The Electrokinetic Potential and Surface Acidity of Titanium Dioxide

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When an insoluble metal oxide is in equilibrium with water, the solid will be covered with surface hydroxyl groups as a result of surface hydration. The present communication deals with the dependence of the electrokinetic potential and the surface acidity of titanium dioxide on its heat treatment in order to clarify the dissociation of surface hydroxyl groups on titanium dioxide.

Titanium dioxide obtained by the hydrolysis of titanium sulfate was treated with ammonium hydroxide to remove contaminating sulfate groups. After having been sufficiently washed with water, the sample was dried and calcined at given temperatures. The electrokinetic potentials obtained in water by the streaming-potential method are shown in Fig. 1. The charge of titanium dioxide is positive on the samples treated at 100 to 700°C, but it changes to a negative value after treatment at higher temperatures. An isoelectric point appears on a sample treated at about 800°C, which agrees with the transition temperature of anatase to rutile.

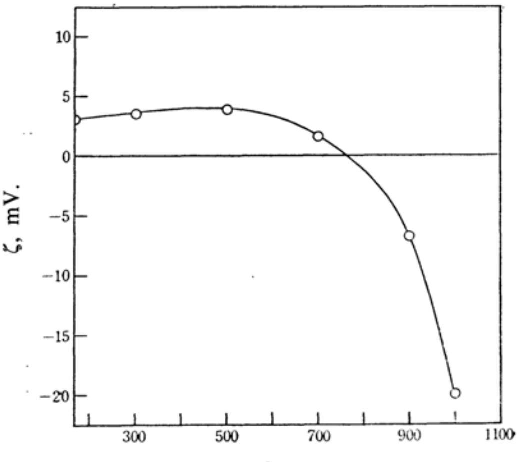

Fig. 1. Electrokinetic potential (ζ) of titanium dioxide.

In the next place, the surface acidity of these samples was examined by the dye-adsorption method. To prepare the dye solution, 10 mg. of methylred was dissolved in 100 ml. of isooctane.[1] 0.2 g. of titanium dioxide was then shaken with 4 ml. of the dye solution. After the adsorption of dye molecules, the

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[1] K. Tanabe and M. Katayama, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **7**, 106 (1959); C. Walling, *J. Am. Chem. Soc.*, **72**, 1164 (1950).

reflectance of the powder was measured by a spectrophotometer. The color of the adsorbed dyestuff was a basic one, yellow, in the samples treated at lower temperatures, but in the samples treated at 1000°C it was an acidic color, red, as is recorded in Fig. 2. Thus the change in the surface acidity of titanium dioxide appears to correspond to the transition temperature of the crystal, as in the case of the electrokinetic potential.

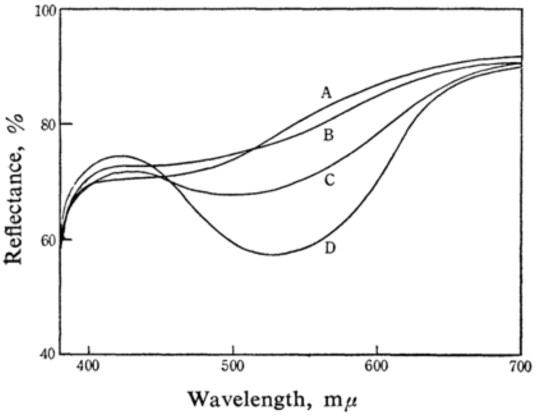

Fig. 2. Reflection spectra of methylred adsorbed on titanium dioxide, treated at A, 100°C; B, 500°C; C, 700°C; D, 1000°C.

It is possibly considered that the surface hydroxyl groups situated on titanium dioxide dissociate as follows:

$$\equiv\text{TiOH} \rightarrow \equiv\text{Ti}^{+} + \text{OH}^{-} \qquad (1)$$

$$\equiv\text{TiOH} \rightarrow \equiv\text{TiO}^{-} + \text{H}^{+} \qquad (2)$$

Dissociation resulting from Eq. 1 will give a positive charge on the surface and a basic color for the indicator, while that from Eq. 2 a negative charge and an acidic color. Judging from the present investigation, it is plausible that, on treatment at temperatures lower than 800°C, the dissociation of surface hydroxyl groups on titanium dioxide follows Eq. 1, while on treatment at higher temperatures it follows Eq. 2.

It is known that the distances between neighboring oxygens are longer than about 3.00 Å in basic metal hydroxide crystals, while in acidic ones they are less than 2.70 Å.²⁾ The crystallographic data on titanium dioxide, described by Cromer and Herrington,³⁾ are represented in Table I. If we assume that the surface of titanium dioxide is hydrated to form surface hydroxyl groups without varying the O–O distances greatly from those given in Table I, it may be expected that rutile has an acidic surface and anatase, a basic one. Rather we may propose from the present results that the exposed surfaces of anatase are rich in longer O–O bonds. In conclusion, the fact that titanium dioxide may have either a positive or a negative charge according to its modifications should play an important role in the interfacial phenomena of titanium dioxide.

TABLE I. OXYGEN-OXYGEN DISTANCES IN ANATASE AND RUTILE, Å

Anatase	Rutile
2.802	2.779
2.446	2.526
3.040	

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2) R. Kiriyama, "Kôzô Muki-Kagaku," Kyôritsu, Tokyo (1955).

3) D. T. Cromer and K. Herrington, *J. Am. Chem. Soc.*, 77, 4708 (1954).