BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1754—1758 (1971)

Studies of the Surface of Titanium Dioxide. I. The Effect of Reduction by Hydrogen on the Heat of Immersion in Water

Toru Iwaki and Masaji Miura
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima

(Received December 28, 1970)

The reduced state of the surface of titanium dioxide was studied by the measurement of the heat of immersion in water. When the titanium dioxide was reduced by hydrogen at 500°C, the heat value decreased appreciably with an increase in the pressure of hydrogen, in contrast to the increase in the heat value due to the reduction by an organic contaminant. The heat value was not restored to the original state even after oxygen had been introduced at 500°C to the reduced sample, while the color of the sample returned to white from bluish gray. These phenomena were interpreted by examining the adsorption of water, the reduced amount, and the reflectance spectrum.

It is well known that titanium dioxide is subject to a change in color from its initial white state to gray or bluish gray when heated *in vacuo* from 300 to 500°C. This color change has been considered to be caused by a removal of oxygen atoms from the surface. Such a reduction of titanium dioxide has been regarded as attributable to organic compounds which come from stopcock grease, diffusion pump oil, *etc.* in a vacuum system, and which are also occluded in titanium dioxide during its preparation.[1,2] When heated at a high temperature, these organic compounds are oxidized, resulting in the removal of oxygen atoms on the surface.

Titanium dioxide is also reduced easily by contact with a reducing gas, such as hydrogen or carbon monoxide, at a high temperature.[3] The removal of one oxygen atom from titanium dioxide produces two electrons which reside in the oxygen vacancy or the titanium ion. Reduced titanium dioxide is also well known to be an *n*-type semiconductor and to play an important role as a catalyst for such chemical reactions as the Fisher-Tropsch synthesis. Therefore, the investigation of the reduction of titanium dioxide is of interest in connection with the nature of the defect structures of solid surfaces. A number of studies of the bulk properties of reduced titanium dioxide have been performed for rutile modification by various methods,[4] but scarcely none have been done for anatase.

In the present study, the effect of an organic contaminant on the surface properties of anatase treated under several conditions was examined by measuring the heat of immersion in water. Further, in order to investigate the properties of the defect structure of the surface, the heat of immersion in water, the adsorption of water vapor, the weight change caused by the reduction, and the reflectance spectra were measured on anatase samples which were reduced by hydrogen

---

[1] J. Gebhardt and K. Herrington, *J. Phys. Chem.*, **62**, 120 (1958).
[2] C. M. Hollabaugh and J. J. Chessick, *ibid.*, **65**, 109 (1961).
[3] T. J. Gray, C. C. McCain, and N. G. Masse, *ibid.*, **63**, 472 (1959).
[4] F. A. Grant, *Rev. Modern Phys.*, **31**, 646 (1959).

and reoxidized by oxygen.

Experimental

Material. Titanium dioxide supplied by Teikoku Kako Co., Ltd., was purified by the method described in a previous paper.[5] X-ray analysis showed well-crystallized anatase for the sample outgassed at 500°C.

The titanium dioxide was treated under the following several sets of conditions in order to investigate the effect of the organic contaminant on the heat of immersion:

(1) Outgassing at 500°C for 5 hr at 10^{-5} mmHg.

(2) Outgassing at 500°C for 5 hr with a liquid nitrogen trap just before the sample in order to prevent the effect of the vapor of the stopcock grease.

(3) After the (1) treatment, introducing oxygen gas through a liquid nitrogen trap for 2 hr at a pressure of 0.5 atm and 500°C and then outgassing at room temperature for 0.5 hr.

(4) After the (2) treatment, introducing oxygen in the manner described above.

(5) After the condensation of diffusion pump oil on the surface of titanium dioxide, outgassing as in the (1) treatment.

(6) After the (2) treatment, introducing hydrogen gas through a liquid nitrogen trap at 0.5 atm and 500°C for 2 hr and then outgassing at 500°C for 0.5 hr.

Further, in order to examine the reduced state of the surface brought about by the reduction with hydrogen, titanium dioxide was treated under the following conditions:

(7) After the (2) treatment, introducing hydrogen gas at various pressures, ranging from about 0.01 to 1 atm, in the same way as in (6).

(8) After the (6) treatment, introducing oxygen gas through a liquid nitrogen trap for 0.5 hr at 0.5 atm and room temperature or 500°C, and then outgassing for 0.5 hr at room temperature.

Heat of Immersion. The heat of immersion was measured at 25°C by using a calorimeter, as was described previously.[6] The detection limit of the temperature difference was $\pm 1.7 \times 10^{-5}$°C, and the heat evolved in the calorimeter could be measured within ±1%. The heat of breaking of a vacant ampoule was found to be 0.3±0.05 J; this was calibrated for the heat-of-immersion data.

Surface Area. The surface area of the sample was determined by nitrogen adsorption at 77°K using the BET method; the area of a nitrogen molecule was assumed to be 16.2 Å^2 at that temperature. The surface area of each sample was 144 m^2/g, independent of the treatment, except for a sample treated with oxygen at 500°C after reduction with hydrogen (treatment (8)); the surface area of that sample was 139 m^2/g.

Adsorption of Water Vapor. The adsorption isotherms of water vapor on several samples were measured volumetrically at 25°C.

Reduced Amount. The amounts of titanium dioxide reduced by hydrogen at 500°C for 2 hr were obtained with a Cahn RG electrobalance.

Reflectance Spectrum. The reflectance spectrum was measured at 25°C with a Hitachi Perkin-Elmer 139 spectrophotometer over the wavelength range from 300 to 900mμ.

TABLE 1. HEAT OF IMMERSION OF TITANIUM DIOXIDE IN WATER

	Treatment	ΔH, erg/cm^2	Color
(1)	500°C, no trap	726	white or brown
(2)	trap	715	white
(3)	O_2	695	white
(4)	trap, O_2	695	white
(5)	oil	731	brown
(6)	H_2 (0.5 atom)	558	bluish gray

Results and Discussion

Effect of Organic Contamination on the Heat of Immersion. The values of the heat of immersion of titanium dioxide treated under the several sets of conditions are represented in Table 1. As is obvious by comparison of the (1) treatment with (2), the heat value is lowered slightly by using the liquid nitrogen trap. The sample became slightly brownish in the case of (1), but did not color in the case of (2). By the (3) or (4) treatment, the heat value was further decreased slightly as a result of the elimination of the organic contaminant by oxidation. Since the heat value was not so remarkably affected by the organic contaminant in the above cases, minute quantities of diffusion-pump oil were condensed on the sample. The results obtained by the treatment are shown in (5) of Table 1; the results indicate that the heat value increased by about 5% as compared with that of the (4) treatment. These results show that the heat of immersion is not influenced by the organic contaminant so remarkably as in the case of rutile reported by Hollabaugh and Chessick; in the latter case, the heat value increased by 120 erg/cm^2. The high value of the immersional heat is considered to arise from the reduced state of the rutile surface.[2] Therefore, the hydrogen gas was admitted to the sample at 500°C as in the (6) treatment in order to produce the reduced state to a considerable degree. In contrast to our expectations, the heat value for the surface decreased appreciably. Moreover, the sample was tinged bluish gray, different from the color caused by an organic contaminant. It seems that the surface state produced by the reduction with hydrogen is different from that produced with an organic contaminant. No further details of the effect of an organic contaminant on the surface properties were examined. Instead, the effect of reduction by hydrogen on the surface state will hereinafter be described.

Reduced State of Titanium Dioxide. In general, the surface of titanium dioxide is covered with hydroxyl groups. When the titanium dioxide is heated *in vacuo* at a high temperature, the surface hydroxyl groups may be removed as follows:

$$2OH^- \longrightarrow H_2O + O^{2-} \tag{1}$$

The resulting oxygen anion may be displaced from its original position to form a bridge, Ti–O–Ti. On the contrary, when dehydrated titanium dioxide is rehydrated, hydroxyl groups are again formed on the surface.

When a hydrogen molecule is introduced to the titanium dioxide at a high temperature, it removes the

---

[5] M. Miura, H. Naono, and T. Iwaki, *J. Sci. Hiroshima Univ. Ser. A-II*, **30**, 57 (1966).

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

oxygen anion as a water molecule, producing a defect structure according to the reaction:

$$O^{2-} + H_2 \longrightarrow H_2O + \square + 2e^- \qquad (2)$$

where $\square$ is an oxygen vacancy.

In many studies of reduced rutile by examinations of the electric conductivity, the paramagnetic resonance, the dielectric relaxation, *etc.*, some results favor the oxygen vacancy as a dominant defect, some favor the interstitial titanium ion, and some favor a combination of the two.[7] At a high temperature, there are interstitial titanium ions, which may form the Magnéli interfaces as a result of the diffusion of oxygen vacancies.[8] Barbanel *et al.* have recently reported, from the measurement of the density of rutile, that the interstitial Ti^{3+} ion appeared when a rutile was heated above 750°C *in vacuo*.[9] In the present study, the reduction of the sample by hydrogen did not occur at 400°C, but it proceeded gradually at 500°C. Therefore, the oxygen vacancies produced may be present for the most part on the surface rather than in the bulk. The surface area of the sample may be expected to be changed by the reduction, but the nitrogen adsorption experiments showed no appreciable change in the surface area, even under the treatment with hydrogen at 1 atm.

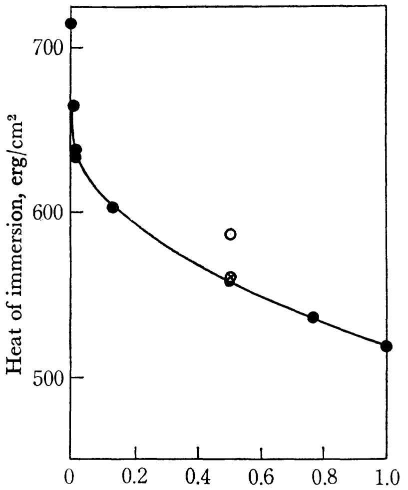

Fig. 1. Heat of immersion of titanium dioxide as a function of the pressure of hydrogen.
●, reduced at 500°C; ⊗, reoxidized at room temperature; ○, reoxidized at 500°C

Effect of Reduction on the Heat of Immersion and Adsorbed Amount of Water Vapor. The values of heat of immersion are shown in Fig. 1 as a function of the pressure of hydrogen, the pressures ranging from 0.01 to 1 atm. The heat value decreased with an increase in the pressure of hydrogen, rapidly in the lower pressure region and gradually in the higher one. The possibility of the removal of hydroxyl groups on the surface by the reduction is present in this case. Morimoto *et al.* have ascertained the water content of anatase treated at 500°C to be *ca.* 0.3 hydroxyl groups per 100Å.[2,10] If the decrease in the heat value by the reduction were responsible only for the removal of hydroxyl groups on the surface, the heat value might decrease by *ca.* 30 erg/cm². The heat of the immersion of the sample in dry benzene was measured to be 155 erg/cm²; this was not altered by the reduction. Therefore, the decrease in the heat may be caused mainly by the reduced state of the surface structure rather than by the hydroxyl groups.

Then, titanium dioxide reduced with hydrogen at 0.5 atm and 500°C was reoxidized by oxygen at 0.5 atm and room temperature or 500°C (treatment (8)). The values of the heat of immersion for the two samples in water are indicated in Fig. 1. In the former case the heat value was not varied at all, while in the latter case it was slightly increased.

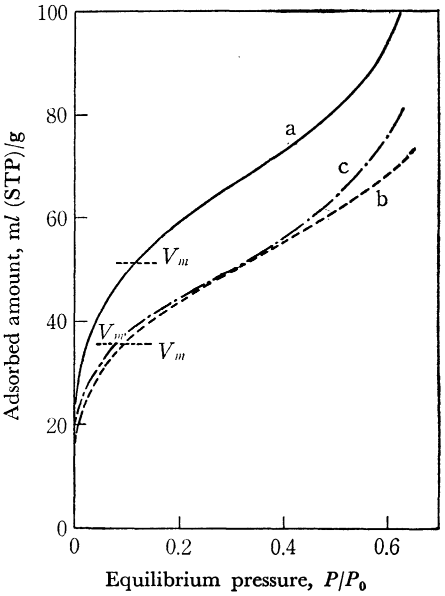

Fig. 2. Adsorption isotherms of water vapor on the surface of titanium dioxide; (a) outgassed at 500°C, (b) reduced with hydrogen at 0.5 atm, and (c) reoxidized at 500°C.

Table 2. Monolayer volume and surface area of water adsorbed on the surface of titanium dioxide

Treatment	V_m, ml (STP)/g	S_{H_2O}, m²/g	S_{H_2O}/S_{N_2}
(a) 500°C	50.7	147	1.02
(b) H_2 (0.5 atom)	36.3	105	0.73
(c) H_2–O_2 (500°C)	36.2	105	0.76

Figure 2 shows the adsorption isotherms of water vapor on the following three kinds of surfaces of titanium dioxide: outgassed at 500°C (a), reduced by 0.5 atm of hydrogen (b), and reoxidized by oxygen at 500°C (c). Table 2 lists the amount of water adsorbed on the surface corresponding to the monolayer obtained by the BET method, the surface area, S_{H_2O} being determined

---

[7] L. A. K. Dominik and R. K. MacCrone, *Phys. Rev.*, **163**, 756 (1967).

[8] J. S. Anderson and B. G. Hyde, *J. Phys. Chem. Solids*, **28**, 1393 (1967).

[9] V. I. Barbanel, V. N. Bogomolov, and S. A. Borodim, *Fiz. Tverd. Tela*, **11**, 537 (1969).

[10] T. Morimoto, M. Nagao, and T. Omori, This Bulletin, **42**, 943 (1969); T. Omori, J. Imai, M. Nagao, and T. Morimoto, *ibid.*, **42**, 2198 (1969).

by assuming the cross-sectional area of water molecule to be 10.8 Å^2, and the ratio of the area to the area being obtained from nitrogen adsorption, S_{H_2O}/S_{N_2}. In the case of (a), the monolayer of water covers the entire surface obtained from nitrogen adsorption because S_{H_2O}/S_{N_2} is nearly one, whereas in the cases of (b) and (c), the surface shows a somewhat hydrophobic character. The number of sites for water to be adsorbed on the surface may be altered by the reduction.

Reduced Amount. The change in the weight of titanium dioxide by the reduction with hydrogen at 500°C is given in Fig. 3 as a function of the pressure of hydrogen. The value at 0.006 atm of hydrogen was obtained by the volumetric method, because it is difficult to get the exact value at pressures lower than 0.05 atm by the gravimetric method because of a thermomolecular effect.

If the composition of titanium dioxide evacuated at 500°C is stoichiometric, the amount of oxygen atoms removed by the reduction with hydrogen at 0.5 atm is calculated from Fig. 3 to be 0.3% of all the oxygen atoms of titanium dioxide; the composition of $TiO_{1.994}$ can thus be obtained. Among all the oxygen ions, those on the surface layer are calculated to be 13.3% for the (001) plane, 10.6% for the (100) plane, and 9.9% for the (101) plane. These planes are the cleavage faces of anatase.[11] If the elimination of oxygen atoms from titanium dioxide is limited to the surface oxygen atoms, which account for 11.3% of the total, the oxygen atoms removed should become 2.7%, resulting in the composition of $TiO_{1.946}$ for the surface layer. Thus, the oxygen vacancies per surface area should become 0.32/100 Å^2. The real surface of reduced titanium dioxide, however, may have fewer oxygen vacancies than the values calculated above since the reduction may occur also in the bulk.

The relationship between the reduced amount and the hydrogen pressure in Fig. 3 resembles fairly well that between the heat of immersion and the hydrogen pressure in Fig. 1. The decrease in the heat of immersion per reduced weight takes a constant value, 210 erg/cm^2 per mg of oxygen vacancy, in the pressure range higher than 0.05 atm. This means that hydrogen atoms eliminate the oxygen atoms on the surface which are active to the water molecule. The weight of the reduced titanium dioxide could not be restored completely to the original weight by oxidation even at 500°C; about three quarters of the weight loss was recovered.

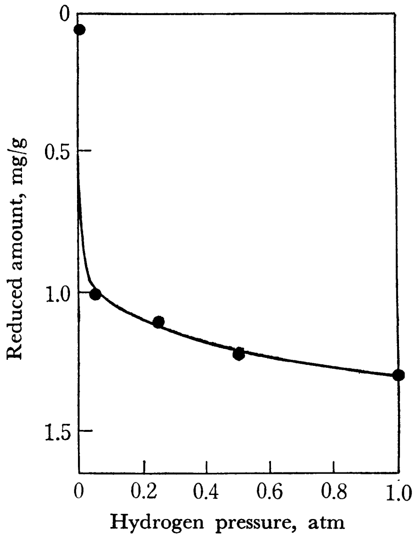

Fig. 3. Reduced amount of titanium dioxide as a function of the pressure of hydrogen.

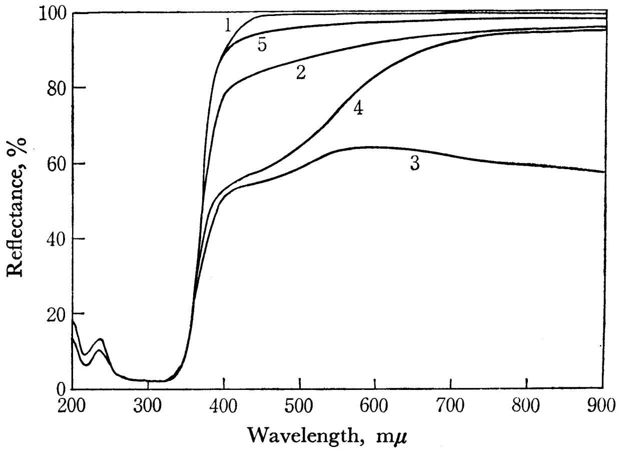

Fig. 4. Reflectance spectra of titanium dioxide; (1) unreduced, (2) outgassed at 500°C, (3) reduced with hydrogen at 0.5 atm, (4) reoxidized at room temperature, and (5) reoxidized at 500°C.

Color Changes by Reduction and Reoxidation. Titanium dioxide reduced by hydrogen was tinged with a bluish-gray color. It showed a brown color after being oxidized by oxygen at room temperature, but it became white when oxidized at 500°C. The reflectance spectra for these samples are shown in Fig. 4. An absorption in the ultraviolet region with an absorption edge of 360 mμ is caused by a transition from the valence band, the $2p$ state of O^{2-}, to the upper conduction band, the $3d$ state of Ti^{3+}, which is the fundamental absorption.[12] For the reduced sample, other absorption bands emerged in the longer-wavelength range: a shoulder at 440 mμ and a broad absorption band with a maximum above 900 mμ. The latter band disappeared when oxygen was introduced to the reduced surface at room temperature, while both bands disappeared after coming into contact with oxygen at 500°C, whereupon the spectrum was similar to the original one. The differences between the reflectances of the reduced samples and that of the unreduced sample are shown in Fig. 5. The increase in intensity of the absorption bands at both 440 mμ and above 900 mμ with an increase in the degree of reduction indicates that these bands are caused by irregularities in the lattice.

The former band is similar to a band resulting from indirect transition which is observed in germanium and silicon.[13] This forbidden transition from valence band to conduction band may be made possible by

---

[11] L. G. Berry and B. Mason, "Mineralogy," W. H. Freeman and Co., San Francisco (1959), p. 377.

[12] G. V. Schultz, *Z. Phys.*, **179**, 473 (1964).

[13] W. C. Dash and R. Newman, *Phys. Rev.*, **99**, 1151 (1955).

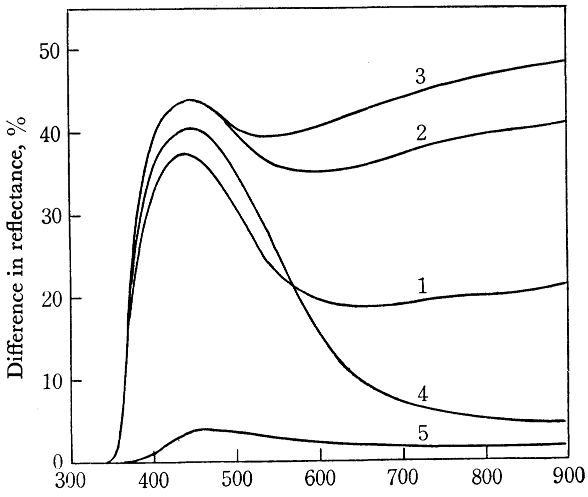

Fig. 5. Differences between reflectance of unreduced sample and those of the samples treated as follows: (1) reduced with hydrogen at 0.1 atm, (2) reduced with hydrogen at 0.5 atm, (3) reduced with hydrogen at 1 atm, (4) reoxidized at room temperature, and (5) reoxidized at 500°C.

crystal imperfections. The latter band may be responsible for the bluish-gray coloration. In a reduced sample of rutile, this coloration is considered to be caused by an excitation of electrons from the donor state as well as from the conduction band to the additional conduction band (absorption band miximum at $h\nu=$ 1 eV).[14] However, the excitation of electrons may be made impossible by the adsorption of oxygen on the reduced surface at room temperature. The adsorbed oxygen molecules become O_2^-[15] by drawing electrons from the donor state and the conduction band, resulting in the formation of a depletion layer near the surface. Oxygen admitted to the reduced sample at 500°C may be incorporated into the crystal lattice as O^{2-} to reproduced a considerably less irregular lattice near the surface.

Conclusion. From the results of the heat of immersion in water, the weight change, and the color change, it may be considered that titanium ions are present, in a considerable part, around oxygen vacancies on the surface when titanium dioxide is reduced. Such a surface may weakly interact with water, since a certain number of active oxygen ions, which strongly attract water molecules to form surface hydroxyl groups, are removed from the surface. When the surface is reoxidized at 500°C, the electronic state of the surface can return to the original unreduced state, but the interaction of the surface with water can not be restored. Even though oxygen is incorporated on the reduced surface as O^{2-}, it may no longer be such an active oxygen ion as that on the unreduced surface.

---

14) J. H. Becker and W. R. Hosler, *J. Phys. Soc. Jap.*, **18**, Suppl. II, 152 (1963).

15) J. H. C. VAN Hoff, *J. Catal.*, **11**, 277 (1968).