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Heat of Immersion of Titanium Dioxide in Water. II. The Effect of the Crystallinity of Anatase

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Two kinds of anatase samples which have very large specific surface areas and low crystallinities were prepared, and the interaction between the solid surface and the water molecule was investigated by measuring the water content, the heat of immersion in water, and the infrared spectrum of each sample. Two characteristic features were found in these samples: first, the plot of the heat of immersion *vs.* the pretreatment temperature did not reveal such a maximum as had been found previously with the crystalline anatase, and second, the heat of surface hydration as calculated from the plot of the heat of immersion *vs.* the water content was found to be remarkably smaller than with the crystalline anatase. These facts have led us to conclude that, with the anatase samples of a low crystallinity, not only does the rehydration reaction of a surface oxide structure produced at an elevated temperature proceed more easily on immersion in water, but also the heat of rehydration is smaller, than in a sample of a high crystallinity. Moreover, it was found from an infrared spectroscopic investigation that the water molecules physisorbed on the surfaces of large-area samples could be desorbed more gradually than those on small-area samples and remained small in quantity up to near 300°C *in vacuo*.

Titanium dioxide is one of the most important white pigments produced on an industrial scale; it has been studied by many investigators from the surface-chemical point of view. Nevertheless, it seems that many problems remain to be worked out with this material. Recently, the investigations have been carried out on the vapor adsorption,[1-3] the heat of immersion,[4] the surface

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[1] C. M. Hollabaugh and J. J. Chessick, *J. Phys. Chem.*, **65**, 109 (1961).

[2] P. T. Dawson, G. T. Rich and D. A. Haydon, *ibid.*, **68**, 3550 (1964).

[3] T. Morimoto, M. Nagao and F. Tokuda, *ibid.*, **73**, 243 (1969).

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

charge,[5,6] and the catalytic activity[7,8] of titanium dioxide; consequently, it has become clear that the surface hydroxyl groups play an important role in these phenomena. The plot of the heat of immersion of most metal oxides in water against the pretreatment temperature reveals a maximum, this phenomenon being also closely related to the presence of surface hydroxyl groups. Since, by analysing the plot, we can estimate the heat of formation of a surface hydroxyl group (the heat of surface hydration), the measurement of the heat of immersion of metal oxides in water makes it possible to make an energetic interpretation of the chemisorption of water on the solid surfaces. Recently, we have discovered two types of heat-of-immersion curves on α-Fe_2O_3; one shows a maximum, while the other does not.[9]

In the present work, anatase samples with large surface areas have been prepared in order to clarify the conditions of the appearance of a non-maximum curve in the plot of the heat of immersion *vs.* the pretreatment temperature. Then the interaction between the solid surface and the water molecule has been investigated by measuring the surface water content, the heat of immersion in water, and the infrared spectroscopy and by comparing the results with those obtained previously for the crystalline anatase.[10] As a result, two typical non-maximum curves have been observed in the plot of the heat of immersion *vs.* the pretreatment temperature; one shows an almost straight line, while the other shows an intermediate type between a maximum curve and a straight line.

Experimental

Materials. Two kinds of anatase were prepared in this study. The first sample was made by repeatedly treating the precipitate of anatase made through the hydrolysis of titanium sulfate with 1 N ammonia water in order to remove a large quantity of contaminated sulfate ions. It was then washed thoroughly with distilled water, and finally treated by means of electrodialysis (sample FA). The second sample was produced by calcining titanium peroxide for 4 hr at 400°C in air; the titanium peroxide had been prepared by the oxidation of metallic titanium with hydrogen peroxide. This sample was washed with distilled water, and finally the contaminating trace of electrolytes was removed by means of electrodialysis (sample SA). These two samples were dried at 110°C for 10 hr. For the sake of comparison, the data on the sample AI obtained in the previous work[10] are also cited, and also some new data were taken on this sample.

Surface-area Measurements. The specific surface areas of the anatase samples were determined by applying the BET theory to the nitrogen adsorption data obtained at the temperature of liquid nitrogen, assuming the molecular area of nitrogen to be 16.2 Å^2.

Heat-of-immersion Measurements. A sample of *ca.* 10 m^2 was used for every immersion measurement. Prior to the calorimetric measurement, the sample was treated in an ampoule at a desired temperature for 4 hr in a vacuum of 10^{-5} Torr, and then the ampoule was sealed off. The calorimeter and the technique of the heat-of-immersion measurements have been reported previously.[11] The measurements were carried out at 25°C. The heat of the breaking of the vacant ampoule was found to be 0.28 J; this was calibrated for the heat-of-immersion data.

Water-content Measurements. The water content of the anatase samples was measured by the successive ignition-loss method reported previously.[11] When the samples of anatase were treated at elevated temperatures *in vacuo,* small amounts of gases other than water vapor were found to be evolved. The amounts of these gases were measured volumetrically by a method described previously;[10] these data were then calibrated for the water content data. For instance, the gases other than water vapor which were evolved at 300, 400, and 600°C for the samples FA and SA were 0.02, 0.10, and 0.16, and 0.39, 0.94, and 1.67 molecules/100 Å^2 respectively.

Infrared Spectroscopy. The apparatus used for the infrared spectroscopic study was one made by the Japan Spectroscopic Co. (IR-G), to which a cell for the powdered sample was attached. The cell was essentially the same as that utilized by Yates.[12] The disk was prepared by pressing the powdered sample under a pressure of *ca.* 300 kg/cm^2. The sample disk set in the cell was first treated at an elevated temperature in a vacuum of 10^{-5} Torr for 4 hr and cooled to room temperature; then an infrared absorption spectrograph was taken. The measurements were repeated successively on one and the same sample after heat treatment at increasing temperatures.

Results and Discussion

The specific surface area of anatase is plotted against the pretreatment temperature in Fig. 1. For the sake of comparison, the surface area of the sample AI in a preceding paper[10] is cited in Fig. 1. The surface area of the sample FA is extremely large at room temperature, but it decreases remarkably with a rise in the temperature of heat treatment, indicating a great sintering. In the case of the sample SA also, a considerable sintering occurs. As a whole, we may conclude about the relation illustrated in Fig. 1 as follows:

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5) T. Morimoto and M. Sakamoto, This Bulletin, **36,** 1369 (1963).

6) T. Morimoto and M. Sakamoto, *ibid.,* **37,** 719 (1964).

7) A. A. Tolstopyatova, I. R. Konenko and A. A. Balandin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk,* **1961,** 38.

8) A. A. Balandin, I. R. Konenko and A. A. Tolstopyatova, *ibid.,* **1961,** 45.

9) T. Morimoto, H. Naono, N. Katayama and M. Nagao, This Bulletin, **42,** 1490 (1969).

10) T. Morimoto, M. Nagao and T. Omori, *ibid.,* **42,** 943 (1969).

11) T. Morimoto, K. Shiomi and H. Tanaka, *ibid.,* **37,** 392 (1964).

12) D. J. C. Yates, *J. Phys. Chem.,* **65,** 746 (1961).

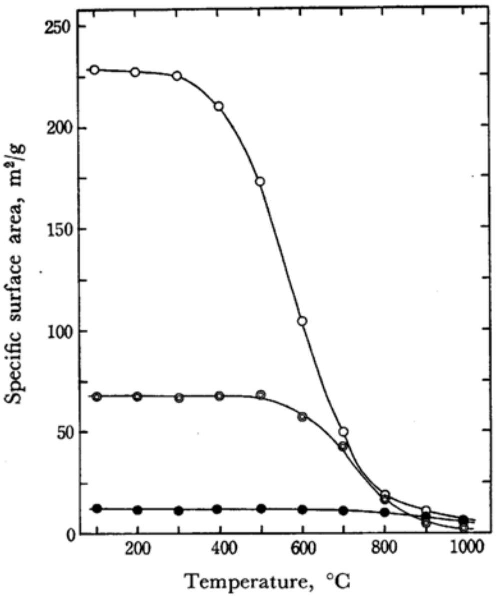

Fig. 1. Dependence of specific surface area of anatase on pretreatment temperature.
○, sample FA; ◎, sample SA; ●, sample AI

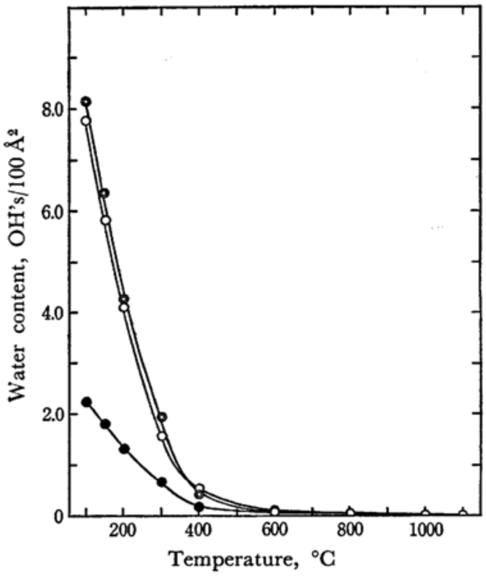

Fig. 2. Water content of anatase at various temperatures.
○, sample FA; ◎, sample SA; ●, sample AI

the larger the specific surface area, the lower the temperature at which the sintering starts.

Figure 2 gives the relation between the water content and the temperature of pretreatment. The water-content value of the samples decreases in the order: SA>FA>AI.

The heat of immersion of anatase in water is plotted as a function of the temperature of pretreatment in Fig. 3. In spite of the large differences between the particle sizes of the three kinds of anatase samples, the particle-size rule investigated in detail by Wade and Hackerman,⁴⁾ which states the increase in the heat of immersion with the increase in the particle size, does not hold in the present case. However, it should be noted that the samples FA and SA do not reveal any maximum in the heat-of-immersion curve, in contrast with the case of the sample AI. Most plots of the heat of immersion of metal oxides in water *vs.* the pretreatment temperature have revealed a maximum. For instance, in the cases of SiO_2,13,14) TiO_2,4,10) ZnO,15) Al_2O_3,11) and $Fe_2O_3$9) all the heat-of-immersion curves showed a maximum, although the maximum value and the temperature at which the maximum appears vary with the nature of the metal oxides. Only in the case of Fe_2O_3, have samples showing no maximum in the heat-of-immersion curve been discovered besides samples showing a maximum. In the present case of anatase, two samples having large surface areas show no maximum in the heat-of-immersion curve, while the sample AI, which has a small surface area, shows a maximum. Moreover, a new type of characteristic feature can be seen from Fig. 3 — the heat of immersion of one sample (FA) increases sharply and almost linearly even after 400°C, whereas that of the other sample (SA) increases sharply at first, but slowly later. The

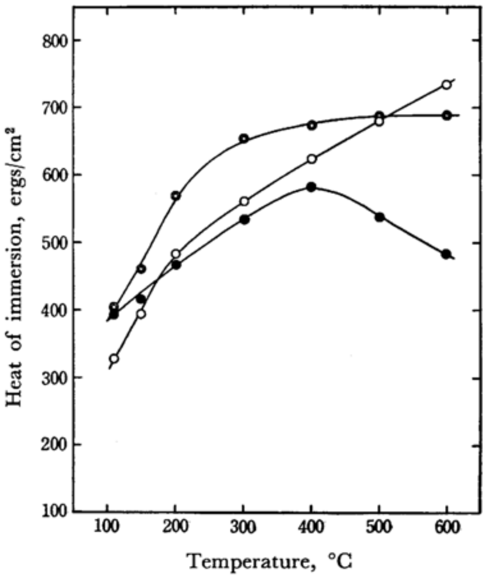

Fig. 3. Dependence of heat of immersion of anatase in water on pretreatment temperature.
○, sample FA; ◎, sample SA; ●, sample AI

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

14) J. W. Whalen, *Advan. Chem. Ser.*, **33**, 281 (1961).

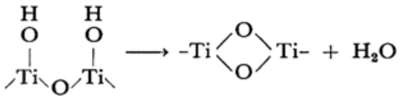
15) T. Morimoto, M. Nagao and M. Hirata, *Kolloid-Z. Z. Polymere*, **225**, 29 (1968).

shape of the non-maximum curve observed on α-Fe_2O_3 rather resembles the case of anatase (the sample SA).

The appearance of the maximum in the heat-of-immersion curve has been elucidated as follows: the surface hydroxyl groups can be removed by pretreatment at elevated temperatures, and the resulting activated sites can easily be rehydrated to form hydroxyl groups on immersion in water. This additional heat evolution due to the rehydration reaction of the activated sites reaches a maximum value with the rise in the pretreatment temperature, since the number of the activated sites increases upon this pretreatment. Over a certain degree of pretreatment temperature, however, the activated surface oxide structure formed is stabilized, making it possible to retard the rehydration reaction on immersion in water. Thus the heat-of-immersion value decreases in the range of higher pretreatment temperatures. This heat of chemisorption of water which varies largely with the pretreatment temperature can be superimposed upon the wetting heat due to the physisorption of water.

When we reported, in a previous paper,[9] the first instance where two groups of samples showing both maximum curves and non-maximum curves in the plot of the heat of immersion were discovered in the same substance (α-Fe_2O_3), this phenomenon was not resolved satisfactorily. However, we suggested that the stabilization of the surface oxide structure formed by treatment at elevated temperatures is insufficient on the samples which give a non-maximum curve in the plot of the heat of immersion. With the sample FA in the present work the heat of immersion increases linearly over the range of pretreatment temperatures from 200 to 600°C; this suggests that little stabilization occurs on the surface oxide structure up to this, the highest temperature of treatment studied. With the sample SA, on the other hand, the heat of immersion increases sharply up to 300°C and then slowly, indicating that only weak stabilization takes place upon pretreatment at elevated temperatures.

The anatase samples were submitted to X-ray diffraction measurements. From these data the crystallite size of the samples can be estimated according to Scherrer's equation;[16] it amounts to 114, 258, and 2260< Å for the samples FA, SA, and AI respectively, with reference to the peak of the (101) plane of anatase. These values are those calibrated by using the data on a well-defined quartz crystal taken under the same conditions. It can be seen from these data that the sample with a larger surface area is of a lower crystallinity, as is to be expected. Thus, we may conclude that the stabilization of the surface oxide structure made by heat treatment occurs with more difficulty on the surface of the sample with a lower crystallinity. In other words, the stabilization of the $-\mathrm{Ti}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Ti}-$ structure on the surface of anatase which is produced by the reaction:



occurs with more difficulty; accordingly, the reverse reaction of this equation proceeds more easily on a surface with an ill-defined crystal structure than on a surface with a well-defined one. This phenomenon can probably be considered to be caused by the irregular bond length and the strained bond angle of the $-\mathrm{Ti}{<}^{\mathrm{O}}_{\mathrm{O}}{>}\mathrm{Ti}-$ structure on the surface, both of which features arise from the lower crystallinity of the sample. The sample SA has the intermediate crystallinity among the three, produces a moderate stabilization of the surface oxide structure, and has a break in the heat-of-immersion curve at a temperature of about 300°C.

In Fig. 4 the heat of immersion of anatase is plotted against the water content in the treatment range up to 400°C. All the plots represent a linear relationship, the slope giving the heat of formation of a surface hydroxyl group, that is, the heat of surface hydration. The value of the heat of surface hydration can be read from Fig. 4 as 11.8 and 14.9 kcal/mol water for the samples FA and SA respectively, whereas the value is 26.4 kcal/mol water for the sample AI. The former two values are quite a bit smaller than the latter, which is the value of a representative crystalline anatase sample. This indicates that the heat of surface hydration is smaller on the surface with a lower crystallinity. Thus, we can conclude that the surface of the sample FA, whose crystallinity is the lowest, can be rehydrated most easily even

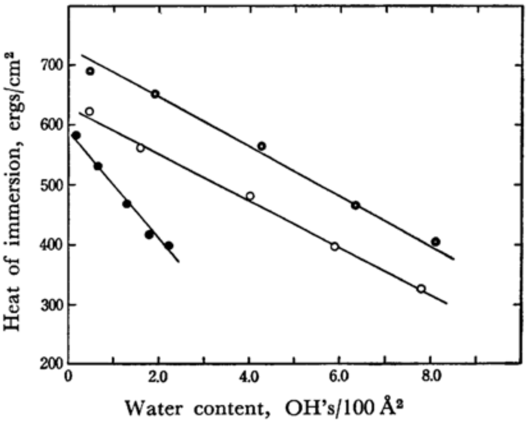


Fig. 4. Relation between heat of immersion and water content on anatase.
○, sample FA; ◎, sample SA; ●, sample AI

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[16] P. Scherrer, *Göttinger Nachrichten.*, **2**, 98 (1918).

after treatment at higher temperatures; moreover, its heat of surface hydration is the smallest. Since, when the activation energy of a reaction is small, the reaction proceeds rapidly, Fig. 3 suggests that the activation energy of the surface hydration reaction on the sample FA is the smallest, while that on the sample AI is the largest. It is known that, as for reactions with the same reaction mechanism, the activation energy of a reaction is larger on the reaction giving the larger reaction heat.[17] In the present examples it seems that this relation holds also in the case of the surface hydration reaction.

Figure 5a illustrates the infrared absorption spectra of the sample FA. After the sample has been degassed at 10^{-5} Torr for 4 hr at room temperature, the spectrum shows a broad absorption band in the range of 3700—2000 cm^{-1} and a shoulder near 3630 cm^{-1}. The former can be assigned to the stretching vibration of hydrogen-bonded hydroxyl groups, and the latter, to the stretching vibration of the isolated surface hydroxyl groups.[18] Another absorption band, near 1620 cm^{-1}, is considered to be due to the bending of hydroxyl groups, indicating the existence of physisorbed water.[12,18] After treatment at 110°C *in vacuo* the intensity of the spectrum generally decreases and the stretching vibration band of hydroxyl groups comes to separate into two parts, indicating a relative increase in the number of free hydroxyl groups. Even after treatment at 200°C there remains a slight bending vibration of hydroxyl groups, but it is extinguished completely after treatment at 300°C. This may be caused by the difficulty of the desorption of the capillary condensed water molecules. The reason why the heat of surface hydration of the sample FA is the least among these three samples may be partially that the desorption of the physisorbed water is most difficult from the sample FA because of the intensive capillary condensation; this results in an apparent increase in the water content at relatively low temperatures and in an apparent decrease in the heat of surface hydration calculated therefrom.

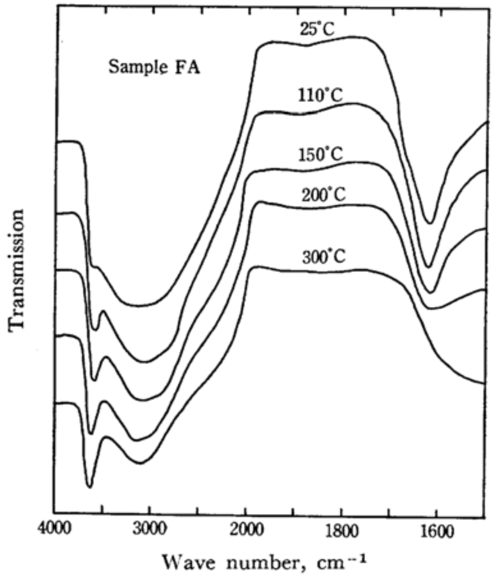

Fig. 5a. Infrared absorption spectra of sample FA under various conditions of treatment.

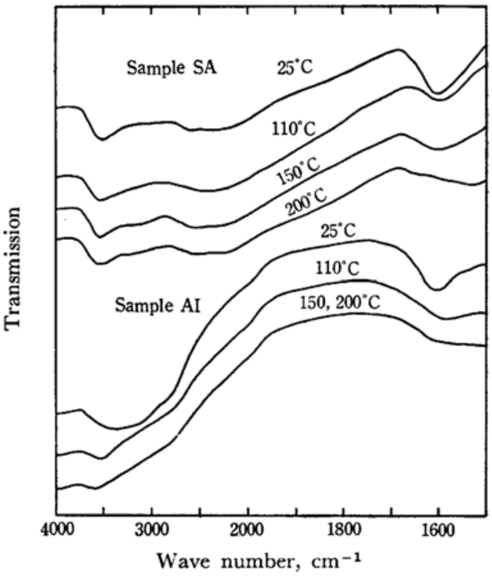

Fig. 5b. Infrared absorption spectra of samples SA and AI under various conditions of treatment.

Figure 5b shows that the water molecules physisorbed on the sample AI can be desorbed by heat treatment up to 150°C in a vacuum of 10^{-5} Torr, while those on the sample SA can be desorbed by heat treatment at a temperature higher than 200°C. Also, the large water content of the sample SA probably comes from the difficult desorbability of the physisorbed water, which may result in the small heat of surface hydration, as in the case of the sample FA.

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17) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y. (1941).

18) K. E. Lewis and G. D. Parfitt, *Trans. Faraday Soc.*, **62**, 204 (1966).