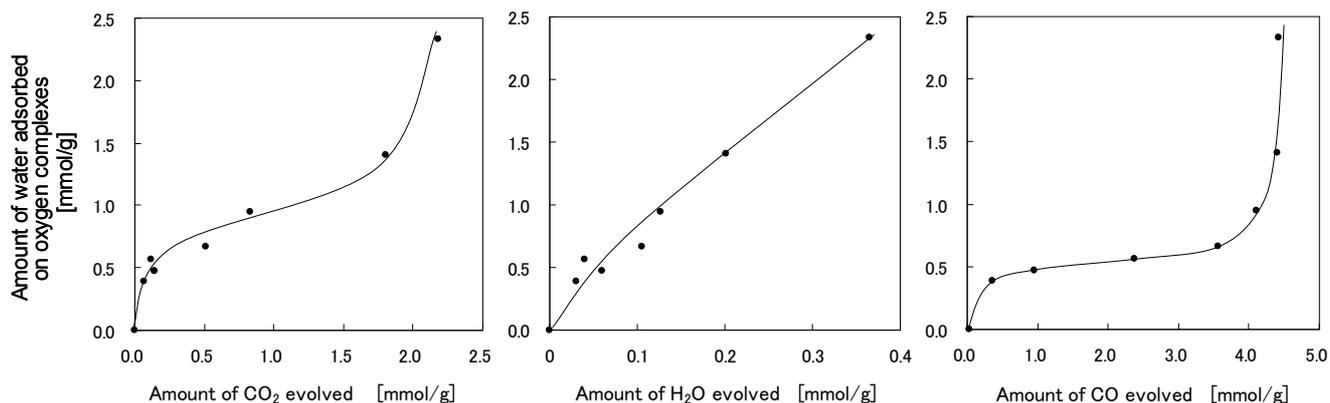


Fig.4. Correlations between amount of water adsorbed on oxygen complexes at  $P/P_0 = 0.1$  and that of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CO}$  evolved.

## CONCLUSION

In this study, an investigation was made to correlate between amount of oxygen complex present on activated carbon and its water adsorption behavior. It was found that the amount of adsorbed water was related to those of oxygen complexes, especially to the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  producing complexes that attracted water molecules at a low vapor pressure range than  $\text{CO}$  producing complexes did.

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