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The Surface Properties of Rutile Prepared by the Hydrolysis of Titanium Tetrachloride. I. The Heat of Immersion in Water

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The surface properties of rutile prepared by hydrolyzing titanium tetrachloride have been studied by measuring the heat of immersion in water as a function of the outgassing temperature. The heat of immersion showed an extremely large value at outgassing temperatures between 300 and 400°C. However, when the rutile was calcined at 800°C, it showed a heat-of-immersion curve similar to those hitherto reported. In order to examine the phenomenon found on uncalcined rutile, the amounts of water physically and chemically adsorbed on the surface were estimated by measuring the water-vapor adsorption. We found that hydroxyl groups were formed in bulk as well as on the surface by means of the chemisorption, resulting in the formation of a hydrous structure because of the low crystallinity of the sample at temperatures below 400°C.

It is well known that the surface hydroxyl groups on such metal oxides as SiO_2, TiO_2, and Al_2O_3 are removed by thermal treatment *in vacuo*, resulting in the formation of an activated oxide structure, $\mathrm{Me}\langle{}^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Me}$, as a result of the condensation of the adjacent hydroxyl groups. The activated site may be rehydrated easily by the adsorptiom of water or may be stabilized by calicing at an elevated temperature. From our examinations of the heat of immersion, the water content, and the features of the adsorption of water, it seems that the nature of the activated site depends also on the nature of the substrate oxide.[1] So far, a number of studies on the heat of immersion of titanium dioxide have been performed by many workers. As for rutile, some studies have been done on samples calcined at high temperatures,[2-4] but none on uncalcined samples.

In the present work, the surface properties of titanium dioxide pretreated at various temperatures from 100 to 800°C *in vacuo* were examined by measuring the heats of immersion in water for uncalcined-rutile samples as well as for calcined ones. The uncalcined samples gave a relation between the heat of immersion and the outgassing temperature different from the results hitherto reported on calcined samples;[1-4] that is, an extremely large maximum occurred at about 300°C. In order to investigate the phenomenon in detail, the adsorption of water was measured for those samples. As a result, it was revealed that the hydroxyl groups were formed in bulk as well as on the surface by means of the chemisorption of water.

Experimental

Material. Three kinds of rutile samples were prepared by the hydrolysis of titanium tetrachloride as follows. An aqueous solution of 1 M titanium chloride was heated at 90°C for 12 hr with vigorous stirring until the deposition of the precipitate had stopped. The precipitate was then washed with distilled water, purified further by means of electrodialysis in order to remove the chloride ions, and then dried at 100°C for two days in air (Sample I). By X-ray analysis this sample was proved to be a rutile modification. The second sample was prepared by calcining Sample I at 800°C for 1 hr in air; then it was exposed to saturated water vapor for a week at room temperature (Sample II). The third sample was obtained by heating Sample II again to 800°C and by then keeping it at that temperature for 1 hr in air. The resulting product was steeped in water and dried at room temperature (Sample III).

The measurements of the differential thermal analysis of Samples I and II were carried out at various temperatures, from 20 to 800°C, in air. A large endothermic peak appeared around 110°C on Sample I, but did not on Sample II. This peak is considered to be connected with the dehydration.

Prior to carrying out the following measurements, each sample was pretreated at various temperatures between 100 and 800°C for 3 hr in a vacuum of 10^{-5} Torr.

Surface Area. The surface areas of the samples were determined from the nitrogen adsorption at 77°K by the conventional B.E.T. method, assuming the area of a nitrogen molecule to be 16.2 Å^2.

Water Content. The water vapor desorbed from the sample by evacuating at a given temperature was condensed in a trap cooled by liquid nitrogen, evaporated in a given system, and then recondensed in a trap cooled by dry ice. The water content of the sample was determined by

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[1] T. Omori, J. Imai, M. Nagao, and T. Morimoto, This Bulletin, **42**, 2198 (1969).

[2] W. H. Wade and N. Hackerman, *J. Phys. Chem.*, **65**, 109 (1961).

[3] A. C. Zettlemoyer, R. D. Iyengar, and P. Scheidt, *J. Colloid Interface Sci.*, **22**, 172 (1966).

[4] T. Morimoto, M. Nagao, and T. Omori, This Bulletin, **42**, 943 (1969).

measuring the amount of reevaporated water volumetrically, assuming the water content at 800°C to be zero.

Heat of Immersion. The heats of immersion of the samples in water were measured at 25°C by using a calorimeter equipped with an automatic recorder; the details have been described elsewhere.[5] In order to prevent the effect of organic contaminants, the sample was outgassed with a liquid nitrogen trap just before the sample.[6]

Water-vapor Adsorption. The adsorption of water vapor on the surface was measured at 25°C gravimetrically by using a Cahn RG electrobalance. After the first adsorption isotherm had been obtained on the sample, this sample was outgassed at 25°C for 24 hr in a vacuum of 10^{-5} Torr in order to remove all the physically-adsorbed water. Then the second adsorption isotherm was determined at 25°C. A series of the first and second adsorption isotherms of water vapor on Sample I outgassed at various temperatures was obtained.

Results and Discussion

Surface Area. The specific surface areas of the three samples are shown in Fig.1 as a function of the outgassing temperature. The surface area of Sample I decreases remarkably as the outgassing temperature rises from 200 to 800°C, whereas that of Sample II is almost constant. The surface area of Sample III was determined at only one temperature because it was considered to be independent of the outgassing temperature, as was the case of Sample II. The progressive decrease in the surface area of Sample I suggests that sintering occurs even at low temperatures such as 300°C. The particle size of Sample I, estimated by using the Scherrer equation from the half-value breadth of the X-ray diffraction line from the (110) plane, increased from 33 to 186 Å with a rise in the outgassing temperature from 100 to 800°C. The surface area was calculated by assuming the shape of the particle to be spherical in order to compare it with the results of nitrogen adsorption, S_N. The resulting values, which are shown in Fig. 1, have the same tendency with regard to the effect of the temperature as in the case of S_{N_2}. However, these values are considerably larger than the nitrogen area. This implies that Sample I does not take as characteristically porous a structure as a result of the removal of water molecules as does Al_2O_3.[7] Therefore, outgassing at higher temperatures may make the particle grow in size, resulting in a decrease in the surface area.

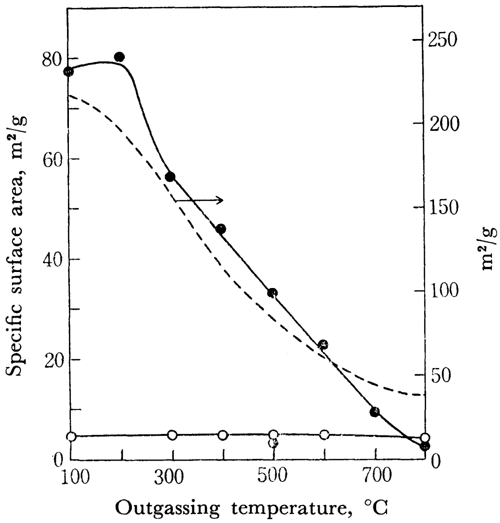

Fig. 1. Specific Surface area obtained from the adsorption of nitrogen as a function of the outgassing temperature; ●: Sample I, ○: Sample II, ◑: Sample III. Dotted line shows the specific surface area of the sample I estimated from the particle size.

Water Content. The water contents of Samples I and II are shown in Fig. 2, where the amounts of water are expressed by the number of hydroxly groups per unit of surface area, S_N. The fact that the amount of water in Sample I was much larger than that in Sample II was supported by the endothermic peak in the differential thermal analysis. The smaller surface area of Sample I at 100°C than at 200°C in Fig.1 may be due to the insufficient desorption of the water which may be present in the capillary, such as in the contacting zone among particles. The large water content may be one of the factors in the sintering at low temperatures.

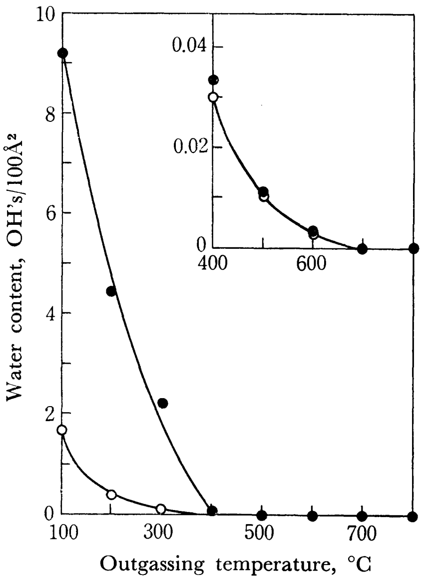

Fig. 2. Water content of rutile as a function of the outgassing temperature; ●: Sample I, ○: Sample II.

Heat of Immersion. Figure 3 shows the relation between the heats of immersion of the three samples in water and the outgassing temperature. Sample I revealed an extremely large heat-of-immersion value at temperatures between 300 and 400°C. The heat of immersion of Sample II was approximately constant above 400°C and did not reveal a maximum. Sample III, however, showed a maximum in its heat-of-immersion curve at a temperature between 400 and 500°C; this curve is similar to that reported by Morimoto *et al.*[3] From these results it is clear that

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[5] M. Miura, H. Naono, T. Iwaki, T. Kato, and M. Hayashi, *Kogyo Kagaku Zasshi*, **69**, 1623 (1966).

[6] T. Iwaki and M. Miura, This Bulletin, **44**, 1754 (1971).

[7] D. Aldcroft, G. C. Bye, J. G. Robinson, and K. S. W. Sing, *J. Appl. Chem.*, **18**, 301 (1968).

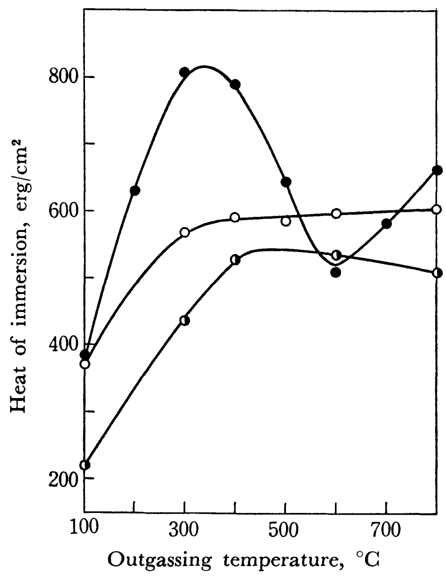


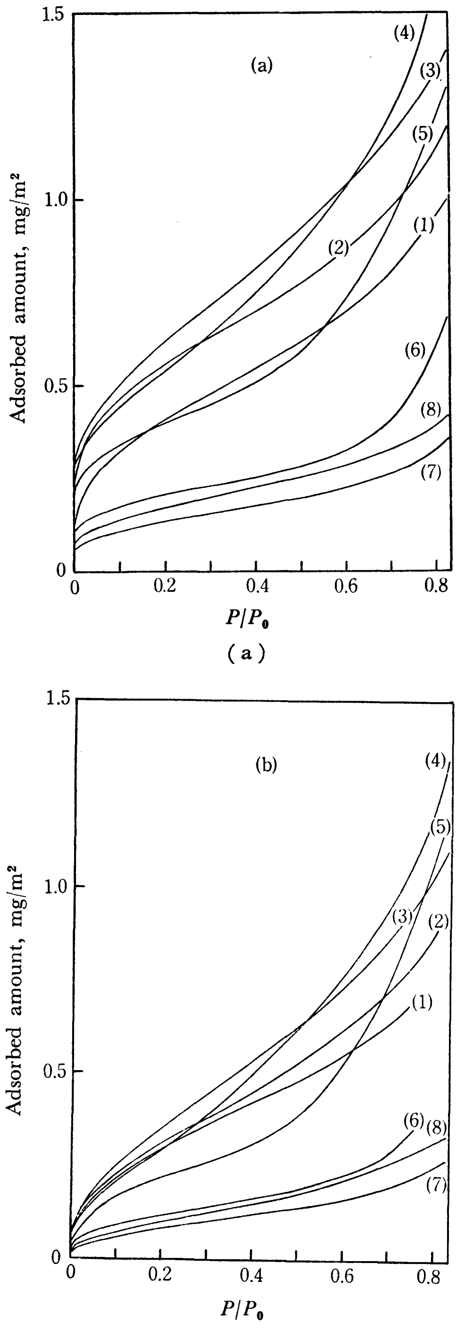
Fig. 3. Heat of immersion of rutile in water as a function of the outgassing temperature; ●: Sample I, ○: Sample II, ◑: Sample III.

the heat of immersion depends remarkably on the initial calcination of the sample.

The appearance of a maxiumm in the heat-of-immersion curve has generally been explained as being caused by the stabilization of the surface oxo-structure during the treatment at high temperatures *in vacuo*. This explanation is applicable to the behavior of Sample III, since it was calcined at a high temperature and may have a well-defined surface oxo-structure. However, it seems strange that an extremely large maximum in the heat-of-immersion curve was found for the sample treated at a low temperature. In order to investigate this phenomenon in detail, the adsorption of water on the surface of Sample I was examined as follows.

Water Adsorption. Figures 4a and 4b show, respectively, the first and second adsorption isotherms of water vapor on the surface of Sample I outgassed at various temperatures between 100 and 800°C. The ordinate in the figure represents the amount of water adsorbed per unit of area, S_{N_2}. The second isotherm obtained lies below and nearly parallel to that of the first run. The difference between these two curves is regarded as the amount of the water adsorbed chemically on the surface as hydroxyl groups. The second isotherm indicates the water adsorbed physically on the hydroxyl groups formed on the surface.

Both the first and second isotherms of the sample outgassed at 300°C indicate the largest adsorbed amounts of all; this phenomenon is similar to that of the heat of immersion, where the maximum occurs at a temperature between 300 and 400°C. By applying the BET method to the second isotherm, the monolayer volume of the physically adsorbed water was calculated. The amount of the hydroxyl groups formed by the chemisorption was estimated from the difference in the initial weights of the two samples on which the first and second adsorption runs were performed. This amount is almost consistent with that obtained from the difference in the amounts of water adsorbed at a high pressure in the two isotherms. The number of the physically-adsorbed water molecules and that of the hydroxyl groups per unit of area obtained from the nitrogen adsorption are plotted in Fig.5 as functions of the outgassing temperature. In the figure there is also plotted the total number of hydroxyl groups per nitrogen area, which is the sum of the amount of the chemisorbed water and the water content. From this figure, it may be considered that the large heat of immersion at about 300°C is attributable



(a)

(b)

Fig. 4. Adsorption isotherms of water on rutile (Sample I) outgassed at various temperatures; (1) 100, (2) 200, (3) 300, (4) 400, (5) 500, (6), 600, (7) 700, (8) 800°C.
(a) First adsorption isotherms, (b) Second adsorption isotherms.

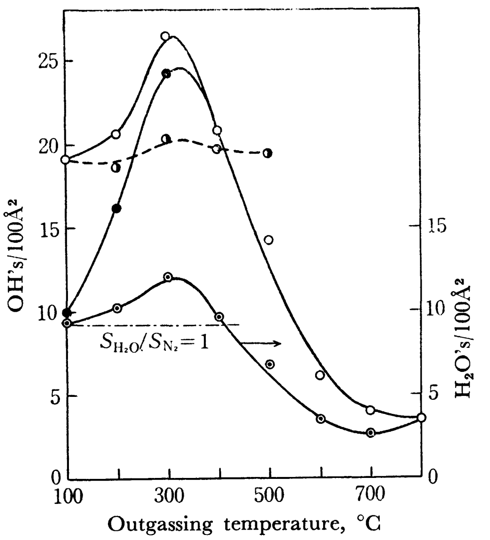
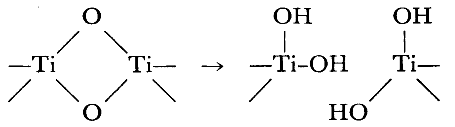


Fig. 5. Amounts of physically and chemically adsorbed water on the surface as a function of the outgassing temperature; ●: the number of hydroxyl groups formed by chemisorption per nitrogen area, ⊙: the number of physically adsorbed water per nitrogen area, ○ and ◑: total hydroxyl groups obtained by summing the chemically adsorbed water and water content per nitrogen area and water area respectively. Dotted line (—·—·—) shows that water area, S_{H_2O}, coincides with nitrogen area, S_{N_2}, at the amount of 9.3 H_2O's/100 Å^2.

mainly to the chemisorbed water.

It should be noted that the total number of hydroxyl groups per unit of area at temperatures between 100 and 500°C is too large to be accommodated to the monolayer coverage because the number of the hydroxyl groups corresponding to the monolayer coverage is 12/100 Å^2, which is calculated by assuming the radius of the hydroxyl group to be 1.45 Å.[8] There is the possibility that the true surface area of the sample is not evaluated by the nitrogen adsorption. Therfore, the surface area, S_{H_2O}, was estimated from the monolayer volume of the physically-adsorbed water by assuming the cross-sectional area of the water molecule to be 10.8 Å^2. The ratio of the water area, S_{H_2O}, to the nitrogen area, S_{N_2}, is related to the amount of the physically-adsorbed water per nitrogen area, as is indicated in Fig. 5. The water area exceeds the nitrogen area in the outgassing temperature range from 100 to 400°C and shows a maximum at about 300°C. The total number of hydroxyl groups per unit of water area is also plotted in Fig. 5; the number at 300°C is about 20/100 Å^2.

The surface of Sample I, when evacuated at a low temperature, may have an ill-defined oxo-structure because of the low crystallinity of the surface. When water molecules adsorb on such a surface, the hydroxyl groups may be formed in bulk as well as on the surface, resulting in the formation of hydrous titanium dioxide in part as in the following scheme:



This reaction is irreversible; in other words, the unhydrated state produced by evacutaion does not return to the original unevacuated state, since the evacuation destroys the structure of the latter state. As the average number of titanium atoms exposed on the surface of rutile modification is 8/100 Å^2,[9] it is calculated that about two or three hydroxyl groups combine with one titanium atom at temperatures below 400°C. This reaction may not occur on the stabilized surface oxo-groups, since the number of hydroxyl groups and also the heat of immersion decrease remarkably above 400°C. Above this temperature, the sample will form the more stable rutile structure in bulk and stabilized oxo-groups on the surface. As a consequence, the rehydration of the surface titanium atoms may be retarded, resulting in a decrease in the heat of immersion. The surface area of S_{H_2O} larger than S_{N_2} around 300°C may be responsible for the large number of hydroxyl groups on the surface, since water molecules adsorb physically on the hydroxyl groups.

Smaple I was tinged bluish gray when evacuated above 600°C. This color change has been considered to be caused by the removal of oxygen atoms from the surface.[10] Samples II and III also underwent a color change at high temperature, but it was slight compared with that of Sample I. The increase in the heat of immersion of Sample I above 600°C may be due to the contribution of the oxygen vacancy and the resulting distorted structure of the surface to the heat value.

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[8] J. A. A. Ketellar, "Chemical Constitution," Elsevier Pub. Co., Amsterdam (1958), p. 29.

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

[10] C. M. Hollabaugh and J. J. Chessick, *ibid.*, **65**, 109 (1961).