

Structural and Morphological Behavior of TiO₂ Rutile Obtained by Hydrolysis Reaction of Na₂Ti₃O₇

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The structural transformation behavior of Na₂Ti₃O₇ by hydrolysis was investigated in mild and strong acidic aqueous medium. Compared with K₂Ti₄O₉, Na₂Ti₃O₇ exhibits quite different structural and morphological transformation behavior despite their similar layered structural characteristics. TiO₂(B) obtained by heat treatment of H₂Ti₃O₇ at 350 °C transforms to rutile TiO₂ at 900 °C. This temperature is much lower than 1200 °C, the temperature for anatase to rutile transition when K₂Ti₄O₉ is used as a starting titanate. A rectangular rod shape and size of TiO₂(B) particles obtained from Na₂Ti₃O₇ is also different from a fibrous structure of TiO₂(B) prepared using K₂Ti₄O₉. Rutile crystals of 100 nm diameter with a corn-like morphology and large surface area are directly obtained when the hydrolysis of Na₂Ti₃O₇ is carried out at 100 °C in a strong acid solution. The structure of starting titanates and the hydrolysis conditions are an important factor to decide the particle size and morphology of TiO₂(B) and TiO₂.

Key Words : Layered titanates, Rutile, Hydrolysis, Morphology

Introduction

A family of alkali metal titanates, represented by the general formula A₂O·*n*TiO₂ or A₂Ti_{*n*}O_{2*n*+1} (A = alkali metal and 2 ≤ *n* ≤ 9), is well known to have characteristic layered- or tunnel-type structures depending on *n* values.¹⁻⁵ These titanates exhibit diverse potential applications associated with their high ion-exchange ability. Thus, they are used for the host materials to intercalate organic guest molecules,⁶⁻⁸ to fabricate porous materials,^{9,10} and to fix the radioactive metal ions.^{11,12} Several non alkali metal members are also prepared by ion-exchange reactions.¹³ Proton exchanged members can be easily exfoliated into single layers by the intercalation of bulky organic amines to fabricate plate-like particles of titania and thin films of protonic titanate.¹⁴ Other properties of interest for A₂Ti_{*n*}O_{2*n*+1} titanates include photoluminescence and photocatalytic activities.¹⁵⁻¹⁷

In particular, the layered members of this series show the catalytic activity to decompose water to hydrogen and oxygen when the ruthenium oxide is dispersed on the surface.¹⁸ During thermal dehydration process of protonated forms H₂O·*n*TiO₂, the intermediate form TiO₂(B) is frequently obtained and shows excellent photocatalytic activity.¹⁹ Since these titanates are very sensitive to the proton exchange reaction, the interlayer spaces are easily hydrated in an aqueous medium and then the crystal structure and morphology degrade and transform to a different structure, size, and shape. For instance, the protonic tetratitanate H₂Ti₄O₉·*n*H₂O, which is derived by the ion-exchange reaction of parent K₂Ti₄O₉, transforms in a series of steps to H₂Ti₈O₁₇, TiO₂(B), anatase, and rutile.²⁰ The transformation temperature and the microstructure of respective phases also significantly change, depending on the reaction environments.

In order to improve functional properties such as photocatalytic activity or ion-exchange ability, it is highly desirable to control the particle size and morphology of the titanates. Moreover, the degradation and transformation behaviors of alkali metal titanates should be understood for an effective application at diverse conditions. In this work, we investigated the structural transformation behavior of Na₂Ti₃O₇ in mild and strong hydrolysis condition. It is interesting that, compared with K₂Ti₄O₉, Na₂Ti₃O₇ exhibits quite different structural and morphological transformation behavior in an aqueous solution despite their similar layered structural characteristics.

Experimental Section

Alkali metal titanate Na₂Ti₃O₇ was prepared by conventional solid state reaction. Stoichiometric mixture of dried Na₂CO₃ and TiO₂ (anatase) was heated at 850 °C for 12 h in air with intermittent grinding. Proton exchange reaction of Na₂Ti₃O₇ was carried out in acidic solution. The powdered Na₂Ti₃O₇ was immersed in 0.5 N HNO₃ solution and stirred at room temperature for 10 h to prepare H₂Ti₃O₇. The resulting product was retrieved by filtration, washed with distilled water several times, and dried at 120 °C. If the final precipitate was dried at room temperature instead of 120 °C, the hydrated H₂Ti₃O₇·*n*H₂O could be obtained. The protonated form was heated in an electrical furnace at 500-900 °C for 10 h in air to investigate its dehydration and structural transformation behavior. As a different reaction procedure, Na₂Ti₃O₇ powder was vigorously stirred in 3 N HNO₃ solution at 100 °C for 6 days to obtain directly the rutile type of TiO₂. The precipitated powder was filtered, washed with distilled water several times, and dried at 120 °C in air.

The formation of Na₂Ti₃O₇, H₂Ti₃O₇·*n*H₂O, H₂Ti₃O₇,

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TiO₂(B), and TiO₂ was confirmed by powder X-ray diffraction (XRD) technique using a rotating anode source installed diffractometer with X-ray source of 40 kV, 300 mA. The CuK α radiation used was monochromated by a curved-crystal graphite. Elemental analysis using the inductively coupled plasma (ICP) gave the stoichiometric sodium composition for Na₂Ti₃O₇ within experimental errors. No sodium component was detected with H₂Ti₃O₇ after proton exchange reaction. Approximate water content (*n*) in hydrated H₂Ti₃O₇·*n*H₂O was determined by thermogravimetric (TG) analysis. A weight loss up to ~200 °C reached to ~0.25 H₂O per formula unit (H₂Ti₃O₇·0.25H₂O). Measurements were made under static air at a heating rate of 5 °C/min. Scanning electron microscopy (SEM) photographs were obtained at 30 kV. Specimens for electron microscope were coated with Pt-Rh for 180 s under vacuum.

Results and Discussion

Schematic structures of Na₂Ti₃O₇, K₂Ti₄O₉, and TiO₂(B) are illustrated in Figure 1. The layered structures of alkali metal titanates are quite similar but consist of different length of zigzag TiO₆ octahedral ribbons.

As a consequence of sequential stacking of zigzag ribbon layers along the *a*-axis, interlayer Na⁺ or K⁺ ions are readily exchanged by protons and resulting proton layers are open to the intercalation of water and organic guest molecules. Three-dimensional framework of TiO₂(B) is built up of four edge sharing TiO₆ octahedral subunits.

The space group (*P*2₁/*m*) and unit cell dimensions (*a* = 8.57(3), *b* = 3.81(5), *c* = 9.11(4), β = 101.7°(1)) of obtained Na₂Ti₃O₇, which was calculated by the least square method, are in good agreement with the literature values (Figure 2a).⁴ Powder X-ray diffraction pattern of proton exchanged form H₂Ti₃O₇ is shown in Figure 2b. Well crystallized structure is retained after exchange reaction at mild acidic solution as evidenced by complete assignments of all reflections. Small shifts of particularly (*h*00) reflection positions toward high angles are consistent with a contraction along the *a*-axis by the topotactic exchange reaction between sodium ions and

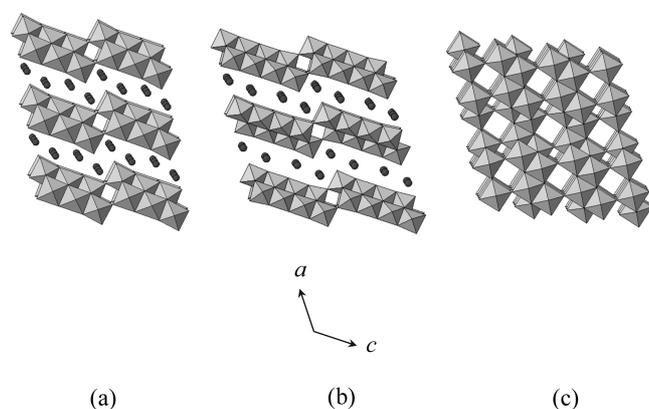


Figure 1. Comparison of idealized structure for (a) Na₂Ti₃O₇, (b) K₂Ti₄O₉, and (c) TiO₂(B). Edge shared rectangular unit and small sphere represent TiO₆ octahedron and Na or K atom, respectively.

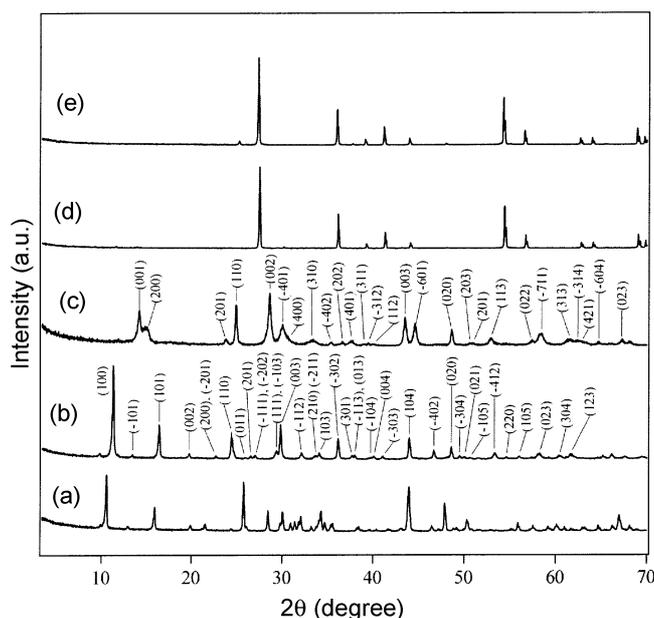


Figure 2. XRD patterns of (a) Na₂Ti₃O₇, (b) H₂Ti₃O₇, (c) TiO₂(B), (d) TiO₂ prepared by heat treatment of TiO₂(B) at 900 °C, and (e) commercial rutile type TiO₂.

smaller protons. In contrast, no noticeable shift of (*00l*) reflections indicates that the TiO₆ octahedral ribbon layers are little influenced by the proton exchange. Figure 2c shows XRD pattern after heat treatment of H₂Ti₃O₇ at 350 °C for 3 h in air. This form is known as TiO₂(B) and all reflections were indexed on the basis of space group *C*2/*m* with unit cell parameters, *a* = 12.18 Å, *b* = 3.74 Å, *c* = 6.53 Å, and β = 107.05°.²¹ TiO₂(B) is one of the intermediate forms induced during the hydrolysis reaction followed by dehydration of A₂O·*n*TiO₂. The metastable TiO₂(B) easily transforms to stable anatase or rutile TiO₂ after heat treatment at higher temperature. Comparing Figures 2d and 2e, XRD pattern after heat treatment of TiO₂(B) at 900 °C for 3 h in air is in accordance with that of commercial rutile. It should be noted that TiO₂(B) transforms to anatase at 1000 °C and then the phase transformation of anatase to rutile is completed at 1200 °C if K₂Ti₄O₉ is used as a starting titanate.²⁰

Both layered titanates, Na₂Ti₃O₇ and K₂Ti₄O₉, undergo proton-exchange reactions, and subsequent dehydration of the exchanged materials results in the formation of TiO₂(B). Several distinct condensations and rearrangements during the dehydration could be different from each other, depending on the number of TiO₆ octahedra constituting layers of starting titanates. However, the phase transformation from TiO₂(B) to TiO₂ is independent of the nature of starting titanates and considered to be a unique process. In this respect, it is of interest that the formation temperature of rutile significantly lowers when TiO₂(B) is prepared from Na₂Ti₃O₇ rather than K₂Ti₄O₉. The crystallinity of TiO₂(B) is strongly dependent on the structure of starting material and dehydration temperature.²¹ In addition, the hydrolysis of K₂Ti₄O₉ frequently gives K_{2-*x*}H_{*x*}Ti₄O₉, *x* value depending on the temperature, pH, and the proportion of liquid.²² Residual

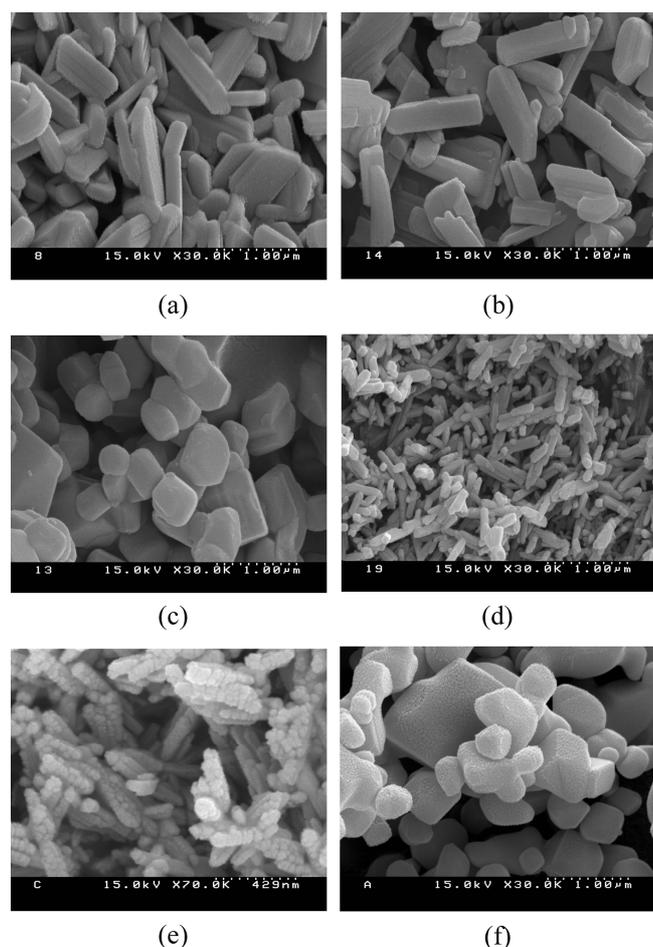


Figure 3. SEM photographs of (a) Na₂Ti₃O₇, (b) TiO₂(B), (c) rutile type TiO₂ transformed from TiO₂(B), (d) rutile type TiO₂ transformed directly from Na₂Ti₃O₇, (e) magnification of (d), and (f) commercial TiO₂ rutile.

K⁺ ions in proton exchanged product would increase the transformation temperature of subsequent TiO₂(B) and anatase. One of the more interesting features is that the hydrolysis of Na₂Ti₃O₇ at 100 °C for 6 days in a concentrated acidic (3 N) solution gives rise to a direct formation of rutile. The transition temperature of TiO₂(B) to anatase and then rutile is strongly affected by the acid concentration of aqueous solution. Such a result could not be induced if only rearrangement of TiO₆ octahedral network is included in the transformation mechanism. Thus, it can be proposed that the phase transformation from TiO₂(B) to TiO₂ proceeds through a dissolution-recrystallization mechanism and therefore depends on the solubility of starting alkali metal titanate in the acidic solution.

Scanning electron micrographs of (a) Na₂Ti₃O₇, (b) TiO₂(B) prepared by dehydration of H₂Ti₃O₇ at 350 °C, (c) rutile type TiO₂ transformed from TiO₂(B) at 900 °C, and (d) rutile type TiO₂ transformed directly from Na₂Ti₃O₇ at 100 °C in Figure 3. A rectangular rod shape and size of TiO₂(B) particles are similar to those of Na₂Ti₃O₇ which was used as a starting material. However, this structure is quite different from a fibrous structure of TiO₂(B) prepared using fibrous

K₂Ti₄O₉ as a starting material.²⁰ Such comparison indicates that the size and morphology of TiO₂(B) particles are dependent on those of starting alkali metal titanates. The new crystallite structure would nucleate at some point on or within a grain of the condensed structure and proceed to grow through grain. The double TiO₆ octahedral ribbons are expected to form by a reconstructive nucleation and growth mechanism to transform to TiO₂(B). Consequently, the grain size and shape of starting titanates would be crucial for the crystal growth behavior and the particle morphology of TiO₂(B).

When the rutile type TiO₂ is obtained by heating TiO₂(B) at 900 °C, the particle size distribution is rather poor and the morphology of TiO₂(B) is essentially retained after structural transformation. In contrast, when rutile is directly prepared from Na₂Ti₃O₇ at 100 °C, much smaller particles are obtained and size distribution is also highly improved as shown in Figure 3d. The magnified SEM image of Figure 3e exhibits a corn-like particle morphology with highly increased surface area. This result implies that the structure of starting titanates and the hydrolysis conditions are an important factor to decide the particle size and morphology of TiO₂(B) and rutile TiO₂. Considerable dependence of rutile morphology on the hydrolysis conditions supports that the phase transformation mechanism includes a dissolution-precipitation process. A study to control the morphology and size of anatase and rutile particles is in progress using diverse starting alkali metal titanates.

Conclusions

Both anatase and rutile structure of TiO₂ can be obtained from the hydrolysis of Na₂Ti₃O₇ and K₂Ti₄O₉. However, the temperature for transformation of anatase to rutile and the morphology of TiO₂ particles are largely different depending on hydrolysis condition. Rutile crystals of 100 nm diameter with a corn-like morphology and large surface area are directly obtained by hydrolysis of Na₂Ti₃O₇ in a strongly acidic solution. The crystallite size increases when rutile TiO₂ results from the transformation of TiO₂(B). The morphology of TiO₂(B) is also largely dependent on that of the alkali metal titanate selected as a starting material.

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