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The Relation between the Amounts of Chemisorbed and Physisorbed Water on Zinc Oxide

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In the system ZnO-H_2O, in which a jump appears in the adsorption isotherm, the relation between the amounts of chemisorbed and physisorbed water has been investigated, on the basis of the measurements of the water adsorption isotherms and the water content. The first adsorption isotherm of water was measured at 18°C on a sample degassed at 450°C. After degassing the sample again at 30°C, the second adsorption isotherm was obtained at the same temperature as before. The water content (V_h) on the surface of the sample was determined by the successive ignition-loss method. In the present system, the amount of water physisorbed in the first layer is composed of two parts: one (V_{p1}) is the amount adsorbed at lower vapor pressures, up to the beginning of the jump in the isotherm, and the other (V_{p2}), the amount adsorbed during the jump. The amount of water chemisorbed (V_c) during the adsorption process could be estimated as the difference between the monolayer capacities of the first and second isotherms, the total amount of chemisorbed water being the sum of V_h and V_c. The ratio of the total amount of physisorbed water ($V_{p1}+V_{p2}=V_p$), expressed in the number of water molecules per unit of area, to that of chemisorbed water (V_c+V_h), expressed in the number of hydroxyl groups per unit of area, was found to be about 1 : 1 in the first physisorption layer for all the samples tested, irrespective of their origin, while the ratio of V_{p1} to V_{p2} varied extensively with the origin of the samples.

The surface of most metal oxides adsorbs water molecules physically and chemically. In a previous paper,[1] it has been found in TiO_2 (rutile) and two kinds of α-Fe_2O_3 (hematite) that the ratio of the number of physisorbed water molecules in the monolayer to the number of surface hydroxyl groups (chemisorbed water) is about 1 : 2. The type of the water adsorption isotherms on these oxides was that of the polymolecular adsorption isotherm, whereas on zinc oxide the type of the isotherm has been found to be quite different from that on the other metal oxides:[2,3] the amount of water adsorbed increases remarkably in the relative pressure range of 0.2—0.3. No such phenomenon has been found in the other oxide-water systems; it was called the "hump" of the adsorption isotherm in previous papers.[2,3] The purpose of the present work is to ascertain the relation between the amounts of water physisorbed and chemisorbed on zinc oxide by analysing the adsorption isotherms, and to investigate the structure of the adsorption layer in this system.

Experimental

Materials. Three kinds of zinc oxide samples were used in the present work. One of them was the same sample as had been studied previously;[2-4] it was presented from Sakai Kagaku Co., being prepared by burning zinc metal in air (sample A). The second sample was made by the pyrolysis of zinc hydroxide in air, the latter being precipitated by mixing 0.37M ammonia water with a 0.34M zinc-nitrate solution. In the present procedure, the precipitate of zinc hydroxide was first washed sufficiently with distilled water, dried at 100°C, and then calcined at 500°C for 4 hr (sample B). The last sample was prepared from zinc oxalate precipitated by mixing 0.20M zinc-nitrate and 0.22M oxalic-acid solutions. This precipitate was treated in the same way as sample B, and was finally calcined at 500°C for 4 hr (sample C). From X-ray analysis, the sample B and C were found to be only pure zinc oxide, their crystallinity being to the same extent as that of the sample A.

Surface-area Measurement. The specific surface area of the ZnO samples was determined by applying the BET theory to the nitrogen adsorption data which had been obtained at the temperature of liquid nitrogen; the cross-sectional area of a nitrogen molecule was assumed to be 16.2 Å^2.

Water-adsorption Isotherm. The adsorption isotherms of water on the surfaces of ZnO samples were

1) T. Morimoto, M. Nagao and F. Tokuda, *J. Phys. Chem.*, **73**, 243 (1969).

2) T. Morimoto, M. Nagao and F. Tokuda, This Bulletin, **41**, 1533 (1968).

3) M. Nagao and T. Morimoto, *J. Phys. Chem.*, **73**, 3809 (1969).

4) T. Morimoto, M. Nagao and M. Hirata, *Kolloid-Z. Z. Polym.*, **225**, 29 (1968).

determined volumetrically by using a usual adsorption apparatus equipped with an oil manometer. About a 10-m² sample was used in each measurement. Initially, the sample was degassed at 450°C under a reduced pressure of 10^{-5} Torr for 4 hr, and then the adsorption isotherm of water was measured at 18°C. After the first adsorption isotherm had been obtained, the sample was degassed at 30°C in order to remove only the physisorbed water;[2,5-8] the measurement of the second adsorption isotherm was then carried out at the same temperature as before. The adsorption equilibrium was attained within 30 min after each dose of water vapor. A preliminary experiment of desorption was done on each sample; it revealed no hysteresis, indicating that the samples used were nonporous.

Water-content Measurement. It has become clear that the surfaces of metal oxides placed in an atmosphere have water molecules adsorbed both physically and chemically. The physisorbed water can be removed *in vacuo* at relatively low temperatures, *i. e.*, even at room temperature, whereas the surface hydroxyl groups (chemisorbed water) can be removed only gradually at higher temperatures. The temperature at which the removal of the surface hydroxyl groups starts has been found to vary with the nature of the metal oxides, and to be about 200°C in the case of ZnO.[2] The amount of chemisorbed water, that is, the water content (V_h), on the surfaces of ZnO samples was determined by the successive ignition-loss method[1,9] using the same apparatus as that used for the water-adsorption measurement: the sample was heated at various temperatures *in vacuo*, and the gas evolved at every stage of the treatment was measured volumetrically.

When the ZnO sample was treated *in vacuo* at elevated temperatures, a small amount of a gas other than water vapor was found. The gas expelled was condensed in a vessel kept in liquid nitrogen, and was determined volumetrically in the measuring system after having been re-evaporated at room temperature. Next, when the gas was allowed to condense again at −72°C, a small part of the gas was found to remain uncondensed. When only the water vapor was present in the gas, however, this procedure did not leave a uncondensed gas phase. Mass spectroscopy showed that this uncondensed gas was, for the most part, composed of carbon dioxide. The values (V_h) given in Table 1 are the true water content; they do not include the amount of gas uncondensed at −72°C.

Results and Discussion

The first and second adsorption isotherms of water on ZnO at 18°C are given in Figs. 1, 2, and 3. The sample A shows a remarkable jump in its adsorption isotherm in the relative pressure range of 0.2—0.3, as has been observed in the previous works.[2,3] From Figs. 2 and 3 it is clear that, in the cases of the samples B and C, the jumps are considerably smaller than that of the sample A, though they all appear in the same pressure region. These results present important problems yet to be solved concerning the adsorption properties of the

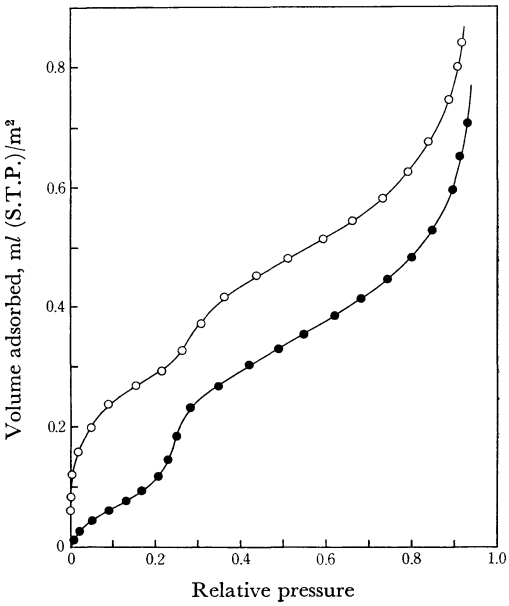

Fig. 1. Adsorption isotherms of water at 18°C on sample A: ○, first adsorption; ●, second adsorption.

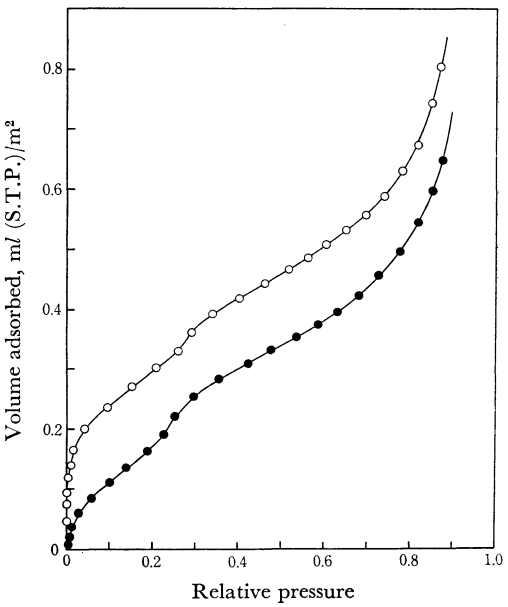

Fig. 2. Adsorption isotherms of water at 18°C on sample B: ○, first adsorption; ●, second adsorption.

5) F. H. Healey, J. J. Chessick and A. V. Fraioli, *J. Phys. Chem.*, **60**, 1001 (1956).
6) G. Srinivasan, J. J. Chessick and A. C. Zettlemoyer, *ibid.*, **66**, 1819 (1962).
7) J. J. Jurinak, *J. Colloid Sci.*, **19**, 477 (1964).
8) V. Pravdic, E. McCaffery and A. C. Zettlemoyer, *Surface Sci.*, **7**, 380 (1967).
9) T. Morimoto, K. Shiomi and H. Tanaka, This Bulletin, **37**, 392 (1964).

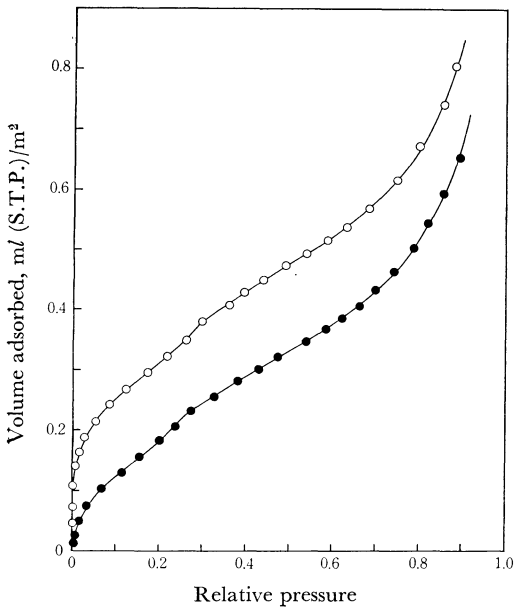

Fig. 3. Adsorption isotherms of water at 18°C on sample C: ○, first adsorption; ●, second adsorption.

system ZnO–H_2O: (1) a jump appears on the adsorption isotherm at relative pressures of 0.2—0.3, (2) the height of the jump depends on the origin of the samples, and (3) the relation between the amounts of physisorbed and chemisorbed water is unclear. The former two problems will be discussed in detail in subsequent papers. Here, mainly the last problem will be dealt with, using, for comparison, the data on the other oxides reported previously.[1]

As was reported in the previous paper, the amount of adsorbed water on metal oxide evacuated at an elevated temperature increases with a rise in the pretreatment temperature. Furthermore, it was found that the adsorption isotherms can be treated by the BET method; the plot of the resulting V_m values against the pretreatment temperature suggests the temperature at which the removal of the chemisorbed water starts.[2] In other words, on the surfaces of metal oxides degassed at elevated temperatures, the chemisorption and physisorption of water occur simultaneously, whereas only the physisorption occurs on the surfaces treated at room temperature.[2,5-8] A conventional application of the BET theory to the first adsorption isotherms of water on various kinds of metal oxides, including both physisorbed and chemisorbed water, has given the monolayer capacity.[5-8] Also, in the present system we can apply the BET theory to the initial part of the isotherms and thus obtain the monolayer capacity. Thus, the V_m value in Table 1 is the monolayer capacity calculated from the first adsorption isotherm, and the V_{p_1}, that calculated from the second one. As has been described above, the former should include the physisorbed and chemisorbed water, whereas the latter, only the physisorbed water. The difference between the values V_m and V_{p_1}, therefore, will indicate the amount of water chemisorbed during the adsorption process. V_c in Table 1 is this amount of chemisorbed water expressed in terms of the number of hydroxyl groups per 100 Å^2 of the surface, by taking into account the fact that one water molecule forms two hydroxyl groups. V_h is the surface water content, being the amount of the water chemisorbed on the surface just before the adsorption process. The sum of V_c and V_h is, therefore, the total amount of water chemisorbed after the adsorption process; this water may act as the sites for the physisorption of water molecules.

On the other hand, by applying the B-point method to the second adsorption isotherm, we can obtain the overall monolayer capacity of physisorption. This value is listed in the V_p column in Table 1. The V_p value may be considered to be composed of two parts: one is the initial part of the adsorption isotherm (V_{p_1}), as has been calculated above, while the other is the part of the jump, the latter being obtained by subtracting V_{p_1} from V_p. Thus, V_{p_2} is the second part of physisorption. In conclusion, the chemisorbed water layer is present as a substrate on which the water molecules are adsorbed physically. Here, we can estimate the relation between the numbers of the molecules present in the two layers up to the attainment of the B point.

This ratio is given in the last column of Table 1, in which the total amount of physisorbed water is

Table 1. The relation between the amounts of chemisorbed and physisorbed water on ZnO

Sample	Calcn. temp. (°C)	Surface area (m^2/g)	V_m (ml(S.T.P.)/m^2)	Physisorbed amount (H_2O molecules/100Å^2)			Chemisorbed amount (OH groups/100Å^2)			$V_p/(V_c+V_h)$ (H_2O/OH)
				V_{p_1}	V_{p_2}	V_p	V_c	V_h	V_c+V_h	
A	—	4.79	0.247	3.47	4.52	7.99	6.27	1.10	7.37	1.08
B	500	1.97	0.308	5.70	1.16	6.86	5.17	3.20	8.37	0.82
C	500	11.3	0.290	5.25	2.15	7.40	5.11	2.48	7.59	0.97
A	—	4.79	0.247	—	—	4.92	6.27	1.10	7.37	0.67

expressed in H_2O molecules/100 Å^2, and that of the underlying chemisorbed water, in OH groups/100Å^2. It may be seen from Table 1 that the ratio is about 1 : 1 for every sample tested.

It is well known that the crystal of ZnO is of the same type as wurtzite. The numbers of the zinc atom on the (0001) and (10$\bar{1}$0) planes, both of which are known to have excellent cleavage,[10,11] can be estimated crystallographically to be 11 and 6/100 Å^2 respectively. If we assume that these two kinds of planes are equally present on the actual surfaces, and that a surface hydroxyl group is bonded to a zinc atom, the total amount of chemisorbed water will become to about 8.5 OH groups/100 Å^2; this figure agrees fairly well with the results in Table 1. Furthermore, the experimental results show that the water molecules are adsorbed on these surface hydroxyl groups in the ratio of 1:1. If the molecular area of water is assumed to be 10.8 Å^2, as usual, it is found that the number of water molecules of 7—8/100 Å^2 is suitable to be adsorbed as a monolayer. When we calculate the ratio of each physisorbed amount, V_{p_1} or V_{p_2}, to the total amount of chemisorbed water, they are very different from each other, depending on the origin of the samples. With the sample A, V_{p_1} is smaller than V_{p_2}, whereas the situation is quite the reverse with the samples B and C; the value of V_{p_2} is only 20% of the value of V_{p_1} in the case of the sample B and only 41% in the case of the sample C respectively, corresponding to the smaller jump in the isotherms with the two samples than with the sample A. Here it is noticeable that the larger the V_{p_1} value, the smaller the V_{p_2} value.

In the cases of α-Fe_2O_3 (hematite) and TiO_2 (rutile), which give the polymolecular adsorption isotherm of water, the ratio of the amounts of physisorbed to chemisorbed water has been found to be nearly 1 : 2, as has been reported previously.[1] In the present work, we could not prepare the sample of ZnO, which gives a usual polymolecular adsorption isotherm of water, though Egorov *et al.*[11] obtained a sample of ZnO in which the jump was not observed in the water adsorption isotherm. It can be seen from Fig. 4 that the second adsorption isotherms of the three samples agree fairly well with one another in the range of relative pressures higher than 0.3 (*i. e.*, above the "B-point"), but at lower relative pressures they are quite different, depending on the origin of the samples. The results show that V_{p_2} decreases when V_{p_1} increases, the sum of V_{p_1} and V_{p_2} keeping almost constant. From the features of the adsorption isotherms observed here, we can

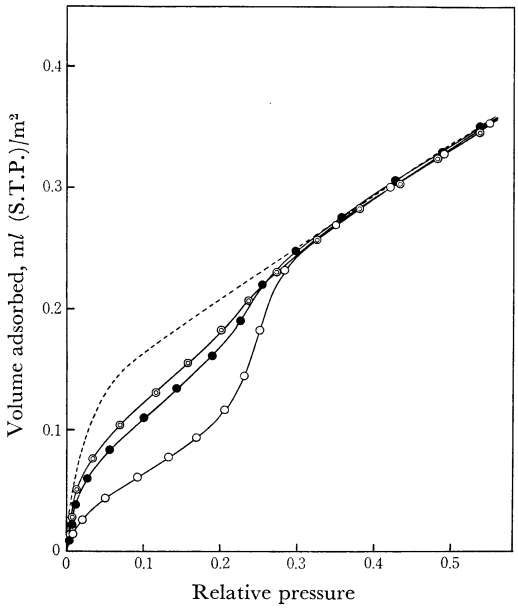

Fig. 4. Second adsorption isotherms of water at 18°C on ZnO samples: ○, sample A; ◎, sample B; ●, sample C; dotted line represents a hypothetical isotherm.

expect, as the limiting case, an adsorption isotherm in which the jump does not appear. The curve expressed by the dotted line in Fig. 4 shows this hypothetical isotherm, which is obtained by extrapolating the upper part of the real isotherms to the lower pressures. By applying the BET theory to this hypothetical isotherm, we can obtain the V_m value and calculate the other quantities as being similar to those obtained in the preceding paper.[1] The values thus obtained are given in the bottom row of Table 1. As a matter of fact, when the initial adsorption amount increases, the slope of the linear part of the adsorption isotherm after the attainment of the monolayer coverage often tends to fall. Therefore, the hypothetical isotherm may scarcely be realized unless all the features of the isotherm are changed. However, there is a great indication in Table 1 that if we prepare a sample of ZnO which does not reveal the jump in the water adsorption isotherm, we can expect the ratio of H_2O : OH to rise to 1 : 2.

Fisher and McMillan[12] and Ross *et al.*[13–17] studi-

10) S. Dana and W. E. Ford, "A Textbook of Mineralogy," John Wiley, New York, N. Y. (1960), p. 480.

11) M. M. Egorov, N. N. Dobrovol'skii, V. F. Kiselev, G. Furman and S. V. Khrustaleva, *Zh. Fiz. Khim.*, **39**, 3070 (1965).

12) B. B. Fisher and W. G. McMillan, *J. Amer. Chem. Soc.*, **79**, 2969 (1957).

13) S. Ross and W. Winkler, *ibid.*, **76**, 2637 (1954).

14) S. Ross and H. Clark, *ibid.*, **76**, 4291, 4297 (1954).

15) S. Ross, J. P. Olivier and J. J. Hinchen, *Advan. Chem. Ser.*, **33**, 317 (1961).

16) J. P. Olivier and S. Ross, *Proc. Roy. Soc.* (London), *Ser. A*, **265**, 447 (1962).

17) W. D. Machin and S. Ross, *ibid.*, *Ser. A*, **265**, 455 (1962).

ed the adsorption isotherms on systems containing a nonpolar adsorbent with homotattic surfaces and found that the nonpolar molecules adsorbed on such surfaces behave like a mobile film according to the two-dimensional van der Waals equation. Furthermore, when the pressure exceeds a limiting value, the film give rise to a two-dimensional phase transition, resulting in a sudden change to a close-packed state of the adsorbed molecules. Also, in the present system a similar circumstance may hold between the surfaces of the ZnO and the water molecules: the amount of water physisorbed on the homotattic layer of surface hydroxyl groups on ZnO is depressed initially, but increases steeply to the adsorption ratio of 1 : 1 (H_2O : OH) when the vapor pressure exceeds a certain value.

Usually, the surfaces of most metal oxides are considered to be inhomogeneous, and it has been reported that, on such surfaces, the adsorption of molecules first occurs on the highest energy sites and later on successively lower energy sites. Moreover, on such surfaces no jump in the adsorption isotherm appears and the stable ratio of H_2O : OH is 1 : 2 in the first layer of adsorption.[1] On the contrary, the present system shows depressed adsorption at lower pressures and a stable ratio of 1 : 1 (H_2O : OH). Also, this comparison makes it possible to predict that the surfaces of ZnO may be homotattic for the physisorption of water molecules. Further investigations will appear in the next paper.