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Heat of Immersion of Titanium Dioxide in Water. I. The Effect of the Hydration Treatment of Titanium Dioxide

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On anatase and rutile, three samples which differ in the extent of hydration treatment have been prepared, and the surface area, the water content, and the heat of immersion have been measured. The hydration treatment of the sample increases the water content of the sample and lowers the sintering temperature. These facts suggest that the condensation dehydration of surface hydroxyl groups from the facing surfaces of contacting particles is effective for sintering. The plot of the heat of immersion *vs.* the pretreatment temperature shows a maximum at about 400°C, and the heat of immersion is larger in the sample subjected to heavy hydration treatment. The heat of surface hydration, calculated from the plot of the heat of immersion *vs.* the water content, does not vary with the hydration treatment; it averages 25.2 and 19.0 kcal/mol H_2O for anatase and rutile respectively.

It has been clarified that, on the surfaces of metal oxides, there exist hydroxyl groups which have a great influence on such surface chemical properties as surface electrification, hydrophilicity, adsorbability, and catalytic action. Recently, investigations have been made of the chemical properties of the surface hydroxyl groups themselves from the following two points of view: first, the temperature at which the surface hydroxyl groups start to desorb *in vacuo*,[1,2] and second, the rate at which the surface hydroxyl groups are formed.[3,4] These properties seem to depend on the nature of the substrate oxides. The same situation may also be expected in properties other than those just described.

The value of the heat of immersion of metal oxides is affected by the combination of solid and liquid, and by the origin and the history of the solid. So far it has been discovered that the particle size of the powdered sample and the heat treatment of the sample performed just before the calorimetric measurement greatly influence the heat of immersion, and that these circumstances make it impossible to consider the heat-of-immersion value as inherent in the solid substance.[5,6] Of course, the coatings on the solid surface modify the oxide surface properties.[7] Of these factors, the pretreatment of the sample at elevated temperatures serves to modify the surface properties by removing the surface hydroxyl groups. Most plots of the heat of immersion in water against the pretreatment temperature reveal a maximum.[6,8-11] The appearance of the maximum has been explained in terms of the cooperative effect of the formation of surface hydroxyl groups and the physical adsorption of water on them. By analyzing the heat of immersion, therefore, we can obtain the heat of surface hydration, that is, the heat of the formation of surface hydroxyl groups.

In the present paper the heat of immersion of titanium dioxide in water has been measured in order to investigate the effects of the hydration treatment of the samples on the heat-of-immersion value obtained and on the heat of surface hydration calculated therefrom. As a result, it has been found that the hydration treatment has a great influence on the sintering of particles, and that it causes the heat-of-immersion value to vary considerably, while it scarcely affects the heat of surface hydration.

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[2] T. Morimoto, M. Nagao and F. Tokuda, *ibid.*, **41**, 1533 (1968).

[3] T. Morimoto and M. Nagao, *Kolloid-Z. u. Z. Polymere,* **224**, 62 (1968).

[4] to be published.

[5] W. H. Wade and N. Hackerman, *J. Phys. Chem.*, **64**, 1196 (1960).

[6] W. H. Wade and N. Hackerman, *ibid.*, **65**, 1681 (1961).

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[8] G. J. Young and T. P. Bursh, *J. Colloid Sci.*, **15**, 361 (1960).

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[10] T. Morimoto, K. Shiomi and H. Tanaka, This Bulletin, **37**, 392 (1964).

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Experimental

Materials. Both the samples used in the present work, anatase and rutile, presented by the Teikoku Kako Co., had been made from titanium sulfate and were free from coatings. These original samples were treated repeatedly with 0.1 N nitric acid to remove basic impurities, and with 0.1 N ammonia water to remove acidic impurities, and then washed with distilled water; finally, the method of electrodialysis was used to clear them of electrolytes as completely as possible. The resulting samples were dried at 110°C for 10 hr in an oven (AI and RI).

A part of each sample (AI and RI) was treated at 800°C for 4 hr in air, and then exposed to saturated water vapor for 5 days at room temperature (AII and RII).

Another part of each sample (AI and RI) was further immersed in hot water at 80°C for 3 days in order to prepare a highly-hydrated sample (AIII and RIII). The samples AII, AIII, RII, and RIII were finally dried at 110°C for 10 hr as before.

Surface-area Measurement. The specific surface area of the samples was determined by applying the BET theory to the nitrogen adsorption data, assuming the area of a nitrogen molecule to be 16.2 Å^2.

Heat-of-immersion Measurement. The heat of immersion was measured at 25°C by means of a calorimeter equipped with a thermistor as the temperature-sensing element, as has been described previously.[10,11] Prior to the measurement, the glass ampoule containing the sample was treated at a desired temperature in a vacuum of 10^{-5} Torr for 4 hr, sealed off *in vacuo*, and then set in the calorimeter. The technique of the measurement of the heat of immersion was the same as has been described previously.[10,11] It has been pointed out that the heat treatment of titanium dioxide *in vacuo* leads to a partial reduction of the sample, leaving nonstoichiometric and gray-colored surfaces on the sample.[12,13] In the present investigation also, a slight color-change of the sample appeared upon pretreatment at elevated temperatures, but the sample was used for the heat-of-immersion measurement in this state.

Water-content Measurement. In a usual atmosphere water molecules are adsorbed on the surface of titanium dioxide both physically and chemically. The physically-adsorbed water can be removed fairly easily *in vacuo*, even at room temperature, whereas the chemisorbed water can be removed only gradually by heating at higher temperatures. Thus, the water contents at various temperatures were determined by the successive ignition-loss method.[10,11] Since the amount of water expelled above 1000°C was found to be negligible, the water contents at various temperatures were calculated cumulatively by the summation of the amount of water evolved at each temperature, assuming the water content at 1100°C to be zero. In these procedures a small amount of gases other than water vapor was found to be evolved at higher temperatures. This was eliminated from the water-content data in the following way. All the gases evolved at an elevated temperature were trapped in a bulb kept at the temperature of liquid nitrogen, and then measured volumetrically at room temperature after the reevaporation of the trapped gases, using an all-glass apparatus[3] equipped with an oil manometer in order to measure sensitively the minute vapor pressure of water. Next, a part of the gases was retrapped at −72°C. When the gas contained only water vapor, all the gas could be retrapped at −72°C. However, in the gases expelled from the sample at temperatures higher than 300°C, a detectable amount of gases remained uncondensed at −72°C. In such cases, only the condensed gas was again determined in the same way as before, after removing the uncondensed gases by the evacuation of the system. The latter value is illustrated in Fig. 2 as the amount of the water content. The gases other than water which were evolved included, for example, 0.09, 0.18, and 0.29 molecules/100 Å^2 at 300, 400, and 600°C respectively, for the sample RI.

Results and Discussion

In Fig. 1 the specific surface area of titanium dioxide is represented as a function of the temperature of pretreatment. The surface areas of the samples of RI, RII, and AII are almost constant up to 800°C, after that they decrease steeply, indicating the occurrence of sintering. The sintering starts at 700°C with AI, whereas it begins at 600°C with AIII and RIII.

Figure 2 shows the relation between the water content and the temperature of pretreatment, where the former is represented in OH's/100 Å^2. The water content of the rutile obtained is quite small over the whole range examined, as is shown in Fig. 2. This may be explained as follows: the surface hydroxyl groups on rutile can be more easily removed by heating *in vacuo*, and therefore the water content of rutile at 250°C to 400°C is unexpectedly less than those of α-Fe_2O_3 or ZnO.[2]

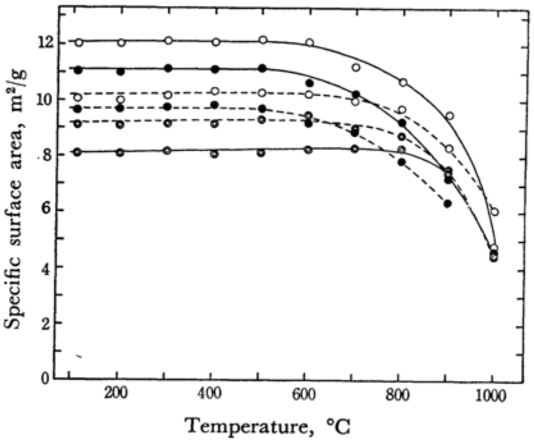

Fig. 1. Dependence of specific surface area of TiO_2 on pretreatment temperature.
—— anatase: ○, AI; ◎, AII; ●, AIII
---- rutile: ○, RI; ◎, RII; ●, RIII

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12) J. Gebhardt and K. Herrington, *J. Phys. Chem.*, **62**, 120 (1958).

13) C. M. Hollabaugh and J. J. Chessick, *ibid.*, **65**, 109 (1961).

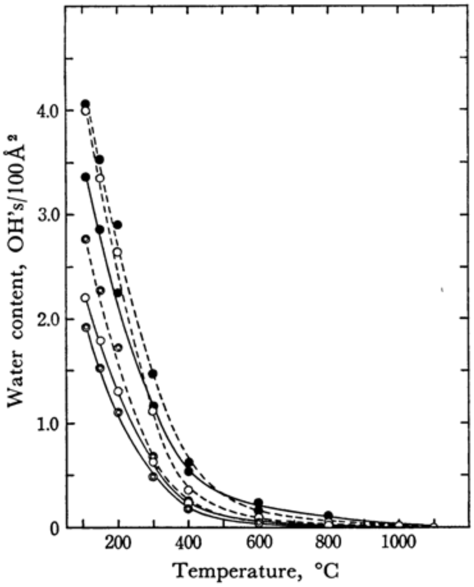

Fig. 2. Water contents of TiO_2 at various temperatures.
—— anatase: ○, AI; ◎, AII; ●, AIII
---- rutile: ○, RI; ◎, RII; ●, RIII

Also, it may be seen from Fig. 2 that the water contents on anatase seems to be slightly less than those on rutile; this may suggest that the surface hydroxyl groups on anatase can be removed as easily as, or more easily than, those on rutile. Furthermore, the water content is the greatest on the samples subjected to heavy hydration treatment in hot water, whereas it is the least on samples exposed to the saturated water vapor after 800°-treatment. In conclusion, the water contents of anatase and rutile decrease in the order: AIII>AI>AII and RIII>RI>RII.

A comparison of Fig. 1 with Fig. 2 leads to an interesting conclusion. On the samples AII and RII, which were once treated at 800°C and then exposed to the saturated water vapor at room temperature, the sintering due to retreatment does not occur below 800°C, but it occurs remarkably over 800°C, as may be expected. On the other hand, the water content of the samples AIII and RIII subjected to heavy hydration procedure in hot water is the largest, and their sintering starts at a lower temperature, 600°C. The temperature at which the sintering of the samples starts rises in the order: AIII<AI<AII and RIII<RI<RII, corresponding to the order of decrease in the water content.

In the present case, the sintering may be initiated by the condensation dehydration of hydroxyl groups from the facing surfaces of contacting particles.[14] The fact that the sintering of the sample with the larger water content starts at a lower temperature seems to support this supposition. When the condensation dehydration occurs from two contacting surfaces facing each other, there is a possibility that a part of the surface hydroxyl groups will be closed into the inner surfaces thus produced. Thus, it is reasonable to consider that it is difficult to remove such surface hydroxyl groups even at elevated temperatures, as is shown in Fig. 2.

The heat of immersion of titanium dioxide is given in Fig. 3 as a function of the temperature of pretreatment. These data show a maximum similar to the results of Wade and Hackerman.[6] The pretreatment temperature at which the maximum appears is about 400°C in the present study, whereas it was between 300°C and 350°C in their experiments. It may be seen from Fig. 3 that the value of the heat of immersion varies with the extent of hydration treatment, while in the experiments of Wade and Hackerman it was dependent on the size of the particles used. The heat-of-immersion value decreases in the order: AIII>AI>AII and RIII>RI>RII, parallel with the order of water content.

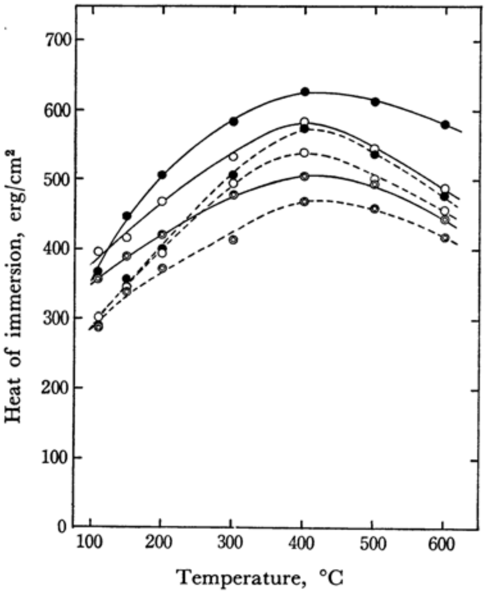

Fig. 3. Dependence of heat of immersion of TiO_2 in water on pretreatment temperature.
—— anatase: ○, AI; ◎, AII; ●, AIII
---- rutile: ○, RI; ◎, RII; ●, RIII

The heat-of-immersion anomaly, the terms of which imply the appearance of a maximum in the plot of the heat of immersion *vs.* the pretreatment temperature, has been explained as a cooperative effect of the chemisorption and physical adsorption of water: in the range of the steep increase in the heat of immersion, the reversible rehydroxylation (chemisorption of water to form surface

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[14] P. J. Anderson and P. L. Morgan, *Trans. Faraday Soc.*, **60**, 930 (1964).

hydroxyl groups) occurs on the site dehydrated by the pretreatment at elevated temperatures.[6,8-11] In the range of temperatures higher than the maximum point of the heat of immersion, the reversible rehydroxylation is delayed by the stabilization of the surface oxide structure, so the additional heat evolution by this reaction within the period of the heat-of-immersion measurement (less than 10 min) is decreased.

If we assume that the energy of the physical interaction on the immersion of a powdered sample in water is constant over the whole range of pretreatment temperatures, and that the appearance of the peak of the heat of immersion results from the additional heat evolution by the chemisorption of water, it may be said, as is shown in Fig. 3, that the contribution of the physical interaction varies considerably with the extent of hydration treatment and is larger on a sample which is subjected to a heavy hydration procedure and which is, therefore, rich in water. In general, three kinds of forces may be considered to be concerned with the contribution of the physical interaction on immersing a solid in a liquid: (1) the interaction between the polar surface and the dipole of the liquid molecule, (2) the effect of the induced dipole of the molecule, and (3) the effect of the dispersion force. Since titanium dioxide is known to be one of the most polar substances, it is valid to consider that the first of these three factors is most effective in the present case, being largely influenced by the surface hydroxyl groups.

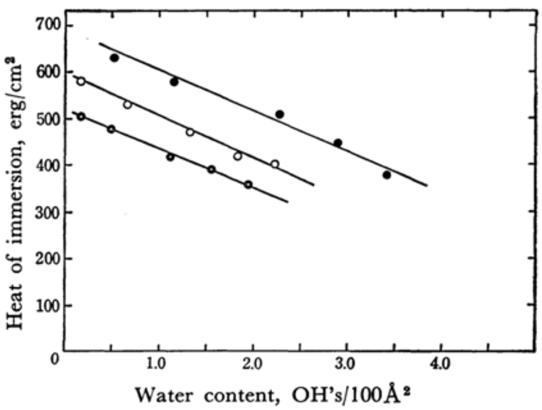

Fig. 4a. Relation between heat of immersion and water content on anatase.
○, AI; ◎, AII; ●, AIII

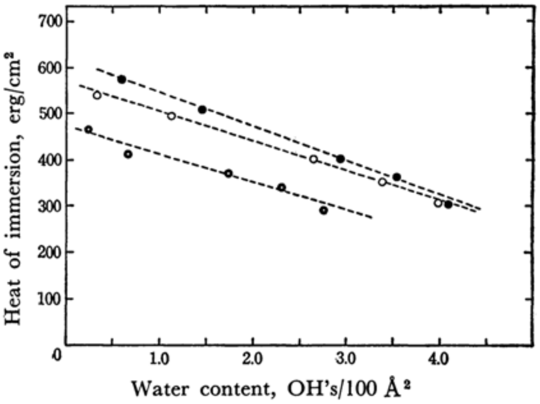

Fig. 4b. Relation heat of immersion and water content on rutile.
○, RI; ◎, RII; ●, RIII

Figure 4 shows the plots of the heat of immersion against the water content in the range of a steep increase in the heat of immersion in Fig. 3. As has been discussed above, in this range the physical adsorption and the chemisorption of water occur simultaneously, and the slope of this plot implies the energy of formation of a hydroxyl group (heat of surface hydration). The heats of surface hydration obtained are tabulated in Table 1; it is found that the variation in the heat due to the extent of hydration treatment is small, the average value being 25.2 and 19.0 kcal/mol H_2O for anatase and rutile respectively. Thus far the heat of surface hydration has been reported for several metal oxides: 16.1,[8] 3.5—6.5,[9] and 4.66[15] for SiO_2, 15.8 and 9.60 for α- and γ-Al_2O_3,[10] and 23.1 for ZnO.[11] The present data on TiO_2 are found to be comparable with those on ZnO.

TABLE 1. HEAT OF SURFACE HYDRATION OF TiO_2 (kcal/mol H_2O)

Sample	AI	AII	AIII	RI	RII	RIII
Heat of surface hydration	26.4	24.3	25.0	18.6	18.3	20.1

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[15] S. Brunauer, D. L. Kantro and C. H. Weise, *Can. J. Chem.*, **34**, 1483 (1956).