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Synthesis of Uniform Anatase TiO_2 Nanoparticles by Gel–Sol Method

1. Solution Chemistry of $Ti(OH)_n^{(4-n)+}$ Complexes[1]

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The mole fractions of hydroxo complexes of titanium(IV) ion in an aqueous solution with 0.10 mol dm^{-3} $NaClO_4$ at 25°C have been determined as a function of pH by a newly developed analytical procedure based on UV spectrophotometry, using a metastable homogeneous solution of 1.25×10^{-4} mol dm^{-3} in total concentration of Ti(IV). Also, the total concentration of the hydroxo complexes in equilibrium with $Ti(OH)_4$ solid, or the solubility of $Ti(OH)_4$ solid in an inhomogeneous system, has been obtained by ICP measurement for the solution phase. A combination of these data yielded the absolute concentration of each complex species in equilibrium with $Ti(OH)_4$ solid. Finally, $Ti(OH)_3^+$ complex has been assigned to the precursor for the formation of anatase TiO_2 nanoparticles transformed from $Ti(OH)_4$ gel from a comparison between the above equilibrium data and a kinetic study on the formation rate of the anatase TiO_2 particles in the gel–sol system. © 2002 Elsevier Science (USA)

Key Words: **titania; anatase; nanoparticles; hydroxo complex; stability constants; titanium hydroxide; gel–sol method.**

INTRODUCTION

Monodispersed anatase titania particles were prepared by the gel–sol method based on a phase transformation process from titanium hydroxide gel or hydrous TiO_2 (1, 2). In this study it was found that spindlelike uniform titania particles (length $\cong 0.3$ μm; aspect ratio $\cong 8$) were obtained in the presence of ammonia as a powerful shape controller and that much smaller nanoparticles of smaller aspect ratios were produced in a lower pH range in the absence of ammonia. For understanding the more detailed background of the gel–sol process, it seems necessary to study the complex chemistry and dynamic behavior of complexes in much simpler systems. Thus, as part 1 of this series, we would like to start with the study on the solution chemistry of titanium hydroxo complexes leading to the formation of anatase titania.

Ti(IV) ion is known to form complexes with a wide variety of anions and other complexing agents, such as hydroxide (3–12), fluoride (12–16), sulfate (3, 4, 17, 18), phosphate (11, 19, 20), chloride (4, 13, 21), carbonate (22), hydrogen peroxide (23, 24), oxalate (25–28), citrate (29–31), lactate (31), tartrate (29, 32, 33), malate (34, 35), ammonia (11, 12), amines (36), 8-hydroxyquinoline (9, 24, 29, 37, 38), thenoyltrifluoroacetone (9, 10), etc. Relevant textbooks (39), reviews (40, 41), and data books (42–44) are also available. The measurements are based on ion-exchange elution (3), batchwise ion exchange (4–7, 17, 21), ion-exchange chromatography (8, 13, 25), liquid–liquid extraction (9, 10, 29, 32, 34, 37), potentiometry (14, 20, 23), dialysis (8, 31), solubility measurement (5, 8, 9, 11, 29, 30, 32), spectrophotometry (37, 38), radiochemical paper electrophoresis (7), NMR (33), etc. For studying the solution chemistry of hydroxo complexes, the pH control has been performed by using inert acids and bases, such as perchloric acid and sodium hydroxide. However, to the best of our knowledge, spectrophotometric analysis on hydroxo complexes of Ti(IV) has never been reported.

The solubility of hydrous TiO_2 is known to be virtually constant above pH 4, but sharply increase below pH 3 (5, 8, 9, 39). The constant solubility above pH 4 may suggest the dominance of the neutral complex, $Ti(OH)_4$, and it seems evident that the dominant species in $HClO_4$ solutions in the pH range, at least, from 1 down to 0 is $Ti(OH)_2^{2+}$ (or TiO^{2+}) from the measurements based on cation-exchange methods (3–7). The pH-dependent solubility of hydrous TiO_2, nearly proportional to the second power of the acid concentration below pH 2, may support the predominance of $Ti(OH)_2^{2+}$ in this pH range.

However, the composition of the hydrous TiO_2 does not appear to have clearly been defined, and there seems to be no definite evidence that a single species, $Ti(OH)_2^{2+}$, is dominant below pH 2. In addition, although the presence of $Ti(OH)_3^+$ has been expected, its reliable data are unavailable as yet probably because of the difficulty in detection by conventional methods (39).

The objectives of the present study are to specify the composition of the hydrous TiO_2, to re-evaluate the contribution of each complex species to the solubility of the hydrous TiO_2, and to

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identify the precursor species for the formation of anatase TiO_2 nanoparticles from the hydrous TiO_2, as essential bases for the mechanistic studies on the formation of anatase TiO_2 nanoparticles in the gel–sol system. For these purposes, a new analytical method, based on the UV spectrophotometry for a metastable homogeneous system of titanium hydroxo complexes, has been introduced.

EXPERIMENTAL

Materials

Reagent-grade titanium (IV) isopropoxide, sodium hydroxide, and perchloric acid have been used as received.

Preparation of Titanium Hydrous Oxide

Titanium hydrous oxide precipitate was prepared by mixing titanium isopropoxide (TIPO: $Ti(OCH(CH_3)_2)_4$) with deionized pure water and washed with pure water three times by centrifugation. The precipitate was then freeze-dried before use or directly used as a suspension without freeze-drying.

Determination of the Composition of the Titanium Hydrous Oxide Powder

Thermogravimetry (TG) and differential thermal analysis (DTA) for the freeze-dried titanium hydrous oxide powder were performed with a Rigaku Thermoflex TAS200 at a heating rate of 20° min^{-1}. The sample weight was 40 mg, and α-Al_2O_3 powder was used as a reference of the heat flow in DTA. From the weight loss in TG, the composition of the titanium hydrous oxide was determined on assumption of the loss of water.

UV Spectrophotometry of the Titanium Hydroxo Complexes

The purified titanium hydrous oxide precipitate was dissolved in an aqueous solution of perchloric acid without freeze-drying to determine the content of titanium ion by inductively coupled plasma (ICP) spectrometry. This acidic solution of titanium ion was diluted with a $HClO_4$ solution to 1.25×10^{-3} mol dm^{-3} in Ti(IV), where the final concentration of $HClO_4$ in this Ti(IV) solution was 1.0 mol dm^{-3}. From this stock solution, solutions of different pH values containing 1.25×10^{-4} mol dm^{-3} in Ti(IV) were prepared by diluting with $HClO_4$ solutions, pure water, or NaOH solutions. The ionic strength was automatically adjusted to 0.1 by this dilution procedure, except for dilution with $HClO_4$ solutions. UV spectra and pH values of these metastable homogeneous solutions of titanium hydroxo complexes at 25°C were measured within 15 min after the final dilution to 1.25×10^{-4} mol dm^{-3} Ti(IV). The purpose of this experiment is to determine the stability constants of the Ti(IV) hydroxo complexes on the assumption of the equilibrium among the solute species before the start of the precipitation of hydrous oxide gel.

Specification of the Dominant Titanium Hydroxo Complex at pH ≅ 1

First, we prepared a calibration curve of pH as a function of the proton concentration by changing the mole number of NaOH dissolved in 100 cm^3 of 0.10 mol dm^{-3} $HClO_4$. Then the pH value of 0.10 mol dm^{-3} $HClO_4$ (100 cm^3) after mixing with a known amount of titanium hydrous oxide precipitate was compared to the calibration curve to determine the mole number of the released OH^- ion, leading to the composition of the dominant hydroxo complex. The exact amount of Ti(IV) in this solution was determined by ICP measurement after the pH measurement. For this experiment, the titanium hydrous oxide precipitate was prepared, purified, and used without freeze-drying. The approximate molarity of Ti(IV) in the stock suspension of titanium hydrous oxide precipitate was predetermined by dissolving a part of the homogenized stock suspension in 1.0 mol dm^{-3} $HClO_4$, followed by ICP measurement.

To check if or not a single species is dominant at pH ≅ 1, the behavior of the UV spectrum was observed with the change of pH around this pH.

Solubility of Titanium Hydrous Oxide as a Function of pH

After preparation and purification of titanium hydrous oxide precipitate, 10^{-3} mol of the titanium hydrous oxide precipitate was directly suspended in 20 cm^3 of water of different pH values, ranging from 1 to 12, with an ionic strength of 0.1, adjusted with $NaClO_4$, and aged at 25°C for 72 h, which was sufficient for establishing the equilibrium between the complexes in the solution phase and the hydrous oxide precipitate, as confirmed by ICP measurement as a function of time for the supernatant solution. After the measurement of the final pH of each aged sample, they were centrifuged at 18,000 rpm for 30 min, and the supernatant Ti(IV) concentrations were measured by ICP.

Formation Rate of Anatase TiO_2 Dependent on pH

Forty cubic centimeters of 0.25 mol dm^{-3} titanium hydrous oxide gel, instantly formed upon mixing titanium(IV) isopropoxide with water at a varying pH containing $HClO_4$ or NaOH and $NaClO_4$ to adjust the final ionic strength to 0.10, was aged for 2 h at room temperature to stabilize the pH and then for 30 min in an oil bath preheated at 100°C. The initial pH of each sample at the start of aging at 100°C ranged from 0.7 to 11.6. The yield of anatase titania particles from titanium hydrous oxide in each sample was determined by dissolving the remaining titanium hydrous oxide in a solution of 2.0 mol dm^{-3} HNO_3 and ICP analysis on the supernatant Ti(IV) after centrifugal separation of anatase TiO_2 settled intact in the 2.0 mol dm^{-3} HNO_3. This method is based on the natures of hydrous TiO_2, readily dissolved in 2.0 mol dm^{-3} HNO_3, and of crystalline anatase TiO_2, virtually undissolved in 2.0 mol dm^{-3} HNO_3.

The mean size of the anatase TiO_2 particles after aging for 24 h at 100°C as a function of pH was measured by transmission electron microscopy.

DATA ANALYSIS

If the hydroxo complexes of titanium(IV) in water are assumed to be generally written as $Ti(OH)_n^{(4-n)+}$ ($n = 2, 3, 4$) the UV absorbance of their homogeneous solution, A_i, in a quartz cell of light path length of 1 cm at a wavelength λ_i may be given as

$$A_i = \varepsilon_a^i c_a + \varepsilon_b^i c_b + \varepsilon_c^i c_c, \qquad [1]$$

where ε_a^i, ε_b^i, and ε_c^i are absorption coefficients ($mol^{-1}\,dm^3\,cm^{-1}$); c_a, c_b, and c_c are the concentrations of $Ti(OH)_2^{2+}$, $Ti(OH)_3^+$, and $Ti(OH)_4$, respectively. The stability constants of $Ti(OH)_3^+$, K_b, and of $Ti(OH)_4$, K_c, may be defined as

$$K_b = \frac{c_b}{c_a[OH^-]} \qquad [2]$$

and

$$K_c = \frac{c_c}{c_b[OH^-]}. \qquad [3]$$

If the total concentration of these complexes is denoted by c_0, it holds that

$$c_a + c_b + c_c = c_0. \qquad [4]$$

A combination of Eqs. [1]–[4] yields

$$A_i = \frac{c_0\left(\varepsilon_a^i + \varepsilon_b^i K_b[OH^-] + \varepsilon_c^i K_b K_c[OH^-]^2\right)}{1 + K_b[OH^-] + K_b K_c[OH^-]^2}. \qquad [5]$$

If the pH is sufficiently low, the contribution of $Ti(OH)_4$ may be ignored and thus Eq. [5] may be approximated by

$$A_i = \frac{c_0\left(\varepsilon_a^i + \varepsilon_b^i K_b[OH^-]\right)}{1 + K_b[OH^-]} \qquad [6]$$

or

$$A_i = -\frac{1}{K_b}\frac{A_i - \varepsilon_a^i c_0}{[OH^-]} + \varepsilon_b^i c_0. \qquad [7]$$

If ε_a^i is known, one may plot A_i against $(A_i - \varepsilon_a^i c_0)/[OH^-]$ ($\equiv X_i$) based on Eq. [7], yielding K_b from the slope of the straight line and ε_b^i from the intercept of the A_i axis at $X_i = 0$. Here, $[OH^-]$ is defined by 10^{-14+pH}.

If the contribution of the third component, $Ti(OH)_4$, becomes significant with increasing pH, one must use the following formula transformed from Eq. [5] without approximation:

$$A_i = -\frac{1}{K_c}\left[\frac{A_i - \varepsilon_a^i c_0}{K_b[OH^-]^2} + \frac{A_i - \varepsilon_b^i c_0}{[OH^-]}\right] + \varepsilon_c^i c_0. \qquad [8]$$

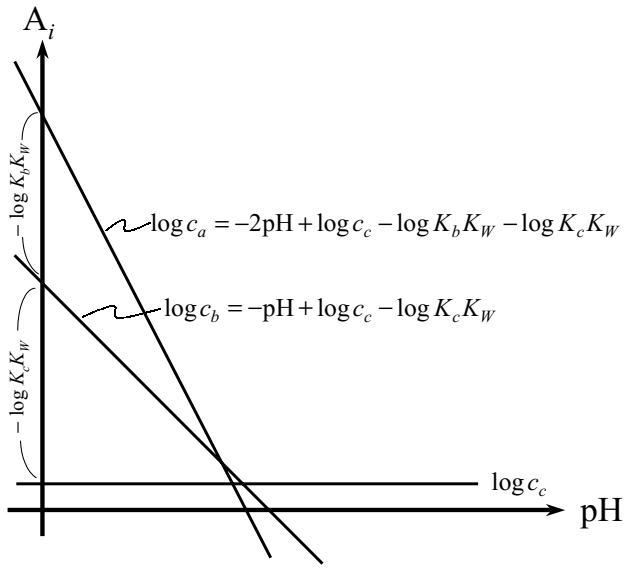


FIG. 1. General relationships among log c_a, log c_b, and log c_c.

Since K_b and $\varepsilon_b^i c_0$ are now known from the plot of Eq. [7], one can plot A_i against $\{(A_i - \varepsilon_a^i c_0)/K_b[OH^-]^2 + (A_i - \varepsilon_b^i c_0)/[OH^-]\}$ ($\equiv Y_i$), yielding K_c from the slope and ε_c^i from the intercept at $Y_i = 0$.

From Eqs. [2] and [3], log c_a and log c_b are given as a function of pH,

$$\log c_a = -2pH + \log c_c - \log K_b K_w - \log K_c K_w \qquad [9]$$

and

$$\log c_b = -pH + \log c_c - \log K_c K_w, \qquad [10]$$

where $K_w = [H^+][OH^-] = 10^{-14}$ $mol^2\,dm^{-6}$. Here, it is noteworthy that c_c, or $[Ti(OH)_4]$, is constant, regardless of pH, in the presence of $Ti(OH)_4$ precipitate, as may be detected as a plateau of the solubility curve of titanium hydroxide precipitate in the higher pH range. Once c_c is determined from the measurement of the solubility of the hydroxide precipitate, log c_a and log c_b are given as fixed straight lines with slopes -2 and -1, against pH, and the relative positions of these two lines and log c_c may be illustrated as in Fig. 1.

RESULTS AND DISCUSSION

Composition of Titanium Hydrous Oxide

Figure 2 shows the TG and DTA curves of the titanium hydrous oxide powder, prepared by mixing Ti(IV) isopropoxide with distilled water, purified by centrifugal rinsing with pure water, and freeze-dried. The stepwise weight loss with the endothermic transition at 70°C, the exothermal transition at 325°C, and the exothermal transition at 540°C may correspond to the evaporation of adsorbed water, the transition from

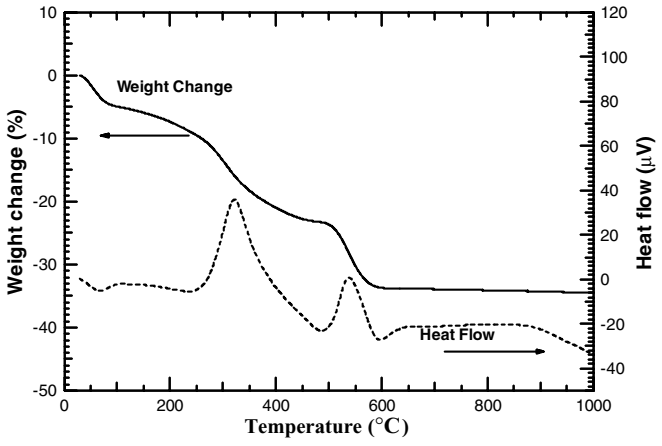


FIG. 2. TG-DTA diagram for titanium(IV) hydrous oxide prepared by mixing Ti(IV) isopropoxide with water, purified by centrifugal washing with pure water, and freeze-dried.

titanium hydrous oxide to $TiO(OH)_2$, and the transition from $TiO(OH)_2$ to TiO_2, respectively. If we assume that the actual weight loss of the titanium hydrous oxide started from 70°C, by which 4% of the original weight had already been lost, the total weight loss of the titanium hydrous oxide may be calculated as $(0.34–0.04) \times 100/(1.00–0.04) = 31.2\%$. This value is very close to the theoretical weight loss of 31.1% with the transition from $Ti(OH)_4$ to TiO_2. Hence, one may conclude that the titanium hydrous oxide assumes a composition of titanium hydroxide, $Ti(OH)_4$.

Characteristics of the UV Spectra in the Ti(IV) Complex System

Figure 3 shows UV spectra of the metastable complex system of 1.25×10^{-4} mol dm^{-3} in total Ti(IV) concentration at different pH values at 25°C. Here, the weak absorption of ClO_4^- below 220 nm was subtracted. One of the most salient characteristics of these spectra may be that they are virtually fixed below pH 1.07 within the tested pH range, suggesting that a single complex species, whose absorption peak seems to be located at a wavelength much lower than 200 nm, is dominant. Another characteristic is that the absorption spectrum at pH 9.31 basically differs from those below pH 3.69, as is obvious from the absorbance at pH 9.31 significantly lower than those at pH 3.30 and 3.69 in the wavelength range between 240 and 340 nm. This may imply that the dominant species in the alkaline range is different from those below pH 3.69.

As is already expected from the spectra at pH 3.30, 3.69, and 9.31 with their relatively high backgrounds in the wavelength range above 340 nm, the solution was more or less unstable as showing some sign of the precipitation of $Ti(OH)_4$ gel in the pH range above pH 3. This fact may suggest the increasing contribution of the neutral complex, $Ti(OH)_4$, in this pH range.

Composition of the Complex at a pH ≤ 1

Figure 4 shows the calibration curve of $[H^+]$ vs pH below pH 2. When 0.0131 mol dm^{-3} $Ti(OH)_4$ was dissolved in 0.100 mol dm^{-3} $HClO_4$, the resulting pH was found to be 1.21, corresponding to $[H^+] = 0.075$ mol dm^{-3}. Thus, 0.025 mol dm^{-3} (=0.100–0.075) of hydroxide ion, OH^-, must have been released from the 0.0131 mol dm^{-3} $Ti(OH)_4$. In other words, the average n value for $Ti(OH)_n^{(4-n)+}$ complexes at pH 1.21 is calculated as 2.09 (=4.00–0.025/0.0131). This means that the complex species at pH 1.21 is mostly $Ti(OH)_2^{2+}$, probably with a small content of a complex of high n, such as $Ti(OH)_3^+$. If we consider the presence of a single complex species below pH 1.07, as suggested from the UV spectra in Fig. 3, the single species must be $Ti(OH)_2^{2+}$. This conclusion is congruent with most data reported before for the overall composition of the complexes

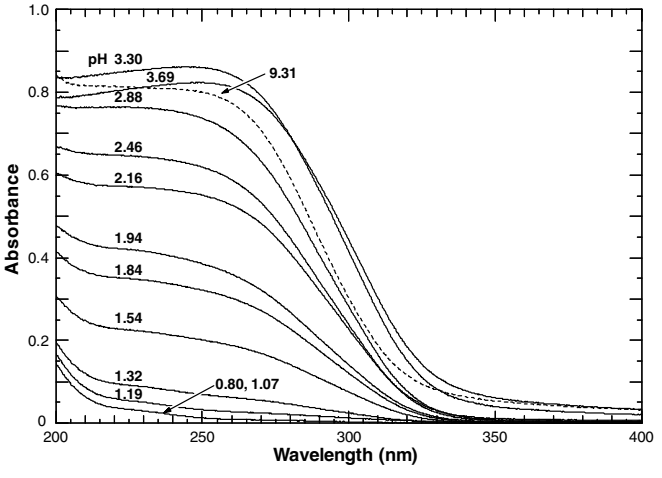


FIG. 3. UV spectra of metastable homogeneous aqueous solutions of Ti(IV) hydroxo complexes of different pH values at 25°C with a total Ti(IV) concentration of 1.25×10^{-4} mol dm^{-3} and ionic strength 0.1 adjusted with ClO_4^-. The UV spectra and pH values were measured within 15 min after the final dilution of 1.25×10^{-3} to 1.25×10^{-4} mol dm^{-3} Ti(IV) of different pH values. The weak UV absorbance of ClO_4^- ion was subtracted from each spectrum.

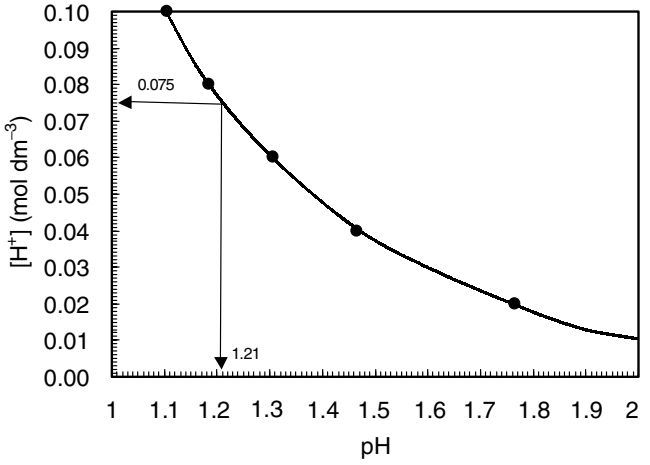


FIG. 4. Calibration curve of $[H^+]$ vs pH below pH 2, used for determining the released OH^- from a known amount of $Ti(OH)_4$ precipitate, to specify the composition of the hydroxo complex below pH 1.

in this pH range (39). As has been confirmed that the complex species below pH 1 is a single species, $Ti(OH)_2^{2+}$, it seems reasonable to consider that the increase in absorbance above pH 1 in Fig. 3 is due to the increasing contribution of $Ti(OH)_3^+$, followed by the increasing weight of the neutral complex, $Ti(OH)_4$, above pH 3.

Stability Constants and Mole Fractions of the Complexes

For the analysis of the spectrophotometric data, the UV spectra at different pH values in Fig. 3 were modified into the absorbance as a function of pH for each wavelength, as shown in Fig. 5. Here, each curve in Fig. 5 was obtained as a sixth-degree polynomial by least squares for the data points.

Figure 6 shows the plot of A_i vs X_i in Eq. [6] for wavelengths 260, 270, 280, 290, and 300 nm, using the data of A_i as a function of pH in Fig. 5. Here, each ε_a^i used in this plot was obtained from the UV spectra at a pH $\leq$1.07 in Fig. 3, as listed in Table 1. We could obtain a linear relationship for A_i vs X_i in the pH range from ca. 1.5 to 2.3, and A_i gradually deviated downward from the straight line with the decreasing X_i or increasing pH, suggesting the increasing contribution of another complex, $Ti(OH)_4$, of a lower absorption coefficient in the higher pH range. From the average slope of the linear range and the individual intercepts for different wavelengths, we obtained log $K_b = 11.9$ and each ε_b^i as listed in Table 1.

Incidentally, if the increasing absorbance with increasing pH from 1 to 2.5 in Fig. 3 is assumed to be due to the increasing contribution of $Ti(OH)_4$ instead of $Ti(OH)_3^+$, there must be a linear relationship in the plot of A_i vs $(A_i - \varepsilon_a^i c_0)/[OH^-]^2$

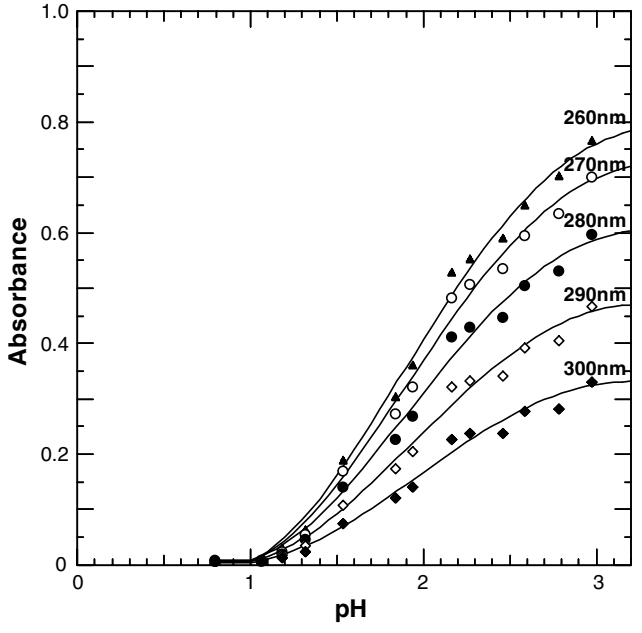


FIG. 5. UV absorbances as a function of pH at different wavelengths, modified from Fig. 3.

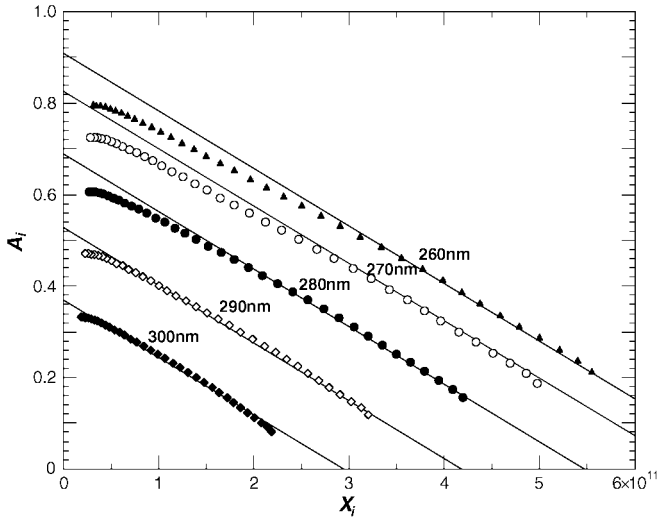


FIG. 6. Plots of A_i vs X_i ($\equiv(A_i - \varepsilon_a^i c_0)/[OH^-]$) in Eq. [7] for determining K_b and ε_b^i at different wavelengths, based on ε_a^i.

and downward deviation in the higher pH range. However, since this plotting resulted in only a curve going up with increasing curvature above pH 1.5, there is no doubt that the increasing absorbance with pH from 1 to 2.5 is not due to the increasing contribution of $Ti(OH)_4$.

Figure 7 shows the plot of A_i vs Y_i corresponding to Eq. [8] for a higher pH range above 2 in Fig. 5. From the average slope and the individual intercepts for different wavelengths, we obtained log $K_c = 10.3$ and each ε_c^i as listed in Table 1.

Figure 8 shows the changes of the mole fractions of the three complex species with pH, as calculated from the stability constants, K_b and K_c. In particular, it is noteworthy that the presence of the $Ti(OH)_3^+$ complex and its significant contribution have clearly been revealed.

Solubility of $Ti(OH)_4$ Precipitate as a Function of pH

The solubility data of the $Ti(OH)_4$ precipitate, obtained from the ICP measurement of the supernatant solutions, are shown as a function of pH in Fig. 9 by closed circles. The straight

TABLE 1
Absorption Coefficients and Stability Constants (25°C, $\mu = 0.1$)

	Absorption coefficients (mol^{-1} dm^3 cm^{-1})		
Wavelength (nm)	ε_a^i	ε_b^i	ε_c^i
260	6.40×10	7.27×10^3	6.18×10^3
270	5.60×10	6.59×10^3	5.42×10^3
280	4.00×10	5.36×10^3	4.58×10^3
290	3.20×10	4.22×10^3	3.29×10^3
300	2.48×10	2.97×10^3	2.32×10^3
Stability constants	log $K_b = 11.9$	log $K_c = 10.3$	

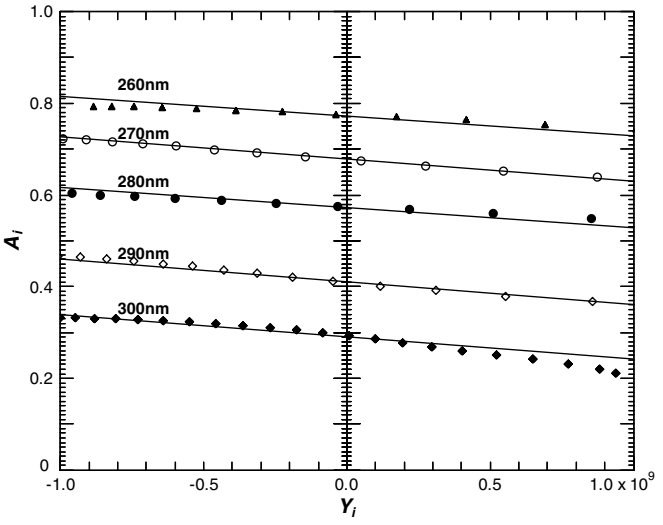


FIG. 7. Plots of A_i vs Y_i ($\equiv(A_i-\varepsilon_a^i c_0)/K_b[\mathrm{OH}^-]^2+(A_i-\varepsilon_b^i c_0)/[\mathrm{OH}^-]$) in Eq. [8] for determining K_c and ε_c^i at different UV wavelengths, based on the predetermined ε_a^i, ε_b^i, and K_b.

lines of log c_a and log c_b as a function of pH were obtained from the experimental data of log $c_c(=-5.5)$, represented by the horizontal line, and the data of K_b and K_c. The dashed curve represents the calculated solubility as the total of c_a, c_b, and c_c. Obviously, there is good agreement between the solubilities obtained directly from the ICP measurement and those calculated from c_c, K_b, and K_c on the basis of UV spectrophotometry.

Although our data for the solubility in the alkaline range, determined by the equilibrium concentration of $Ti(OH)_4$ complex, agree with most of the preceding data in the literature (39), those below pH 2 are somewhat higher than the preceding data. This may probably be due to the nature of the hydroxide gel. For example, we used freshly prepared $Ti(OH)_4$ precipitate without drying, and its solubility was likely to be lowered even with

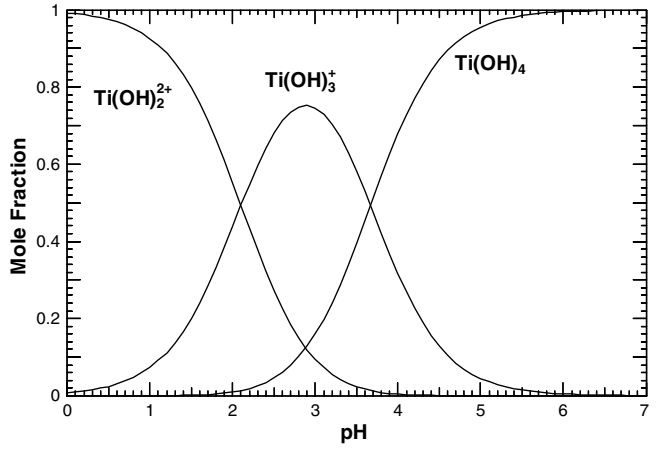


FIG. 8. Mole fractions of $Ti(OH)_2^{2+}$, $Ti(OH)_3^+$, and $Ti(OH)_4$ complexes as a function of pH at 25°C and ionic strength 0.1.

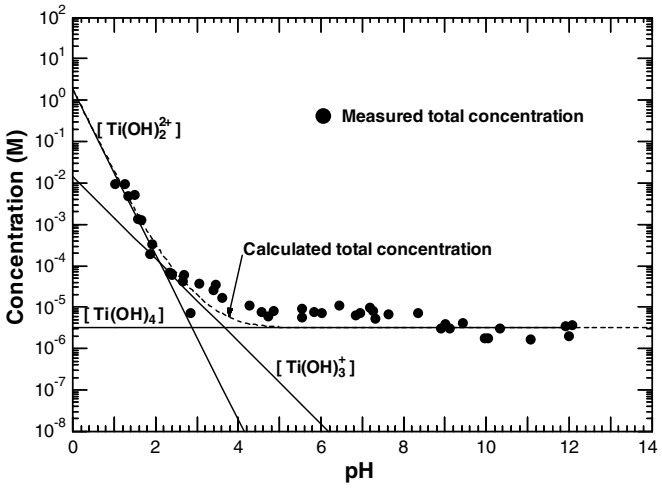


FIG. 9. Concentrations of $Ti(OH)_2^{2+}$, $Ti(OH)_3^+$, and $Ti(OH)_4$ complexes, in equilibrium with $Ti(OH)_4$ precipitate, as a function of pH at 25°C and ionic strength 0.1, as determined from UV spectrophotometry and ICP measurement of $c_c(=[Ti(OH)_4])$. The dashed curve indicates the total concentration of the complexes estimated from the calculated concentrations of the individual complexes, whereas the closed circles stand for the experimental data of solubility from ICP measurement after establishing the equilibrium between the $Ti(OH)_4$ precipitate and the complexes in the solution phase by aging at 25°C for 72 h.

freeze-drying or with aging for a long time or at a relatively high temperature. In fact, we observed a dramatic reduction of the solubility of $Ti(OH)_4$ gel during the first aging period at 100°C in a gel–sol system for the synthesis of uniform anatase TiO_2 particles in the presence of triethanolamine and with the elevation of temperature to 140°C for the following second aging period (1, 2). These effects of aging time and temperature may be explained in terms of transition to a more rigid gel structure with the progress of hydrogen bonding. If the $Ti(OH)_4$ solids used in the foregoing studies were subjected to some of such effects, the somewhat lower solubility below pH 2 in the literature may readily be understood. If it is the case, the actual equilibrium concentration of $Ti(OH)_4$ complex in the literature may possibly be somewhat lower than reported.

In the solubility curve of Fig. 9, one may find a pH range from 3 to 8 where the experimental data are a little higher than the average solubility level. The slightly higher solubilities were not affected by variation of the rotation rate for the centrifugal separation of the $Ti(OH)_4$ precipitate up to 50,000 rpm for 30 min. In view of the virtually pH-independent deviation from the average solubility level, this may not be due to the contribution of dehydrated, dimerized, or trimerized clusters of a charged complex, such as $Ti(OH)_3^+$, since their concentrations must be proportional to the first, second, or third power of the concentration of the coexisting charged single complex, respectively. On the other hand, the measured solubilities above pH 10 appear to be lower than the average level. Hence, the most likely is the variation of the concentration of $Ti(OH)_4$ complex in equilibrium with the $Ti(OH)_4$ gel whose rigidity, or degree of hydrogen bonding, may depend on pH to some extent.

The contribution of complexes of higher coordination of OH^-, such as $Ti(OH)_6^{2-}$, leading to the increase in solubility in the high pH range, was not observed in the tested range.

Formation Rate of Anatase TiO_2 as a Function of pH

Figure 10a shows the yield of anatase TiO_2 transformed from $Ti(OH)_4$ gel (0.25 mol dm^{-3}) with $[NaClO_4] = 0.10$ mol dm^{-3} as a function of initial pH after aging for 30 min in an oil bath preheated at 100°C. The pH was measured after quenching to room temperature. The pH-dependent yield of TiO_2 within a limited time, 30 min, may represent the formation rate of TiO_2 from $Ti(OH)_4$ gel as a function of pH. One may find that the formation rate of TiO_2 significantly increases with the reduction of pH, especially in the acidic range. Figure 10b shows the final mean size of TiO_2 as a function of initial pH after aging for 24 h at 100°C in the same system, where the yield of TiO_2 after 24 h was virtually 100% below pH 7, but ca. 70% at pH 9.0 and ca. 0% at pH 11.6. Obviously, the final particle size is reduced with decreasing pH to ca. 2 but a slight increase below pH 2. From the comparison between Figs. 10a and 10b, one may conclude that the nucleation rate of TiO_2 is greatly accelerated with the reduction of pH to ca. 2. If the nucleation rate of TiO_2 were simply described only by the supersaturation for TiO_2, there would be no pH dependence in its nucleation rate since the supersaturation for TiO_2, represented by the concentration of $Ti(OH)_4$ complex virtually in equilibrium with the $Ti(OH)_4$ precipitate, is constant for all pH. In other words, the strong pH dependence in the nucleation rate of TiO_2 reveals that some specific complex is responsible for the nucleation of TiO_2 as a precursor intermediate. The sharp increase of the formation rate, or nucleation rate, with the reduction of pH from 6 to 2 in Fig. 10a may be closely related to the increase in the equilibrium concentration of $Ti(OH)_3^+$ in Figs. 8 and 9. Moreover, the increase in the formation rate of TiO_2 below pH 3 is rather small, as compared to the dramatic increase of the equilibrium concentration of $Ti(OH)_2^{2+}$ species in proportion to the square of $[H^+]$. Therefore, the $Ti(OH)_3^+$ species is assigned to the precursor complex to anatase TiO_2 in the gel–sol system.

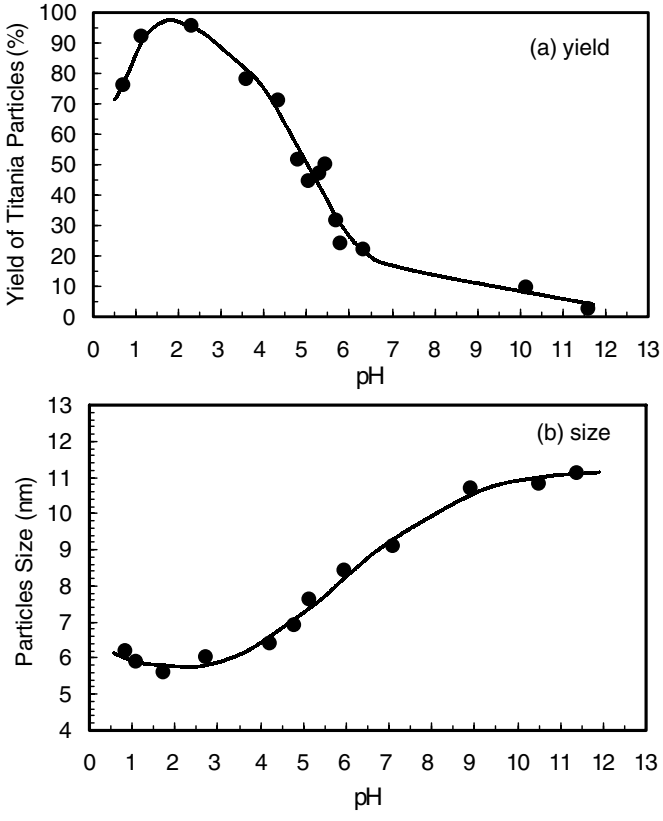
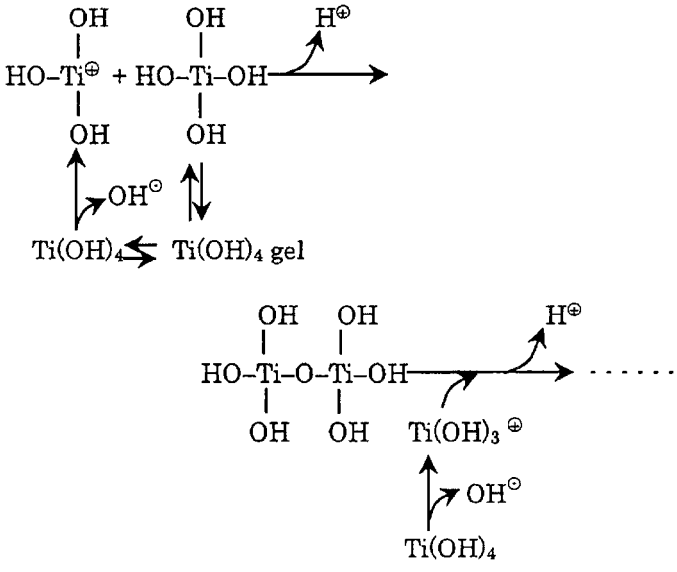


FIG. 10. (a) The yield of TiO_2 particles, as a function of the initial pH, after aging 0.25 mol dm^{-3} $Ti(OH)_4$ gel at 100°C for 30 min in the presence of $NaClO_4$ to adjust the ionic strength to 0.10. (b) The mean size of TiO_2 as a function of the initial pH after aging the $Ti(OH)_4$ gel at 100°C for 24 h, where TiO_2 yield ~100% for a pH <7, ~70% at pH 9.0, and ~0% at pH 11.6.

On the other hand, if we take into account that the overall reaction for the transformation from $Ti(OH)_4$ gel to TiO_2 sol is $Ti(OH)_4 \rightarrow TiO_2 + 2H_2O$, the precursor complex must only be a catalyst or an intermediate, and thus $Ti(OH)_4$ complex, constantly furnished from the $Ti(OH)_4$ gel with the progress of the reaction, may also contribute to the polycondensation reaction in the formation of TiO_2 particles. Therefore, the following elementary processes may be involved in the overall reaction.



The decrease in the formation rate of TiO_2 below pH 2 in Fig. 10a may be due to the reduction of the concentration of $Ti(OH)_4$ complex after the total dissolution of $Ti(OH)_4$ gel in this pH range. This fact may support the above scheme in which $Ti(OH)_3^+$ complex can play the role of the precursor to TiO_2 in collaboration with $Ti(OH)_4$ complex.

CONCLUSIONS

(1) The composition of the freshly prepared hydroxide precipitate was found to be $Ti(OH)_4$, as determined from the TG-DTA measurement.

(2) The predominant hydroxo complex of Ti(IV) in the pH range below 1 is $Ti(OH)_2^{2+}$, as confirmed by UV spectrophotometry and pH measurement of released OH^- from $Ti(OH)_4$ gel.

(3) The concentrations of the $Ti(OH)_2^{2+}$ and $Ti(OH)_3^+$ complexes, c_a and c_b, in equilibrium with the $Ti(OH)_4$ precipitate were determined as a function of pH from the stability constants of $Ti(OH)_3^+$ and $Ti(OH)_4$ complexes, K_b and K_c, determined by UV spectrophotometry, and from the concentration of $Ti(OH)_4$ complex, c_c, in equilibrium with $Ti(OH)_4$ precipitate, determined by ICP measurement. In particular, the presence of $Ti(OH)_3^+$ complex was clearly manifested in the diagram for the mole fractions of the individual complexes as a function of pH. The total solubility as a function of pH, calculated from c_a, c_b, and c_c, was in good agreement with those directly measured by ICP.

(4) The precursor complex to anatase TiO_2 has been specified to be $Ti(OH)_3^+$ in the gel–sol system.

(5) Elementary processes in the transformation of $Ti(OH)_4$ gel to TiO_2 sol, involving the neutral complex, $Ti(OH)_4$, as a counterpart of $Ti(OH)_3^+$, has been suggested.

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