Adsorption Sites for Water on Graphite. 1. Effect of High-Temperature Treatment of Sample

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The adsorption sites for H_2O on the surface of graphite were investigated by measuring the adsorption isotherm of H_2O and the amount of gas evolved on heating the sample. It has been found that when the graphite sample is pretreated at higher temperatures, the shape of H_2O adsorption isotherm transfers from the type II to III, the isosteric heat of H_2O q_{st} remarkably decreases, and at the same time the amount of surface oxygen compounds decreases. In other words, the heat treatment of the sample results in an enhancement of the surface hydrophobicity of graphite. Especially, the q_{st} curve on the 1000 °C treated sample reveals a distinct minimum which lies under the level of the heat of liquefaction of H_2O. Such a change in the shape of the q_{st} curve was well explained in connection with the amount of evolved gas. Also, it was found that the chemisorption of H_2O occurs on the graphite surface treated at higher temperatures.

Introduction

It has been known that various kinds of oxides are present on the surface of carbon and they play a significant role for H_2O adsorption.[1-17] From the investigation of H_2O adsorption on three kinds of charcoals, McDermot and Arnell have concluded that the initial adsorption sites for H_2O are oxygen atoms chemisorbed on the surface.[5] Puri et al. reported that the adsorbability of H_2O increases when the amount of oxygens bonded to the surface as the CO_2-desorbing species increases.[10] Walker and Janov have found that the amount of H_2O adsorbed on activated Graphon is proportional to the surface area covered by chemisorbed oxygens.[12] Barton et al. concluded that the initial adsorption sites for H_2O on carbon are the CO-desorbing oxides.[13] Stoeckli et al. have suggested that the carbonyl-type sites are the primary adsorption centers for H_2O on various kinds of charcoals.[15]

On the other hand, Pierce et al. have found that surface complexes are formed through the reaction between the Graphon surface and H_2O molecules, on the basis of the result that the adsorbed amount of H_2O on the Graphon surface exposed to H_2O vapor at 80 °C is greater than that on the unexposed sample.[18] Smith et al. have confirmed that the reaction products between carbon and H_2O at temperatures from 25 to 200 °C are both H_2 and surface oxygen complexes, the latter being decomposed to form CO_2 and CO.[19]

Moreover, it has been reported that surface oxides are bonded to the terminal edges, $(10\bar{1}0)$ and $(11\bar{2}0)$, of the graphite layers of carbon.[20,21] Most of carbon samples used in the researches cited above are carbon materials with low degree of crystallinity. In spite of the fact that a lot of researches have been done on the adsorbability of H_2O on carbon surfaces, it appears that the adsorption sites for H_2O on carbon surfaces are not clarified yet. We have undertaken to make clear the adsorption sites for H_2O on carbon, by measuring the adsorption isotherm of H_2O and the quantity of surface oxygen compounds on natural graphite.

Experimental Section

Materials. The graphite sample used here was supplied from Nippon Kokuen Co., being produced in Sri Lanka. According to the maker's assay, the sample is 99.5% in purity and contains 0.5% ashes, the particle size being 1–30 μm in diameter. The sample was subjected to extraction with benzene for 6 days to remove organic contaminations, degassed in a vacuum of 10^{-5} torr (1 torr = 133.3 Pa) at room temperature, and then treated for 5 h at 25, 700, and 1000 °C (respectively G-25, G-700 and G-1000). The specific surface area of the samples, measured by the N_2 adsorption at −196 °C, was found to be equal to one another, (8.63 ± 0.20) m^2/g. Furthermore, the adsorption and desorption isotherms of N_2 were in accordance with each other, which denies the presence of mesopores. The scanning electron microscopic observation was carried out by using an electron microscope, JEOL JSM-35.

Measurement of the Water Adsorption Isotherm. Just after the pretreatment at temperatures of 25, 700, and 1000 °C, 10 g of each sample was employed for the measurement of the H_2O adsorption isotherm at 25 °C, where both the heat treatment and the adsorption measurement were carried out in situ to avoid the exposure of the sample to the atmosphere. After the first adsorption isotherm was measured up to a relative pressure of about 0.8, the sample was exposed to saturated H_2O vapor for 48 h at 25 °C and degassed at 25 °C for 10 h in a vacuum of 10^{-5} torr, and then the second adsorption isotherm was measured repeatedly on the same sample at temperatures of 10, 18, and 25 °C. The adsorption equilibrium was attained within 30 min after every dose of H_2O for the measurements of the second adsorption

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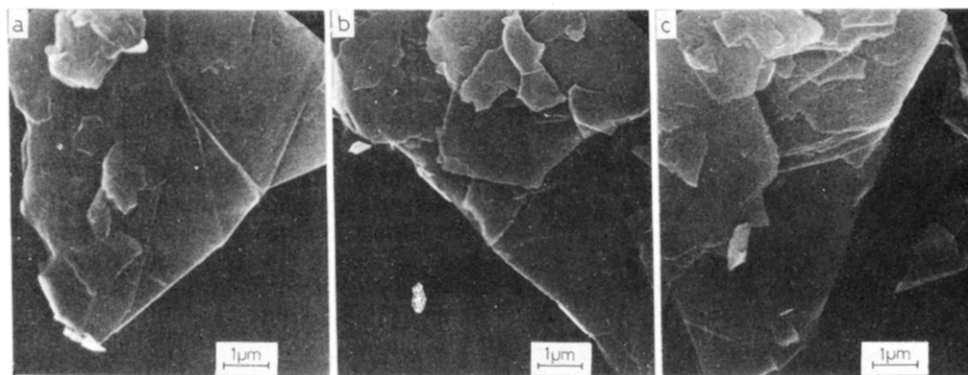[‡] Tsuyama Technical College.

Figure 1. Scanning electron micrographs of graphite: (a) G-25; (b) G-700; (c) G-1000.

isotherm on every sample and of the first adsorption isotherm on G-25, whereas it took more than 1 h for the first adsorption measurement on G-700 and G-1000. The adsorption measurement was carried out volumetrically by using a conventional adsorption apparatus, equipped with an oil manometer.

Determination of Surface Compounds. A preliminary test was carried out to analyze the gas evolved on heating graphite samples in vacuo by means of both gas chromatography and mass spectrometry. The results showed that the released gas contains H_2O, CO_2, CO, H_2, and CH_4. Therefore, the gas evolved by heating a 10-g sample at every 100 °C interval of rising temperature from room temperature to 1000 °C was determined by the two-step trapping.[22] First, the total gas evolved is determined volumetrically and cooled to −196 °C, and the uncondensed gas is analyzed by means of gas chromatography. By this method, the quantities of CO and H_2 can be determined. The amount of CH_4 contained in the uncondensed gas is calculated by subtracting the content of CO and H_2 from the total amount of uncondensed gas. On the other hand, the total amount of condensed gas, i.e., the sum of CO_2 and H_2O, is determined volumetrically after reevaporation at room temperature. The cooling of the gas at −78 °C and the succeeding evacuation of it at −78 °C leave only solid H_2O, whose amount can be determined again volumetrically after reevaporation at room temperature. Thus, the final amount of CO_2 can be obtained by subtracting the amount of H_2O from the sum of CO_2 and H_2O.

The acidic surface oxides[23] were measured through the reaction with four kinds of bases, $NaOC_2H_5$, NaOH, Na_2CO_3, and $NaHCO_3$.[20,24] Ten grams of each sample was stirred in 50 cm³ of a base solution, the supernatant solution was separated by the centrifugation, and then it was titrated conductometrically with a standard HCl solution. It took about 100 h for the attainment of the reaction equilibrium of acidic surface oxides with $NaOC_2H_5$, about 50 h with NaOH, and about 24 h with Na_2CO_3 and $NaHCO_3$. The concentration of the bases used was 0.005–0.2 M.

Results

The electron micrographs of graphite samples are shown in Figure 1. It is found from Figure 1 that the apparent change in the shape of graphite through high-temperature treatment cannot be observed; this is consistent with the result that the surface area also is not altered by the same treatment.

The adsorption isotherm of H_2O on graphite is illustrated in Figure 2, where the adsorbed amount is expressed in cm³(STP)/m², based on the surface area measured by the N_2 adsorption. The results in Figure 2 show that the first and second adsorption isotherms are in agreement with each other on G-25, while they differ individually on G-700 and G-1000. On the G-700 sample, the second adsorption isotherm lies over the first one. In the course of
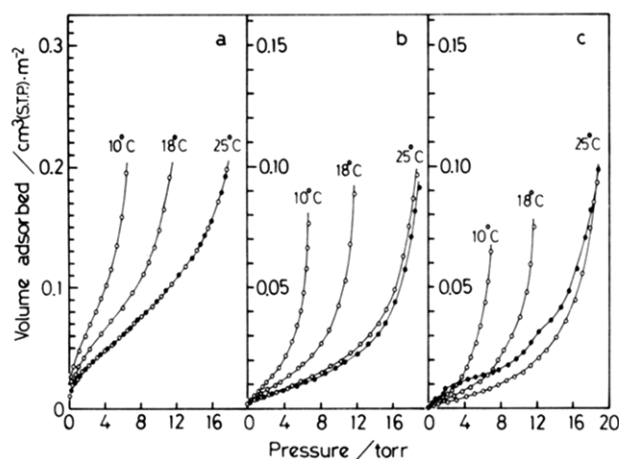
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Figure 2. Adsorption isotherms of water on graphite: (a) G-25; (b) G-700; (c) G-1000. (Closed circle) First adsorption isotherm and (open circle) second one.

the first adsorption measurement, it took about 60 min for the attainment of the adsorption equilibrium after every dose of H_2O vapor. On the other hand, the first adsorption isotherm of H_2O on G-1000 lies over far from the second one. Moreover, the first adsorption isotherm goes irregularly; i.e., the adsorbed amount first increases linearly until the equilibrium pressure reaches 0.3 torr, where it takes about 40 min for the attainment of the adsorption equilibrium. After that the isotherm rises slowly and it takes 1–2 h for the adsorption equilibrium. Finally, the adsorbed amount increases abnormally near the equilibrium pressure of 12 torr. A small knee is found in the second adsorption isotherm on G-25, but it becomes smaller and at the same time the adsorbed amount decreases remarkably when the sample is pretreated at higher temperatures. In other words, the heat treatment of graphite results in the change in the shape of adsorption isotherm from type II to III according to Brunauer's classification.[25] This implies a remarkable enhancement of the surface hydrophobicity of graphite through heat treatment of the sample.

Figure 3 gives the histogram of the gas evolved from the samples which was measured after the second adsorption isotherm of H_2O. Here, the amount of gas is expressed in the number of molecules per nanometer squared. It is found from Figure 3 that the integrated amount of gas evolved from G-25 increases in the order H_2 > CO > H_2O, CO_2 > CH_4. In addition, the histogram of H_2O on G-25 has two peaks in the ranges 100–300 and 500–600 °C, and that of CO_2 also has two peaks in the ranges 200–300 and 500–600 °C, respectively. The desorption of CH_4 reveals

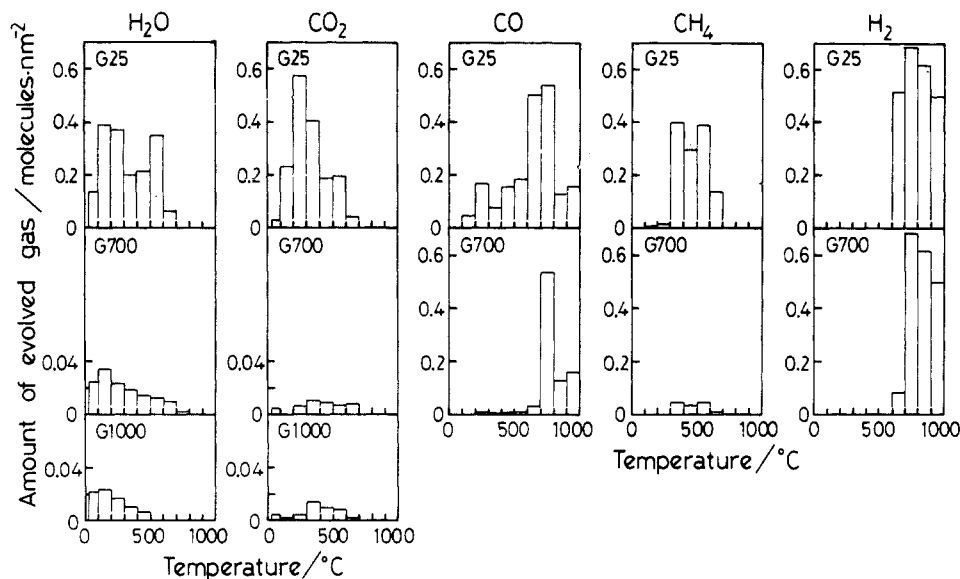(25) Brunauer, S.; Deming, L. S.; Deming, W. E.; Teller, E. *J. Am. Chem. Soc.* **1940**, *62*, 1723.

Figure 3. Amount of gas evolved from graphite when heated at every 100 °C interval of rising temperature. Integrated amounts of CO, CH_4, and H_2 evolved from G-1000 were found to be 0.117, 0.107, and 0.229 molecule/nm^2, respectively.

Table I. Monolayer Volume of Water V_m and Surface Contents of Gases

	$V_m{}^a$	surface content^a				
		H_2O	CO_2	CO	CH_4	H_2
G-25	1.740	1.710	1.644	1.952	1.233	2.294
G-700	0.349	0.134 (0.004)	0.039 (0.000)	0.882 (0.821)	0.126 (0.000)	1.949 (1.784)
G-1000	0.305	0.070 (0.000)	0.035 (0.000)	0.117 (0.000)	0.107 (0.000)	0.229 (0.000)

^{a} Expressed in molecules/nm^2 on the basis of N_2 area.

a broad peak in the temperature range from 300 to 600 °C. These three components cease to evolve at temperatures higher than 800 °C. On the other hand, the desorption of CO shows a large peak between 600 and 800 °C, increases at temperatures higher than 800 °C, and appears to continue even at temperatures over 1000 °C. H_2 is not desorbed till 700 °C and reveals a desorption peak near 700–800 °C. From the mass spectrometric measurement, Barton and Harrison confirmed the evolution of H_2, CO, CO_2, and H_2O during the course of ignition of graphite in vacuo,[26] whereas the present sample was found to evolve a large amount of CH_4 besides the other four kinds of gases.

After exposing the samples, G-700 and G-1000, to saturated H_2O vapor, an extra amount of every gas component was detected at temperatures below each pretreatment temperature, 700 or 1000 °C, as shown in Figure 3. This suggests that a small amount of surface compound is reproduced on exposing the sample to H_2O vapor.

For the calculation of the isosteric heat of adsorption q_{st}, we cannot utilize the first adsorption isotherms, because they include both chemisorbed and physisorbed water or because they are of irreversible character, while the second adsorption isotherms are reversible and therefore adequate for this purpose. The q_{st} curves calculated by applying the Clausius–Clapeyron equation to the second adsorption isotherms in Figure 2 are illustrated in Figure 4. The q_{st} values given in Figure 4 alter within the error of ±6.3 kJ/mol at the adsorption range less than 0.5, 0.2, and 0.05 molecules/nm^2 for G-25, G-700, and G-1000, respectively, while the error becomes very much smaller, i.e., less than ±2.1 kJ/mol, when the adsorbed amount exceeds the values indicated above. In spite of these experimental errors, we can perceive interesting results from Figure 4
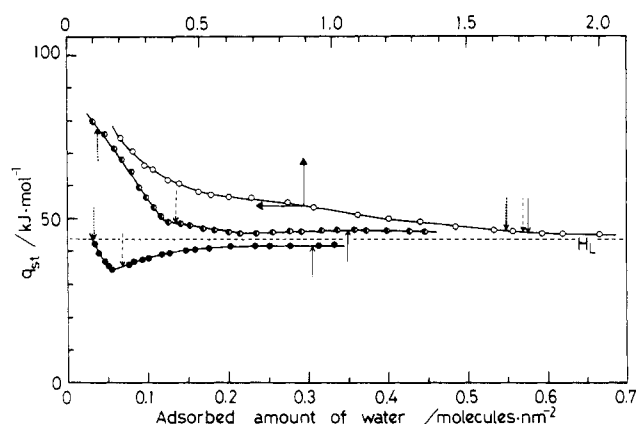
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Figure 4. Isosteric heat of adsorption of water q_{st} on graphite: (○) G-25; (◐) G-700; (●) G-1000. Arrows indicate V_m (solid line), H_2O content (broken line), and CO_2 content (dotted line). Horizontal broken line indicates heat of liquefaction of water at 25 °C (H_L).

as follows. The q_{st} value on G-25 decreases monotonously with increasing coverage θ of H_2O and approaches the heat of liquefaction H_L of H_2O, 43.99 kJ/mol at $\theta = 1$. The q_{st} value on G-700 initially decreases more sharply than that on G-25, approaches the H_L value at θ of about 0.5, and after that keeps those close to the H_L value. With G-1000, the q_{st} value drastically decreases and crosses the H_L value, passes a minimum near $\theta = 0.2$, and increases and approaches the H_L value. These results imply that from the viewpoint of interaction energy the surface hydrophobicity of graphite increases with increasing temperature of pretreatment. Young et al. reported that the q_{st} curve of H_2O measured on Graphon evacuated at 400 °C passes a minimum value less than the H_L value at $\theta = 1$.[4]

In Table I, the monolayer volume of H_2O V_m and the surface gas content are listed; the former was computed

Table II. Amounts of Acidic Surface Oxides

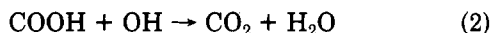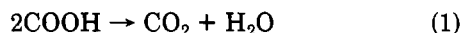|	acidic surface oxides[a]				
	carboxyl H_2O, CO_2	lactone CO_2	phenol H_2O, CO	carbonyl CO	total
G-25	1.12	0.28	0.94	1.02	3.36
G-700	0.00	0.00	0.09	0.62	0.71
G-1000	0.00	0.00	0.11	0.48	0.59

[a] Expressed in groups/nm^2 on the basis of N_2 area.

by applying the BET method to the second adsorption isotherms, and the latter was calculated as the sum of gas evolved from the pretreatment temperature to 1000 °C as shown in the bracket. As stated above, when a high-temperature-treated sample is exposed to H_2O vapor at room temperature, a small amount of surface compounds is reproduced. The amount of gas evolved from the reproduced compounds was also determined and added to the value in the bracket, and the sum of them is listed outside the bracket; the final value corresponds to the surface gas content of the sample used for the measurement of the second adsorption isotherm. The amount of reproduced compounds due to the exposure to H_2O vapor depends upon the pretreatment temperature of graphite as well as upon the nature of gas. When the pretreatment temperature is raised, the increment of H_2O, CO_2, and CH_4 decreases, while that of CO and H_2 increases.

Table II demonstrates the amount of the acidic surface oxides, measured by the neutralization with four kinds of bases.[20,24] Every kind of acidic oxide is on the surface of G-25 most, and decreases when the pretreatment temperature is raised. On the samples pretreated at temperatures over 700 °C, the carboxyl and lactone groups could not be detected. These data demonstrate that an increase in the surface hydrophobicity of graphite through the heat treatment is closely related to the concentration of acidic oxides.

Discussion

Decomposition of Acidic Surface Oxides. The gas evolved by heating the sample at higher temperatures can be considered to have come from surface oxides. The decomposition reactions of acidic surface oxides to form H_2O and CO_2 are as follows.[27-33]

$$2COOH \rightarrow CO_2 + H_2O \quad (1)$$

$$COOH + OH \rightarrow CO_2 + H_2O \quad (2)$$

$$COOH \rightarrow CO_2 \quad (3)$$

$$2OH \rightarrow H_2O \quad (4)$$

$$lactone \rightarrow CO_2 \quad (5)$$

Reaction 1[29,31] will occur when two carboxyls are present in adjacent sites.[21,34] However, this reaction seems to be unlikely on the suface of the present sample, because the density of carboxyls on the prism surface of G-25 is small,
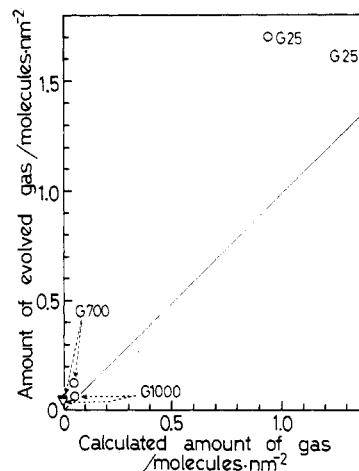
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Figure 5. Relation between amount of gas evolved by igniting sample and that calculated from decomposition reactions: (○) H_2O; (▽) CO_2.

2.54 groups/nm^2, as estimated by introducing the method of Barton et al.[13,26] Therefore, reaction 2[29,31] will take place at the first stage, since the surface density of phenolic hydroxyls is fairly large (Table II). As a result, the carboxyl or hydroxyl groups remaining after reaction 2 will decompose following reaction 3[21,28,29] or 4.[31] Since reaction 5[27,29-31] must occur independently, we can compute the amounts of H_2O and CO_2 formed by the decomposition of acidic surface oxides (Table II) following a series reaction 2, 3, and 5 or reaction 2, 4, and 5.

The amounts of H_2O and CO_2 thus calculated can be plotted against the amounts of H_2O and CO_2 evolved as determined by actually igniting the samples, as shown in Figure 5. If the two sets of data, obtained by the calculation from the amount of acidic surface oxides and by the ignition loss determination, are equal to each other, namely, if the 1:1 relationship holds between them, we can understand that all of acidic surface oxides determined by the titration have been decomposed into two kinds of gases, H_2O and CO_2, on igniting the samples according to the series reaction 1–4. However, the results obtained represent that actually determined amounts of H_2O and CO_2 are always larger than those calculated from the titration data; e.g., the latter values for H_2O and CO_2 on G-25 are about 55% and 85%, respectively, of the former ones. This may be due to the fact that basic oxides[21,35-37] are also present on the surface of graphite. We can suppose various reaction sequencies of the four reactions, (1)–(4), and try to plot the data similar to Figure 5. Though all of them are not cited here, it was proved that the analysis due to the reaction sequence (1)–(4) as shown in Figure 5 was closest to the 1:1 relationship.

Water Adsorption Sites on Graphite. In Figure 4, the monolayer volume V_m as well as the amounts of the evolved gases, H_2O and CO_2, are indicated by arrows, all of them being expressed in the number of molcules per nanometer squared. At a glance, it seems that the change in the shape of the q_{st} curve is closely related with these quantitites. First, the amount of evolved H_2O from G-1000 is very close to that of adsorbed H_2O at which the q_{st} minimum appears. Moreover, the amount of evolved CO_2 is very similar to that of adsorbed H_2O at which the q_{st}

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curve crosses the H_L value. These facts suggest that the initial adsorption of H_2O principally occurs on the sites that evolve H_2O and CO_2 simultaneously on heating the sample, i.e., a pair of carboxyl and phenol groups. As stated above, when the G-1000 sample is exposed to H_2O vapor, a small amount of surface oxygen compound is reproduced, and the amounts indicated by arrows for G-1000 in Figure 4 come from these compounds. After the pair sites of carboxyl and phenol groups have been covered by adsorbed H_2O molecules, the singly H_2O desorbing oxides will act as the adsorption sites for H_2O, which can be decomposed following eq 4. That the q_{st} value in this range of coverage is less than the H_L value may be due to the fact that the neighboring two hydroxyls are situated so that a stable adsorption of H_2O is difficult to occur on them. When θ exceeds 0.2, the adsorption of H_2O will occur on the preadsorbed H_2O, leading to cluster formation,[4,5,12,38,39] which results in an increase in the q_{st} value and finally it approaches the H_L value.

The q_{st} value of H_2O on G-700 initially decreases sharply with increasing θ, but it does not traverse the H_L level. At the knick point of the q_{st} curve, the amount of evolved H_2O is almost that of adsorbed H_2O. On the other hand, the amount of evolved CO_2 corresponds to a small value of adsorbed H_2O, at which the q_{st} value is higher than the H_L value. This feature is quite different from that shown on G-1000. The reason there appears such a difference between the q_{st} curves of the two samples, G-700 and G-1000, may be due to the difference in the contents of the CO-desorbing oxides on them. It has been reported that the CO-desorbing oxides on carbon act as the adsorption sites for H_2O[13] and that the q_{st} value of H_2O on the oxides of Graphon that comes off as CO is similar to the H_L value of H_2O.[12] Virtually, the CO content can be read from Table I to be 0.882 and 0.117 molecule/nm^2 on G-700 and G-1000, respectively. Thus, the CO content is extremely high on G-700 compared with that on G-1000, and exceeds the V_m value of H_2O. Therefore, it may be reasonable to infer that on the surface of G-700 the CO-desorbing oxides act as the adsorption sites for H_2O, cooperatively with the H_2O- and CO_2-desorbing sites. Thus, it follows that after the H_2O- and CO_2-desorbing oxides have been completely

covered with H_2O molecules, the q_{st} value of H_2O on G-700 remains almost constant and is similar to the H_L value.

The q_{st} value of H_2O on G-25 is considerably larger than those on G-700 and G-1000 over the whole range of θ, decreases gradually with increasing θ, and attains the H_L value at the point where the amounts of the evolved gases, H_2O and CO_2, and the V_m value are all equal to one another. No significant relationship has been discovered between the q_{st} value and the content of CH_4 or H_2, though their quantities are very large.

In conclusion, the q_{st} minimum lying under the H_L level has been found to appear only when the quantities of the H_2O- and CO_2-desorbing oxides as well as that of CO-desorbing ones are all extremely small. This should be demonstrated by other examples in the future.

Reaction between Graphite Surface and Water Molecules. As shown in Figure 2b,c, the first and second adsorption isotherms of H_2O on graphite treated at higher temperatures do not agree with each other, and it takes much time for the attainment of the adsorption equilibrium in the first adsorption process. At the same time, a small amount of surface oxygen compounds is found to be reproduced (Figure 3 and Table I). A series of these phenomena are closely related to each other as follows. Clearly, a long time duration for the establishment of the adsorption equilibrium is proof for chemisorption. The surface compounds reproduced by the chemisorption of H_2O will reasonably be the hydrophilic sites, i.e., the physisorption sites for H_2O, so that the chemisorption of H_2O results in an enhancement of the physisorption of H_2O. Evidently, this feature can be observed on G-1000 (Figure 2c), while on G-700 the situation seems to be different (Figure 2b). However, this discrepancy can be elucidated as follows. The chemisorption of H_2O on G-700 is so slow at room temperature that it can be accomplished with difficulty by exposing the sample to saturated H_2O vapor for a long time. Thus, the resulting surface can physisorb more H_2O than the unexposed surface.

Registry No. H_2O, 7732-18-5; graphite, 7782-42-5.

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