The Electrokinetic Potential of Titanium Dioxide

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Recently attention has been drawn by many investigators to the behavior of hydroxyl groups on the surface of insoluble metal oxides, especially from the viewpoints of the adsorption and the catalytic center of the solid surface.

The existence of hydroxyl groups on the surface of insoluble oxides has been demonstrated by the determination of the water content of powders,[1] by studies of wetting heat[2] and, more directly, by the measurement of infrared absorption spectra.[3-5] It has also been reported that a solid retains a small amount of water even after it has been evacuated at a high temperature.[6]

If an insoluble metal oxide is equilibrated with water, a good many hydroxyl groups will be produced on the solid surface; this formation has a serious effect on the physico-chemical properties of the surface. For this reason, it is of special interest to ascertain the dissociation property of surface hydroxyl groups. In the present work, therefore, the dependences of the electrokinetic potential of titanium dioxide in water on the temperature of the pretreatment and on the concentration of added electrolyte in water have been investigated, in connection with the behavior of surface hydroxyl groups on the solid.

Since the surface properties of a solid, such as the surface charge, are usually affected by the presence of impurities, the effect of sulfate groups contaminating the sample on the electrokinetic potential has also been investigated in detail.

Experimental

Materials.—Titanium dioxide was prepared by the hydrolysis of titanium sulfate*. The raw material thus obtained was contaminated with sulfate groups, the amount of which was 54 mg. SO_4/g. of the sample. X-Ray tests showed the raw material to be anatase in form. The sulfate contained in the raw material was removed by treatment with a definite amount of ammonia water. The conditions of the treatment and the amount of sulfate remaining are shown in Table I. After the raw material had been treated with ammonia water for two hours at 70°C, the sample was thoroughly washed with water. Three kinds of samples thus prepared were dried and calcined in a platinum crucible placed in an electric oven held at a given temperature.

TABLE I. CONDITIONS FOR PREPARING SAMPLES AND THE RESULTS OF THEIR ANALYSIS

	Amouut of ammonia water used	Sulfate remained (mg./g. TiO_2)
TiO_2-0	0	54
TiO_2-1.1	1.1 equivalent of sulfate	12
TiO_2-18	18 equivalent of sulfate	0

Electrokinetic Measurement. — The streaming potential method was used for the determination of the electrokinetic potential (ζ-potential). Both the techniques of the measurement of the streaming potential and the method of calculation used to obtain the ζ-potential were the same as have been reported previously.[7]

Results and Discussion

The Electrokinetic Potential of Titanium Dioxide in Water.—The ζ-potentials of titanium dioxide in water are shown in Fig. 1. The ζ-potential vs. the pretreatment temperature curves of three samples agree almost entirely with one another. In the cases of the samples TiO_2-0 and TiO_2-1.1, especially, when treated at 300°C and 500°C, the streaming potentials showed fairly high values at the beginning of the measurement, but thereafter they decreased continuously for many hours, accompanied with a decrease in the electrical conductance. On the other hand, the potential measured on the TiO_2-18, sample which contains no sulfate, remained constant for many hours. Consequently, the decreases in the streaming potentical and electrical conductance in the case of the samples contaminated with sulfate are possibly due to the decontamination of the samples in the course of the streaming operation.

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

[3] J. B. Peri and R. B. Hannan, ibid., **64**, 1526 (1960).

[4] R. S. McDonald, *J. Am. Chem. Soc.*, **79**, 850 (1957).

[5] M. R. Basila, *J. Chem. Phys.*, **35**, 1151 (1961).

[6] G. J. Young, *J. Colloid Sci.*, **13**, 67 (1958).

* This sample was prepared in the laboratory of Teikoku Kakô Co.

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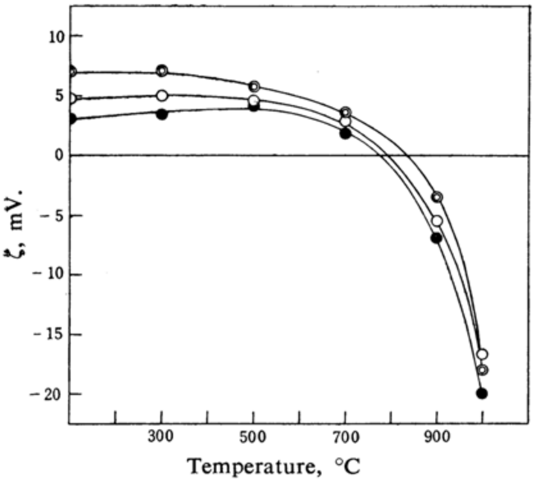

Fig. 1. Dependence of the ζ-potential of TiO_2 on the pretreatment on temperature.
◎ TiO_2-0, ○ TiO_2-1.1, ● TiO_2-18

The results shown in Fig. 1 were obtained after the streaming operation had continued for a long time. It is, therefore, obvious that the values of the streaming potentials on contaminated samples approach those of pure samples when washed with streaming water. Thus, the dependence of the ζ-potential of the TiO_2-18 sample on the pretreatment temperature is considered to be characteristic of titanium dioxide. It may, therefore, be seen from Fig. 1 that titanium dioxide is positively charged in water when it is treated at lower temperatures, whereas it is negatively charged when treated at 1000°C. The inversion of the sign of the surface charge occurs when the sample is treated at about 800°C, a figure which corresponds to the temperature of the transition of anatase to rutile. X-Ray tests on these samples showed that the samples heated at temperatures lower than 700°C are anatase in form, whereas those heated at 1000°C are rutile in form. In order to verify these results, the ζ-potential of rutile powder obtained by the pulverization of the single crystal was measured in water and found to be −36 mV. These results convinced us that the charge of anatase is positive and that of rutile is negative. Although several authors have studied the dependence of the ζ-potential of metal oxides upon their pretreatment temperature,[8-10] no such clearly-established relation has ever been found between the signs of the ζ-potential and the crystal modifications.

When the oxide surface is equilibrated with water, the surface hydroxyl groups will be formed by surface hydration. Further, these hydroxyl groups may be dissociated in two ways:

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

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

If the dissociation of the surface hydroxyl groups occurs according to Eq. 1, it will make the surface positive and basic at the same time. On the contrary, if the dissociation proceeds as in Eq. 2, the surface will become negative and acidic. In our previous study,[11] the surface acidity was observed on the sample of TiO_2-18, which contains no sulfate. Methyl red used as a dyestuff was dissolved in isooctane, a nonpolar solvent. After the dye solution had been shaken with titanium dioxide, the color of the adsorbed dye molecules was observed. When the treatment temperature rises, the color changes from yellow to orange and finally to red, indicating that the surface acidity changes from a basic to an acidic property with an increase in the pretreatment temperature. This proves that the surface hydroxyl groups on titanium dioxide are dissociated following either Eq. 1 or Eq. 2, according to the modifications of the substrate crystal of titanium dioxide.

The crystallographic data of anatase and rutile[12] show that in both crystal forms one titanium atom is surrounded by six oxygen atoms, which are situated on the tops of an octahedron. The bond distances of Ti–O and O–O in anatase and rutile are listed in Table II.[13] It has been reported that the distances of O–O bonds in basic metal hydroxide crystals are longer than about 3.00 Å, while in acidic crystals they are less than 2.70 Å.[14] If we assume that the O–O distances remain almost unchanged when the surface of titanium dioxide is hydrated to form surface hydroxyl

TABLE II. BOND DISTANCES IN TiO_2, Å

	Anatase	Rutile
4 Ti–O	1.937	1.946
2 Ti–O	1.964	1.984
O–O	2.802	2.779
O–O	2.446	2.526
O–O	3.040	

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[8] D. J. O'Connor and A. S. Buchanan, *Austr. J. Chem.*, 6, 278 (1953).

[9] D. J. O'Connor, P. G. Johansen and A. S. Buchanan, *Trans. Faraday Soc.*, 52, 229 (1956).

[10] D. J. O'Connor and A. S. Buchanan, ibid., 52, 397 (1956).

[11] T. Morimoto and M. Sakamoto, This Bulletin, 36, 1369 (1963).

[12] R. W. G. Wyckoff, "Crystal Structure," Interscience Pub. Inc., New York, N. Y. (1948).

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

[14] R. Kiriyama, "Kôzô Muki-Kagaku," Kyôritsu, Tokyo (1955).

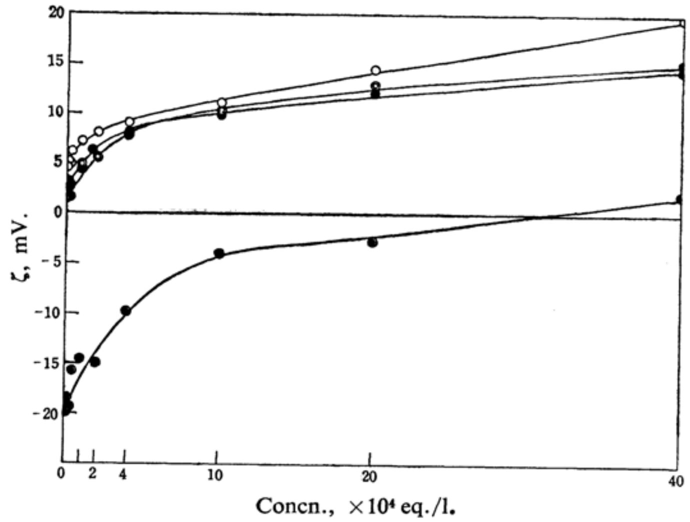

Fig. 2. Effect of barium chloride on the ζ-potential of TiO_2 treated at ● 300°C, ○ 500°C, ◎ 700°C, ◉ 1000°C.

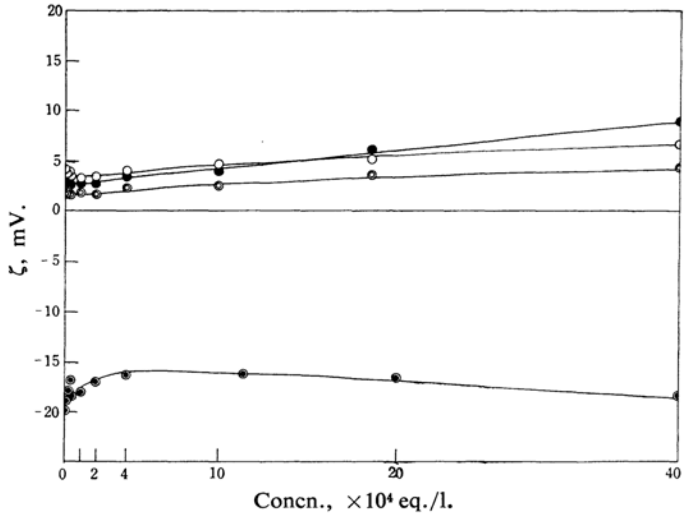

Fig. 3. Effect of potassium chloride on the ζ-potential of TiO_2 treated at ● 300°C, ○ 500°C, ◎ 700°C, ◉ 1000°C.

groups, it may be expected that the surface of rutile is acidic and that of anatase is basic. From this point of view, the present results lead us to postulate that, among the three kinds of O–O bonds of anatase, the longer ones are exposed on its surface to a larger extent.

Electrokinetic Potential in an Electrolyte Solution.—The effect of elctrolytes on the ζ-potential of titanium dioxide has been investigated on the TiO_2-18 sample, which contains no sulfate. The results obtained are shown in Figs. 2—6. Barium chloride seriously affects the ζ-potential of the samples treated at various temperatures (Fig. 2). In this case, the ζ-potential increases with the increasing concentration of barium chloride, independently of the signs of the surface charge of titanium dioxide in water. This indicates that the effect of barium ions is more pronounced than that of chloride ions. The effect of barium ions is greater on the negatively-charged surface than on the positivery-charged surface, and the inversion of the negative charge occurs at a higher concentration. On the other hand, the effect of potassium chloride is much less than that of barium chloride, indicating that the adsorption forces of potassium ions and chloride ions are comparable (Fig. 3). Although at lower concentrations of potassium chloride, the oppositely-charged ions adsorb on the surface of titanium dioxide, at higher

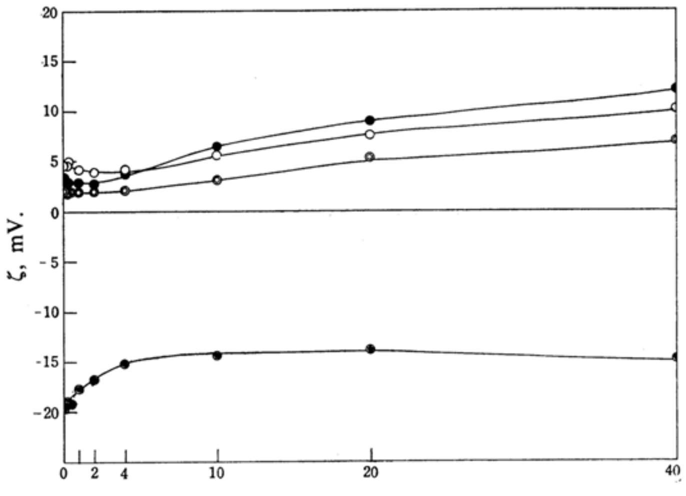

Fig. 4. Effect of hydrochloric acid on the ζ-potential of TiO_2 treated at ● 300°C, ○ 500°C, ◎ 700°C, ◉ 1000°C.

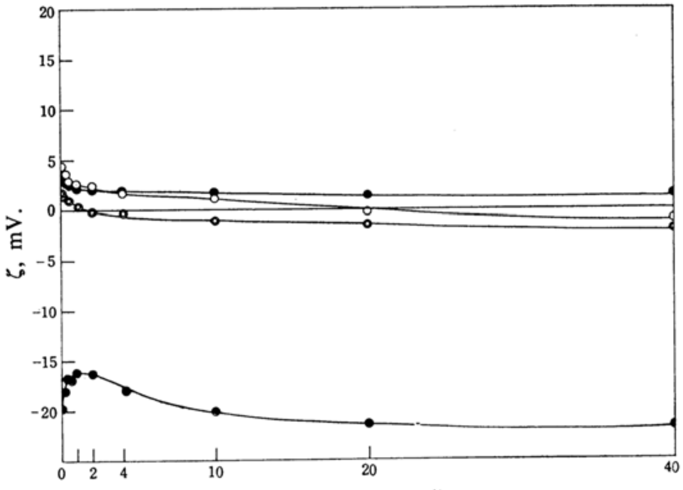

Fig. 5. Effect of potassium hydroxide on the ζ-potential of TiO_2 treated at ● 300°C, ○ 500°C, ◎ 700°C, ◉ 1000°C.

concentrations the counter ions seem to cooperate. The change in ζ-potential in the presence of hydrochloric acid is almost identical with that in the presence of potassium chloride, except that hydrogen ions act more strongly on the solid surface than do potassium ions (Fig. 4). The effect of potassium hydroxide is fairly remarkable, especially in the case of samples treated at moderate temperatures, where the inversion of charge is observed. In the case of a sample treated at 1000°C, the negative potential decreases at first and then increases with the increasing concentration of potassium hydroxide (Fig. 5). In this latter case, the following surface reaction may be considered to take place:

$$\equiv TiOH + KOH \rightarrow \equiv TiOK + H_2O \qquad (3)$$

This reaction will promote the dissociation to form the negatively-charged surface, resulting in the increase in the negative potential.

Sodium triphosphate has an extraordinary influence on the ζ-potential of titanium dioxide (Fig. 6); the positively-charged surfaces in water are all inverted by the addition of triphosphate, and the negatively-charged rutile surface becomes more negative, even at an extremely low concentration of triphosphate. This is obviously caused by the strong adsorption force of triphosphate, suggesting the formation of a complex compound on the surface of titanium dioxide.

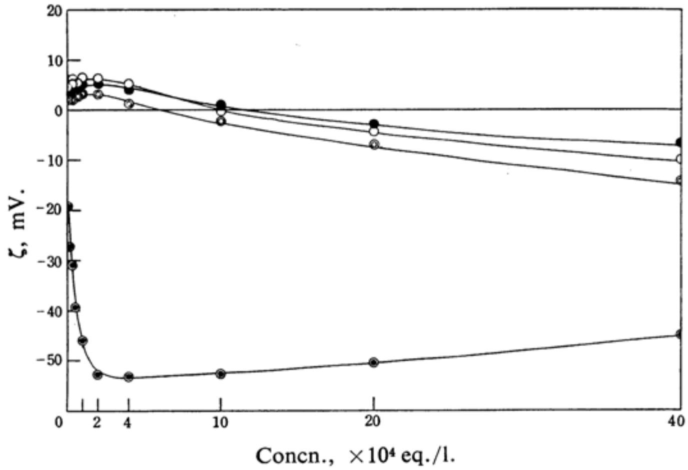

Fig. 6. Effect of sodium triphosphate on the ζ-potential of TiO_2 treated at ● 300°C, ○ 500°C, ◎ 700°C, ◉ 1000°C.

Summary

1) The surface property of titanium dioxide has been investigated by measuring the ζ-potential. The ζ-potential of titanium dioxide in water depends on the temperature of the pretreatment, and its sign changes from positive to negative at about 800°C. This fact has been interpreted in terms of the way of the dissociation of hydroxyl groups on the surface of titanium dioxide, the ways of which depend on its modifications. This phenomenon seems to be supported by crystallographic data.

2) The effects of electrolytes on the ζ-potential of titanium dioxide have been studied. Barium has a chloride greater influence on the ζ-potential of titanium dioxide than does potassium chloride or hydrochloric acid. Hydroxide ions have a fairly great influence on the surface of the solid. The effect of sodium triphosphate is extraordinarily great; by the addition of the electrolyte, the positive potentials of titanium dioxide are inverted to negative potentials and the negatively-charged rutile surface becomes more negative, and this development suggests the formation of a complex compound on the surface of titanium dioxide.

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