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New types of hydrous titanium oxides obtained by homogeneous precipitation from (titanium (III) chloride + urea) solutions

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Four kinds of hydrous titanium oxide (HTiO) were prepared by refluxing 1 mol dm^{-3} titanium (III) chloride ($TiCl_3$) solutions containing urea (urea to titanium mole ratio = 2.0, 3.0, 4.5, and 6.0; the ($TiCl_3$ + urea) system) at 371 K. Their physicochemical properties were investigated by means of X-ray diffraction (XRD), differential thermal analysis (DTA–TG), electronmicroscopy, colour measurement, and nitrogen adsorption–desorption at 77 K. A rod-like sample 0.2 μm wide and 1.0 μm long was obtained in the case of urea to titanium mole ratio of 2.0. The transmission electronmicrograph showed that the rods were aggregates of acicular crystals in a parallel arrangement. Blue samples of microcrystalline rutile were obtained in the case of an urea to titanium mole ratio above 3.0. The electron spin resonance (ESR) measurement showed that the blue colouration was ascribed to the presence of stable paramagnetic titanium (III) ions.

A chemical mechanism for the formation of rod-like and blue-coloured HTiOs is proposed.

1. Introduction

Hydrous titanium oxide (HTiO) has attracted attention as, for example an adsorbent [1–3], and photocatalyst [4]. The adsorptive or catalytic activity of HTiO depends strongly on its physicochemical properties. There have been extensive studies on the method of preparation and the properties of HTiO [5–25].

The thermal hydrolysis from solutions of titanium salts is one of the common methods for the preparation of HTiO. This method gives a variety of HTiOs whose nature depends on the starting titanium salt compound [16, 18, 23, 24] and on precipitation conditions [5, 6]. Moreover, the addition of water-soluble material during precipitation results in HTiOs with different physicochemical properties. The addition of polyvinylpyloridone and polyethylene glycol leads to a remarkable increase in the surface area, as well as an increase in the pore volume of HTiO [12]. The addition of Na_2SO_4 to a highly acidic solution of $TiCl_4$ gives the HTiO sols consisting of spherical particles of narrow size distributions [10]. The homogeneous precipitation method gives precipitates which have uniform physicochemical properties and little coprecipitation. We have tried a method involving the addition of urea to $TiCl_4$ solution, in analogy to the homogeneous precipitation method. The added urea has been found to stabilize the anatase structure and depress any changes in the pore structure during heat ageing [17].

The present paper describes the bulk and surface studies of the HTiOs obtained by thermal hydrolysis from ($TiCl_3$ + urea) solutions and discusses the formation process of the new types of HTiOs. Since the hydrolysis of titanium (III) ions occurs at higher pH values than that of titanium (IV) ions, $TiCl_3$ is the most suitable starting titanium salt to obtain a HTiO with homogeneous physicochemical properties.

2. Experimental procedure

2.1. Preparation of HTiO

1 mol · dm^{-3} titanium (III) chloride solution (1 dm^3) containing urea (urea to titanium mole ratio = 2.0, 3.0, 4.5, and 6.0) was refluxed with vigorous stirring at 371 K. After 8 h of reflux, the precipitates were aged for 12 h at room temperature, then filtered, washed with distilled water until it was free from chloride ions, and dried at 343 K. The samples were designated TU-2, TU-6, etc. so that the numbers corresponded to the starting urea to titanium mole ratio. A small amount of suspension (20 cm^3) was sampled at a known time during the reflux, and then the pH value of the solution and the weight of solid in the suspension were measured at room temperature. Although these pH values are not equal to the actual pH values at 371 K, they may be useful as a measure of the proton concentrations in the reacting solutions.

2.2. Measurement of physicochemical properties

XRD analyses were made with a Nihon–Denshi (JEOL) JDX-8P X-ray diffractometer using nickel-

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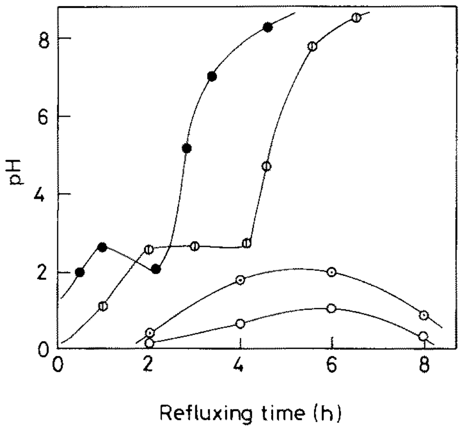

Figure 1 Time dependences of the pH value of the reacting solution, (urea to titanium mole ratio, ○ 2, ⊙ 3, ⦶ 4.5, ● 6).

filtered $CuK\alpha$ radiation. Transmission and scanning electronmicroscope (TEM and SEM) observations were made using Hitachi H-800 and JEOL JSM-T3 electronmicroscopes, respectively. DTA–TG analyses were carried out with a Rigaku–Denki thermoflex (model 8001) at a heating rate of $10\,K\,min^{-1}$. Colour measurements were made with a Nihon–Denshoku–Kogyo ND-1001DP apparatus for powder samples. The *L* value in Hunter's equation [26] was used for referring to the brightness; the increase in the *L* value corresponds to the increase in the brightness. The tint (*a*, *b*) was expressed by the right-angled coordinates system of the colour-body. ESR spectra were obtained with a JEOL JES-RE3X ESR spectrometer at 123 K. Nitrogen adsorption–desorption isotherms were obtained on a Carlo Erba 1800 sorptmatic with outgassed samples for 3 h below 10^{-3} mmHg at 343 K. Specific surface areas were calculated by the BET method and pore volumes from the amounts of adsorbed nitrogen at relative pressure (P/P_0) of 0.95. The pore size distribution was analysed by BJH method from a desorption branch of the isotherm [27].

3. Results and discussion

3.1. Bulk properties

Time dependences of the pH values of the reacting solutions are given in Fig. 1. The pH values increased with an increase in the reflux time up to about pH 2, owing to the formation of ammonia through decomposition of urea ($CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2NH_3$). However, they did not increase monotonously with an increase in the refluxing time. The decrease of pH values was observed for all systems at about pH 2. Further refluxing of the reacting solutions caused an increase in the pH value in the cases of an urea to titanium mole ratio of 4.5 and 6.

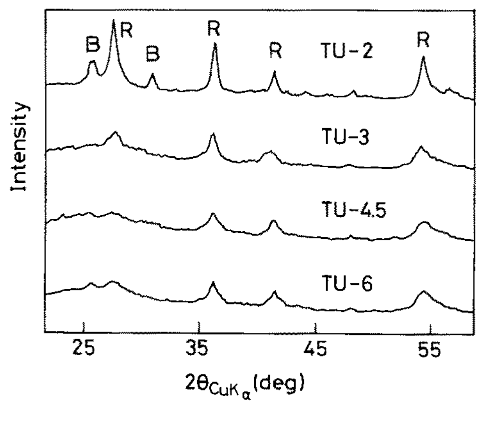

Figure 2 X-ray diffraction patterns (R–Rutile, B–Brookite).

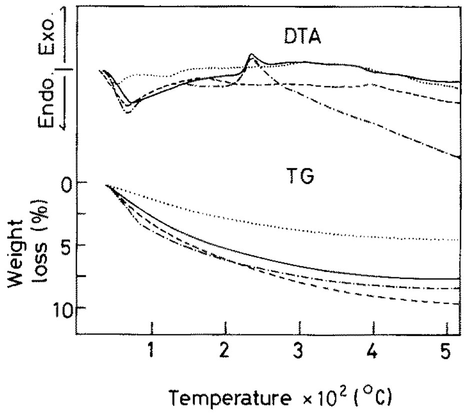

Figure 3 DTA–TG curves. (···· TU-2, – – – TU-3, —— TU-4.5, —·— TU-6).

The XRD patterns of the HTiOs are given in Fig. 2. Sample TU-2 showed a diffraction pattern corresponding to a rutile phase (ASTM 21-1276), accompanied by weak peaks corresponding to brookite phase (ASTM 29-1360). The crystallite size calculated by the Scherrer's equation [28] was about 13.6 nm from the half-width of rutile (110) peak. The other three samples had XRD patterns corresponding to rutile phase with weak diffraction peaks. The diffraction patterns had such a feature that the relative intensity of rutile (110) peak was markedly weak compared to that of the ASTM card. The diffraction intensity decreased with an increase in the starting urea to titanium mole ratio.

The DTA–TG curves showed an endothermic peak below 373 K due to an elimination of water (Fig. 3). The curves of samples TU-4.5 and TU-6 showed an exothermic peak at about 513 K, probably due to a crystallization of amorphous component.

A SEM photograph showed that sample TU-2 consisted of rod-like particles with 1.0 μm in length and 0.2 μm in width (Fig. 4). The TEM observation indicated that the rod-like particles were aggregates of acicular crystals in parallel arrangement. The width of the acicular crystals was about 5 nm, which agreed comparatively well with the crystallite size calculated from XRD analysis. Sample TU-3 was an aggregate of small particles about 50 nm in size (Fig. 5). The particles had a double-layer structure with outside layer about 5 nm in width.

The colour measurement showed that sample TU-2 was yellowish white while the other samples were blue (Table I). The *L*-value was the lowest for the sample TU-3 and increased with an increase in the starting urea to titanium mole ratio. This blue colour was stable even at 450 K and did not fade after several months at room temperature. In order to clarify the origin of the blue colouration, an ESR measurement was carried out. The ESR signals were not observed for all the HTiOs at room temperature. However, the signals were detected at 123 K for only the blue-

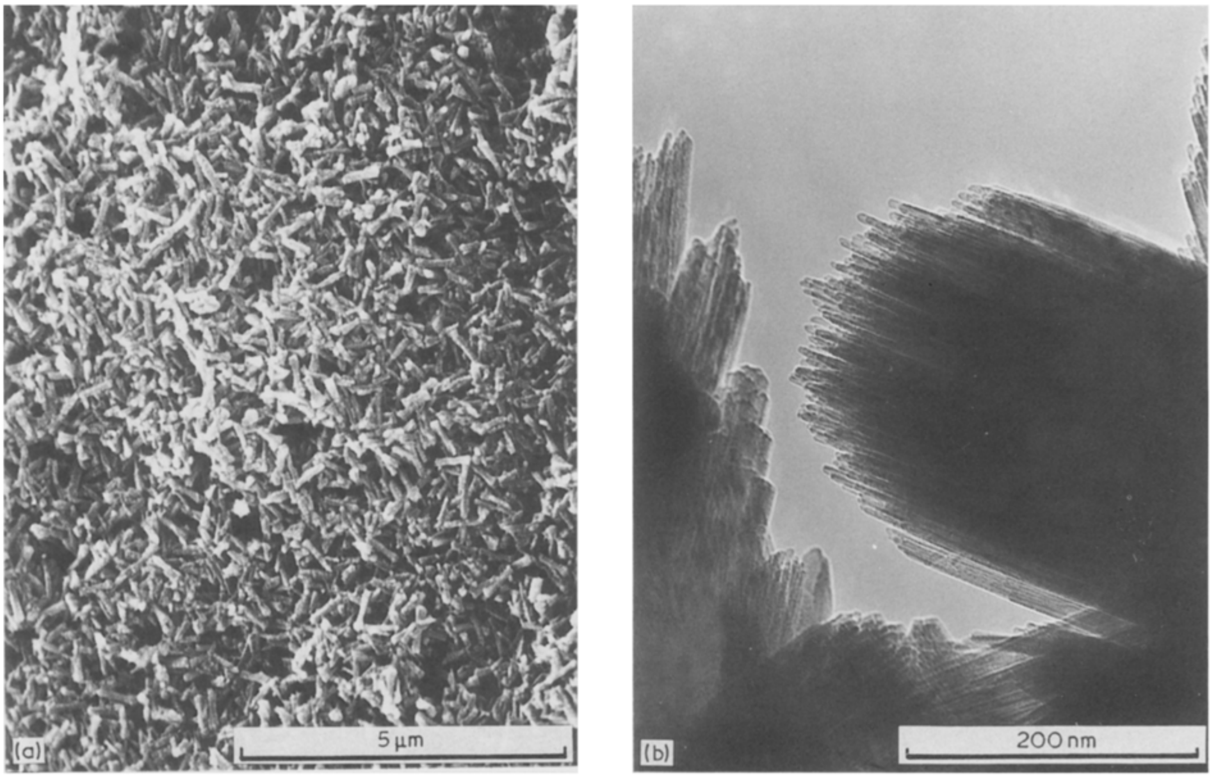

Figure 4 (a) SEM and (b) TEM images of sample TU-2.

coloured HTiOs (Fig. 6). The *g* value was estimated to be 1.92, which was similar to that [29] of the titanium (III) ions obtained by photolysis of colloidal titanium dioxide at 77 K or 4.2 K. The signal intensity increased with a decrease in the *L*-value in the colour measurement. As a result, the blue colouration was ascribed to the presence of stable paramagnetic titanium (III) ions at either stitutial or interstitial positions.

3.2. Surface properties

The nitrogen adsorption–desorption isotherms were classified into two types (Fig. 7): the BDDT III type (sample TU-2) and the BDDT IV type (samples TU-3, TU-4.5, and TU-6). The BDDT III type is characteristic to the nonporous materials while the BDDT IV type to the mesoporous materials [30]. The hysteresis loop shifted to lower relative nitrogen pressure with an

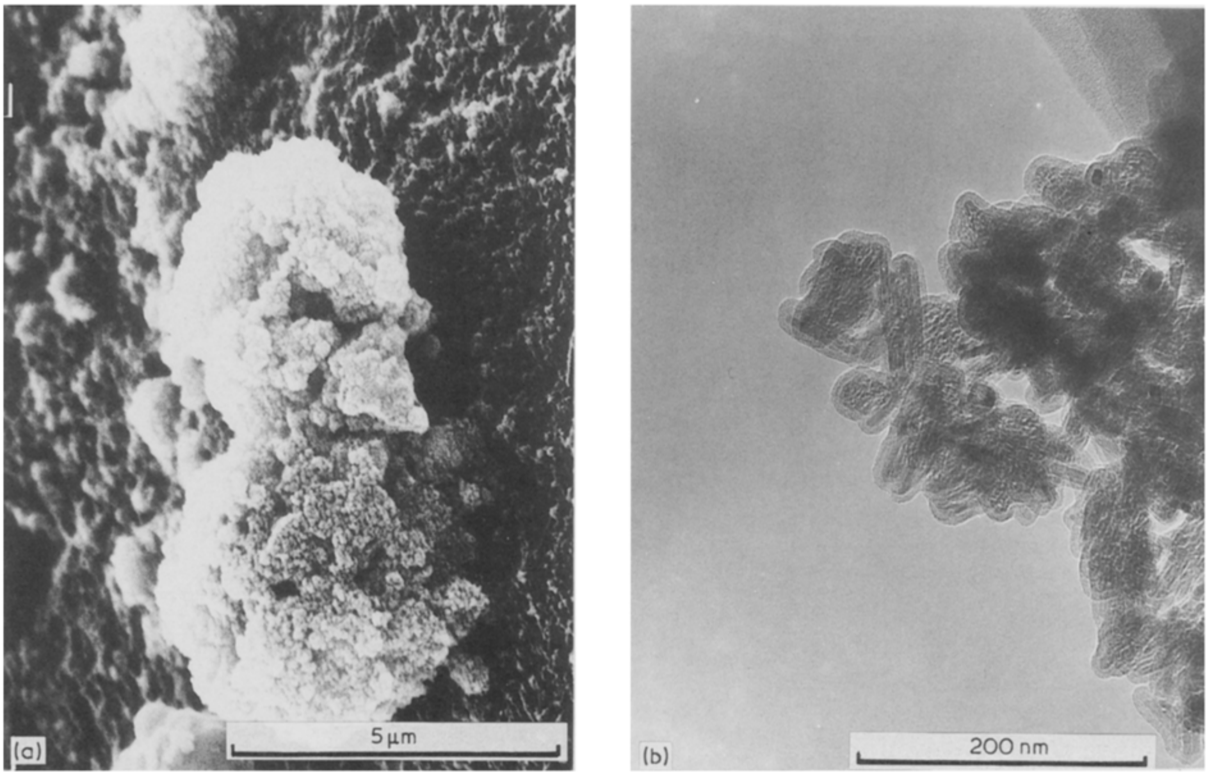

Figure 5 SEM and TEM images of sample TU-3.

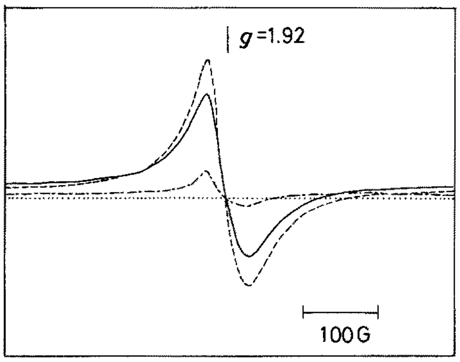

Figure 6 ESR spectra of HTiOs at 123 K. The symbols are the same as those in Fig. 3.

increase in the urea to titanium mole ratio. This indicates the decrease of pore size with an increase in the urea to titanium mole ratio; a pore size calculation indicates that the samples TU-3, TU-4.5, and TU-6 had mesopores around 3.8, 2.7 and 2.0 nm in radius, respectively.

The specific surface area and the pore volume increased with an increase in the urea to titanium mole ratio (Table I). Similar tendencies of specific surface area and pore volume have been observed for the HTiOs obtained from the ($TiCl_4$ + urea) solutions [17, 20]. The experimentally determined surface area of sample TU-2 was remarkably small compared with the external surface area (S_c) which was evaluated by a summation of the external surfaces of primary acicular crystals using the following equation [30]

$$S_c = 4/D_s\varrho$$

where D_s is the surface-averaged diameter. Since the D_s value of the acicular crystals for sample TU-2 was estimated to be 5 nm from the electronmicrograph, the S_c value was calculated to be 190 $m^2 g^{-1}$ using the assumption that ϱ was equal to that of rutile (4.2 $g cm^{-3}$). This suggests that the nitrogen molecules do not enter the vacant spaces among the acicular crystals in parallel arrangement.

3.3. Formation process of the HTiOs

The HTiOs obtained in the ($TiCl_3$ + urea) system have very unique characters. Both of the rod-like crystals and the blue-coloured particles have not yet been obtained by the usual hydrolysis from titanium (IV) salt solution. The HTiO obtained in the ($TiCl_4$ + urea) system is usually an aggregate of microcrystalline anatase about 10 nm in size [19, 20]. A blue-coloured HTiO has been obtained by irradiation of ultraviolet light to titanium (IV) oxide [29]. However, this blue colour is not so stable as that in the present study; it changes to white easily above room temperature. We will discuss below the formation process of the present unique HTiOs.

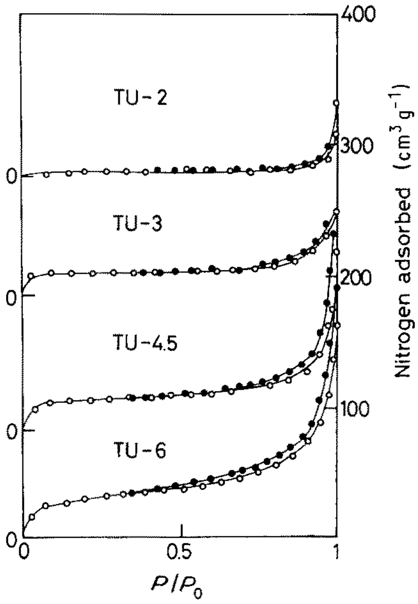

Figure 7 Nitrogen adsorption–desorption isotherms at STP (○ adsorption, ● desorption).

The formation process of the blue-coloured HTiO was studied from a urea-containing $TiCl_3$ solution (urea to titanium mole ratio = 3.0) at 371 K. The precipitates obtained during the reflux were characterized through XRD analysis and electronmicroscopic observation (Figs 8 and 9). The precipitates after 4 h reflux consist of disc-like particles about 200 nm in diameter and its yield was about 12%. It was yellowish white and had a diffraction pattern corresponding to rutile phase with relatively sharp peaks. The precipitates after 6 h reflux were dark blue. The electronmicrograph showed a formation of new type particles (probably correspond to blue-coloured HTiO) within or on the old disc-like particles. The XRD pattern showed a marked decrease of the diffraction intensities corresponding to rutile phase. By comparing these results with the results of pH measurement (Fig. 1), it is suggested that the blue-coloured HTiO is precipitated around pH 2 while the yellowish white one with large particle size below about pH 1.5.

The hydrolitic process of titanium (III) ions is complex compared with that of titanium (IV) ions, because the following oxidation Reaction 1 of titanium (III) ions occurs in aqueous phase including the hydrolysis reaction

$$Ti^{3+} + 2H_2O \rightarrow Ti(OH)_2^{2+} + \tfrac{1}{2}H_2 + H^+ \quad (1)$$

TABLE I Properties of the precipitates

Sample	Urea to titanium mole ratio	Yield (%)	Specific surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Colour		
					L	*a*	*b*
TU-2	2.0	52	7	0.03	92.9	−1.9	8.6 (Yellow)
TU-3	3.0	57	52	0.08	69.5	−2.5	−6.8 (Blue)
TU-4.5	4.5	97	70	0.15	71.0	−2.4	−7.8 (Blue)
TU-6	6.0	99	100	0.21	83.8	−2.4	−2.5 (Blue)

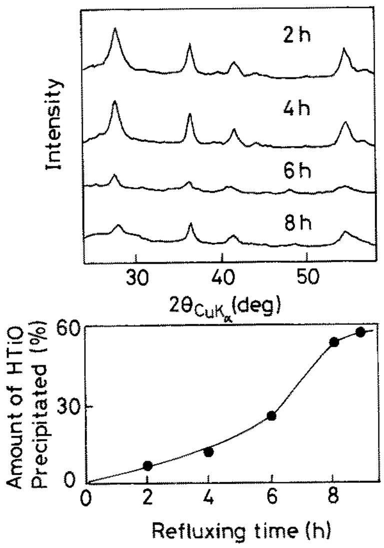

Figure 8 Time dependences of the yield of HTiO and its X-ray diffraction pattern in the case of urea to titanium mole ratio 3.0.

Several authors have investigated hydrolysis reactions of titanium (III) ions [31–33]. They have proposed the following two hydrolysis reactions

$$\mathrm{Ti^{3+} + H_2O \rightleftarrows TiOH^{2+} + H^+} \tag{2}$$

$$\mathrm{Ti^{3+} + 2H_2O \rightleftarrows Ti(OH)_2^+ + 2H^+} \tag{3}$$

Based on these equations, we propose the following precipitation reactions from $\mathrm{TiCl_3}$ solutions at different pH values

$$\nearrow \mathrm{Ti(OH)_2^{2+}} \xrightarrow{\mathrm{pH} \lesssim 1.5} \mathrm{TiO_2}\ \text{crystal (disc or rod)} + n\mathrm{H^+} \tag{4}$$

$$\mathrm{Ti^{3+}} \rightleftarrows \underline{\mathrm{Ti(OH)_2^{2+}, TiOH^{2+}, Ti(OH)_2^{+}}} \xrightarrow{\mathrm{pH} \doteqdot 2} \begin{matrix}\text{coprecipitates}\\ \text{(microcrystalline)}\end{matrix} + n\mathrm{H^+} \tag{5}$$

$$\xrightarrow{\mathrm{pH} \gtrsim 3} \text{polymer gel} \xrightarrow{\mathrm{O_2}} \begin{matrix}\text{precipitates}\\ \text{(amorphous)}\end{matrix} + n\mathrm{H^+} \tag{6}$$

Reaction 4 explains the formation of the yellowish white HTiO with large particle size. In this case, the concentration of titanium (IV) ions ($\mathrm{Ti(OH)_2^{2+}}$) may control nuclei production and crystal growth. The $\mathrm{Ti(OH)_2^{2+}}$ concentration in the present study is markedly lower than that in the usual hydrolysis from titanium (IV) salt solution, because the oxidation Reaction 1 scarcely proceeds in highly acidic solution [31]. The low $\mathrm{Ti(OH)_2^{2+}}$ concentration may cause a small number of nuclei as well as a slow crystal growth, consequently may give a large size of particles. A similar mechanism has been propsed on the formation of uniform spherical particles of titanium dioxide in highly acidic solutions of $\mathrm{TiCl_4}$ containing sulphate ions [10, 21].

Reaction 5 explains the formation of the blue HTiO. The precipitation of titanium (III) ions may occur along with the precipitation of titanium (IV) ions around pH 2 and give a complex titanium oxide containing titanium (III) and titanium (IV) ions. The temporary decrease of the pH values around pH 2 indicates that the rate of proton production due to the irreversible precipitation Reactions 4 and 5 exceed that of the proton consumption due to a decomposition of urea. A stiking feature in the present case is that the titanium (III) ions in the precipitate exist in a stable form against the oxidation by air. The formation of stable titanium (III) ions may arise from the present characteristic conditions of slow and

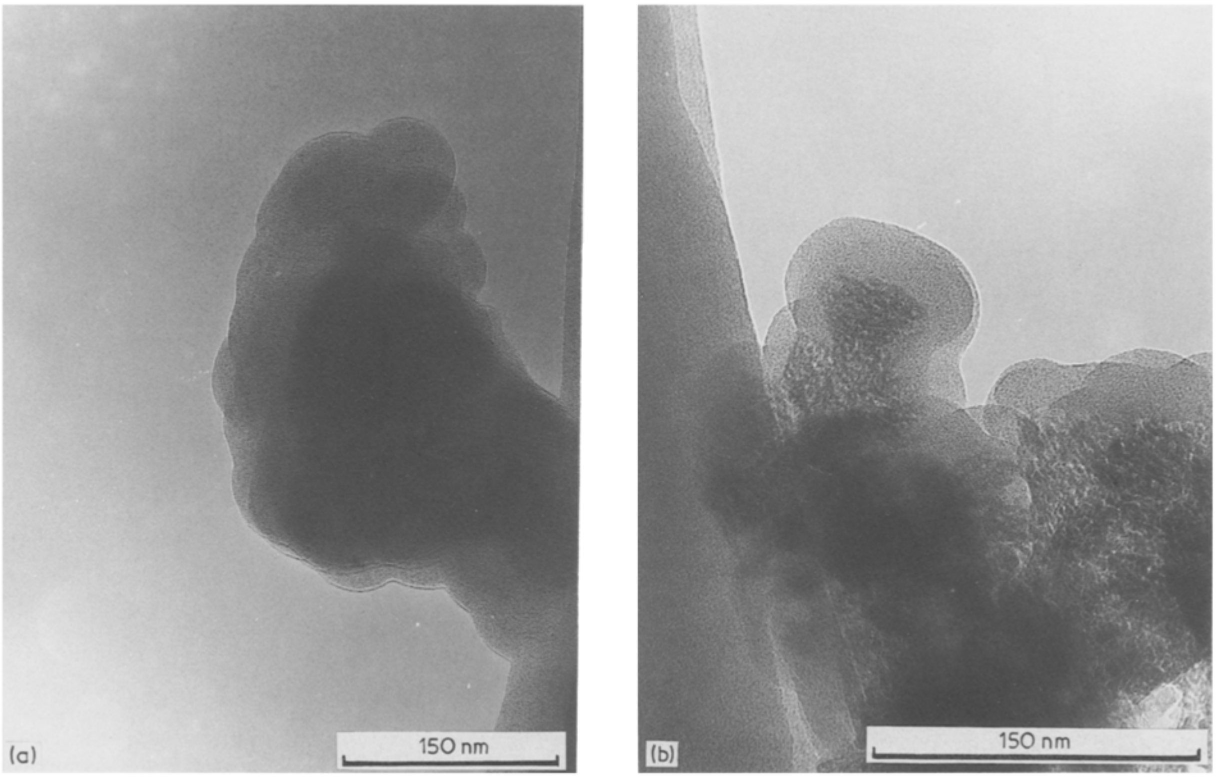

Figure 9 TEM images of precipitates during refluxing in the case of urea to titanium mole ratio 3.0. (Refluxing time a : 4 h, b : 6 h).

cooperative precipitation of titanium (III) and titanium (IV) ions. It needs further study to determine the detailed structure of the blue HTiOs.

The last Reaction 6 can be presumed from the fact that samples TU-4 and TU-6 contain amorphous component (detected by DTA curve) and have larger L-values than that of sample TU-3. Ragai *et al.* have prepared amorphous HTiOs by adding ammonium hydroxide or ammonium carbonate to aqueous solutions of $TiCl_3$ [13–16]. They have reported that the dark-coloured gel was easily oxidized to white HTiO by passing oxygen. The oxidation of amorphous component may be responsible for large L-values of samples TU-4.5 and TU-6 in the present case.

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