

Facile synthesis of >99% phase-pure brookite TiO₂ by hydrothermal conversion from Mg₂TiO₄

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Abstract:

The synthesis of pure brookite is generally much more difficult than that of pure anatase. The hydrothermal conversion, recently developed by Kozawa et al., is a facile method to synthesize brookite TiO₂ from inverse spinel-type Mg₂TiO₄ under a mild hydrothermal condition *e.g.* in 1 M HCl solution at 100°C. However, slight rutile TiO₂ is usually co-existed under the reported conditions. The aim of this study is to prepare a high-purity brookite TiO₂ powder by the hydrothermal conversion from Mg₂TiO₄. We investigated the conditions of Mg₂TiO₄ preparation and hydrothermal conversion, and it was found that the most important factor for the high-purity brookite synthesis, *i.e.* decreasing the co-existing rutile TiO₂, was to prepare the Mg₂TiO₄ precursor without MgTiO₃. Using an MgO-rich composition and adding a second calcination step for the Mg₂TiO₄ preparation yielded a high-purity (99.3 wt %) brookite powder with a surface area of 27.7 m²/g. Under the current experimental conditions, addition of a surfactant or an alcohol for the hydrothermal treatment was not apparently effective for the high-purity brookite synthesis.

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1. Introduction

Titanium dioxide (TiO₂) is a representative photocatalyst with several useful functions, such as antibacterial [1,2], deodorizing [3], antifouling [4], NO_x removal [5], self-cleaning [6,7], and antifogging. TiO₂ has three naturally occurring polymorphs, i.e., rutile, anatase and brookite. Rutile and anatase are widely used for practical applications since they are easily synthesized and cost-effective. In our previous study [8], we reported that the excessive oxidizing ability of anatase TiO₂ caused some problems in the self-cleaning; it formed CaSO₄ white precipitates on a window from atmospheric pollutants. Hence, in our recent study [9], we have focused on brookite TiO₂ with a *mild* oxidizing ability, which is suitable for the self-cleaning.

The synthesis of pure brookite is generally much more difficult than that of pure anatase. Several groups used TiCl₄ as a precursor for the brookite synthesis [10-12]. However, TiCl₄ is relatively difficult to handle, and in many cases, the resulting TiO₂ became a mixture of brookite and rutile. Meanwhile, Tomita et al. [13] developed an excellent protocol to synthesize a single-phase brookite powder using a hydrothermal treatment of a water-soluble complex precursor, (NH₄)₆[Ti₄(C₂H₂O₃)₄(C₂H₃O₃)₂(O₂)₄O₂] \cdot 4H₂O, but this protocol required many experimental steps.

Recently, Kozawa et al. [14] have reported another protocol using a hydrothermal treatment of a simple double-oxide precursor, Mg₂TiO₄. The hydrothermal conversion of Mg₂TiO₄ to brookite proceeds under a mild hydrothermal condition, e.g. in 1 M HCl solution even at 100 °C. The advantages of the Kozawa method are to use stable and cost-effective ingredients and its easy experimental operations. It is practical to obtain brookite TiO₂ powder, but its phase purity is not as prominent as the Tomita method [13]. In our recent work on the self-cleaning [9], we have synthesized brookite powders via the Kozawa method. Actually, the obtained TiO₂ was a mixture of brookite and rutile, and the highest purity of brookite was 97.2 wt % [9]. Such residual rutile TiO₂ can be also seen in the original report by Kozawa et al. (Fig. 1(b) [14]).

Here, we investigated a synthetic condition for high-purity brookite (>99%) by optimizing the Mg_2TiO_4 preparation and the hydrothermal conversion. The additive effects of a surfactant and an alcohol for the hydrothermal treatment are also reported.

2. Experimental procedures

2.1 Mg_2TiO_4 preparation

The experimental conditions were similar to our previous report [9]. At first, Mg_2TiO_4 powder was synthesized by a solid-state reaction between MgCO_3 (basic) [or more precisely, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$] and anatase TiO_2 powders (both 99.9% purity, Kojundo Chemical Laboratory). Prior to weighing, TG-DTA analysis (up to 1000 °C, DTA-50, Shimadzu) was conducted on the MgCO_3 (basic) powder to determine the weight-loss during the heating. Taking into account the compositional calibration using the TG-DTA results, the MgCO_3 (basic) and the anatase TiO_2 powders were weighed to be stoichiometric ratio of $\text{MgO}:\text{TiO}_2=2:1$: sample **(a)**. The other was weighed so as to be 5 wt % excessive MgO rather than the stoichiometric Mg_2TiO_4 composition: sample **(b)**.

These powders were planetary ball-milled (acceleration: 4 G, Pulversette 6, Fritsch) with ZrO_2 balls in ethanol (EtOH) for 2 h. The mixed slurries were vacuum dried, and the dried powders were placed in an oven at 80 °C for 1 h. The mixed powders were calcined at 1250 °C for 2 h in air. As for the powder sample **(b)**, after calcination at 1250 °C for 2 h, it was pulverized in an agate mortar, and then it was re-calcined at 1270 °C for 2 h in air: sample **(c)**.

2.2. Hydrothermal treatment and phase analysis

Table 1 summarizes typical compositions for the hydrothermal treatment. Note that to emphasize the effects of hydrothermal conditions, 2 g loading (instead of 1 g [9]) of Mg_2TiO_4 was mainly tested; i.e., if the hydrothermal conversion was not sufficient, the brookite yield became much smaller. The synthesized Mg_2TiO_4 powder, namely sample **(a)**, **(b)** or **(c)**, and HCl aq. solution were put into an autoclave with a polytetrafluoroethylene inner container, and the hydrothermal conversion was conducted at 150 °C for 24 h in a static condition. Each resulting product was collected using a membrane filter, washed with distilled water, and dried at 80 °C.

Since a surfactant may act as a structure-directing agent to preferentially yield brookite during the hydrothermal treatment, laurylamine hydrochloride (LAHC) was added to the above sample **(a)** or **(c)** so that the weight ratio of Mg_2TiO_4 :LAHC was 4:1. These powders and HCl aq. were put into an autoclave, and the hydrothermal conversion was also conducted at 150 °C for 24 h.

Also, since an alcohol addition to hydrothermal conversion may shorten the reaction time (via a solvothermal effect) with reducing the nucleation and growth of rutile TiO_2 , EtOH was added to HCl aq. so that the volume ratio of HCl aq.:EtOH was 2:1. Sample **(a)** or **(c)** and the mixture of HCl aq./EtOH were put into an autoclave, and the solvothermal treatment was conducted at 150 °C for 8 h.

The constituent phases of the samples were analyzed by X-ray diffraction (XRD, Multiflex, Cu-K α , 40 kV and 40 mA, Rigaku) at a scanning rate of 4 °/min. The microstructure of the brookite TiO_2 powders was observed by scanning electron microscopy (SEM, SU-70, Hitachi High-Technologies). Specific surface area of the brookite powder was determined by BET method using a nitrogen gas sorption analyzer (Autosorb-3-AG, Quantachrome).

3. Results and discussion

Figure 1 shows XRD patterns of the powders before the hydrothermal treatment. Main peaks of the sample **(a)** were identified to Mg_2TiO_4 . Sample **(b)** was quite similar to sample **(a)**. However, there were several peaks corresponding to MgTiO_3 at 2 θ ~33°, 41°, and 49.5°. Therefore, strictly speaking, the samples **(a)** and **(b)** were Mg_2TiO_4 / MgTiO_3 mixtures. Although excess MgO was added to the sample **(b)**, MgTiO_3 could not be fully removed. Meanwhile, the sample **(c)**, which was re-calcined at 1270 °C of sample **(b)**, did not contain the MgTiO_3 peaks. Hence, sample **(c)** consisted of single-phase Mg_2TiO_4 , at least under the standard XRD resolution. Excess MgO may exist as amorphous $\text{Mg}(\text{OH})_2$ and MgCO_3 (by reactions with atmospheric H_2O and CO_2). Also Mg_2TiO_4 with inverse spinel structure may accommodate some excess MgO, although a report MgO- TiO_2 phase diagram depicts Mg_2TiO_4 as a line compound (without a solid solution) [15]. From this result, in order to prepare single-phase Mg_2TiO_4 , it is effective to add excess amount of MgO and to add a second calcination step.

Figures 2 and **3** show XRD patterns of the powders after the hydrothermal treatment of

the samples **(a)** and **(b)**, and the sample **(c)**, respectively. The weight fractions of brookite and rutile TiO₂ can be estimated from the following empirical equation proposed by Zhang and Banfield [16, 17]:

$$W_B = \frac{2.721A_B}{A_R + 2.721A_B} \quad (1)$$

where W_B represents the weight fraction of brookite, and A_B and A_R represent the integrated intensities of the peaks of brookite 121 and rutile 110, respectively. **Table 1** summarizes the weight fractions estimated using the Eq. 1. Because the sample **(d)** was synthesized using the same conditions in our previous report [9], the XRD pattern and the brookite fraction of sample **(d)** (97.2 wt %) are used as the benchmarks in **Figs. 2, 3** and **Table 1**.

In the XRD pattern of sample **(e)**, synthesized from the MgO-rich Mg₂TiO₄ precursor (sample **(b)**), the rutile 110 peak appears larger than the sample **(d)**. The brookite fraction (92.8 wt %) of the sample **(e)** was smaller than that of the sample **(d)**. In the XRD pattern of sample **(f)**, synthesized with LAHC surfactant, the rutile 110 peak appears a little broader and lower height than the sample **(d)**. The brookite fraction (95.0 wt %) of the sample **(f)** was smaller than that of the sample **(d)**. In the XRD pattern of sample **(g)**, synthesized with EtOH (for 8 h), the rutile 110 peak seems clearly higher than the sample **(d)**. The brookite fraction (92.8 wt %) of the sample **(g)** was smaller than that of sample **(d)**.

In the XRD pattern of sample **(h)**, synthesized from the sample **(c)**, the rutile 110 peak was the smallest. The brookite fraction of the sample **(h)** was 99.3 wt %, which was the highest purity brookite powder we had ever synthesized. As for sample **(j)** synthesized with LAHC surfactant, and sample **(k)** synthesized with EtOH, these powders had smaller brookite fractions, similarly to the samples **(f)** and **(g)**. However, by comparison between same hydrothermal conditions, the use of the sample **(c)** as a precursor became larger brookite fraction than that of the sample **(a)**. Throughout this study, the purity of Mg₂TiO₄ is a dominant factor to synthesize purer brookite powder.

Figure 4 shows a SEM micrograph of the brookite powder, sample **(h)**, with the surface area of 27.7 m²/g. Similarly to the previous work [9], the brookite powder retained macroscopic shape of micrometer-sized Mg₂TiO₄ particles, but was actually composed of a large number of

minute particles (ca. 50-100 nm). Facetted growth with dipyramidal idiomorphs of brookite TiO₂ was observed.

4. Conclusions

To prepare a high-purity brookite TiO₂ powder by the hydrothermal conversion from Mg₂TiO₄, improved conditions of the Mg₂TiO₄ preparation and the hydrothermal conversion were investigated. The most important factor for the high-purity brookite synthesis is to prepare the Mg₂TiO₄ precursor without MgTiO₃. It is effective to use an MgO-rich composition and to add a second calcination step for the Mg₂TiO₄ preparation, which yielded a high-purity (99.3 wt %) brookite TiO₂.

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Tables

Table 1 Hydrothermal conditions and final weight fractions of brookite and rutile.

Samples	Precursor powder	Surfactant (LAHC)	Alcohol (EtOH)	HCl aq.	Hydrothermal duration (h)	Brookite (wt %)	Rutile (wt %)
(d)	1 g (a)			1M 30 mL	24	97.2	2.8
(e)	2 g (b)			2M 30 mL	24	92.8	7.2
(f)	2 g (a)	0.5 g		2M 30 mL	24	95.0	5.0
(g)	0.5 g (a)		10 mL	2M 20 mL	8	92.8	7.2
(h)	2 g (c)			2M 30 mL	24	99.3	0.7
(j)	1 g (c)	0.25 g		2M 30 mL	24	95.9	4.1
(k)	0.5 g (c)		10 mL	2M 20 mL	8	96.6	3.4

(a) Stoichiometric Mg₂TiO₄, (b) 5% MgO-rich Mg₂TiO₄, and (c) re-calcination at 1270 °C for 2 h of sample (b).

(d) Best conditions in Ref. 9.

Figures

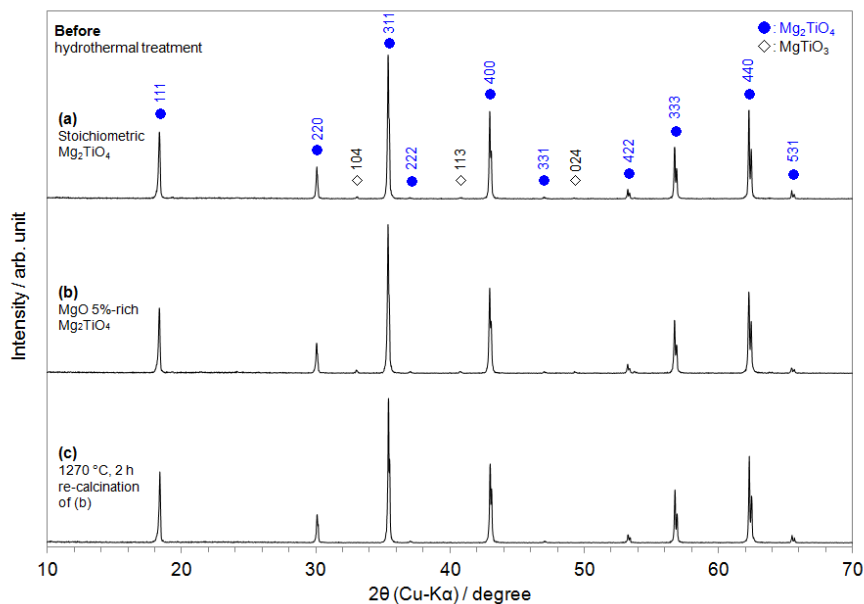


Fig. 1 XRD patterns of the samples before the hydrothermal treatment: (a) stoichiometric Mg_2TiO_4 , (b) 5% MgO-rich Mg_2TiO_4 and (c) re-calcination at 1270 °C for 2 h of sample (b).

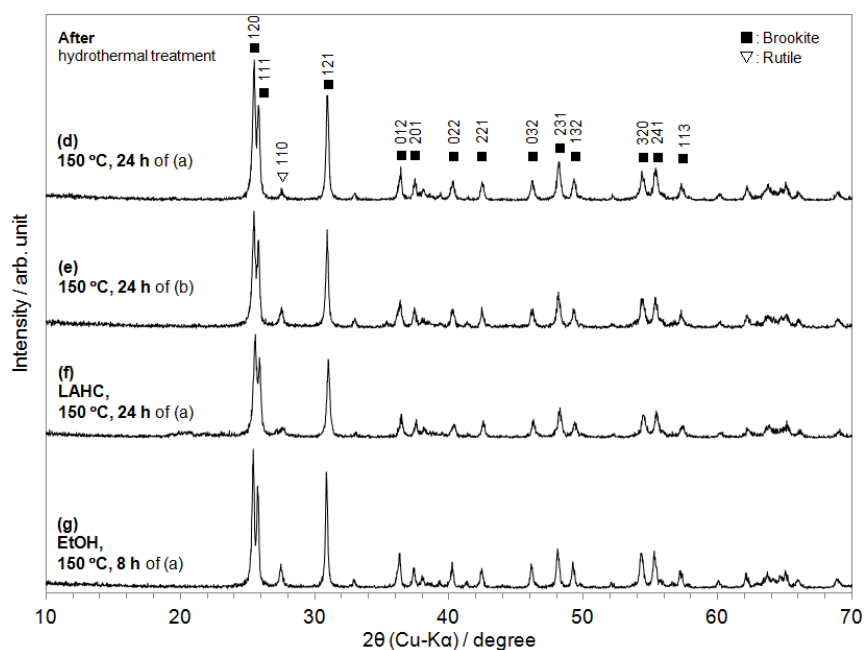


Fig. 2 XRD patterns of the samples after the hydrothermal treatment using sample (a) or (b): (d) at 150 °C for 24 h, (e) at 150 °C for 24 h, (f) at 150 °C for 24 h with LAHC, and (g) at 150 °C for 8 h with EtOH.

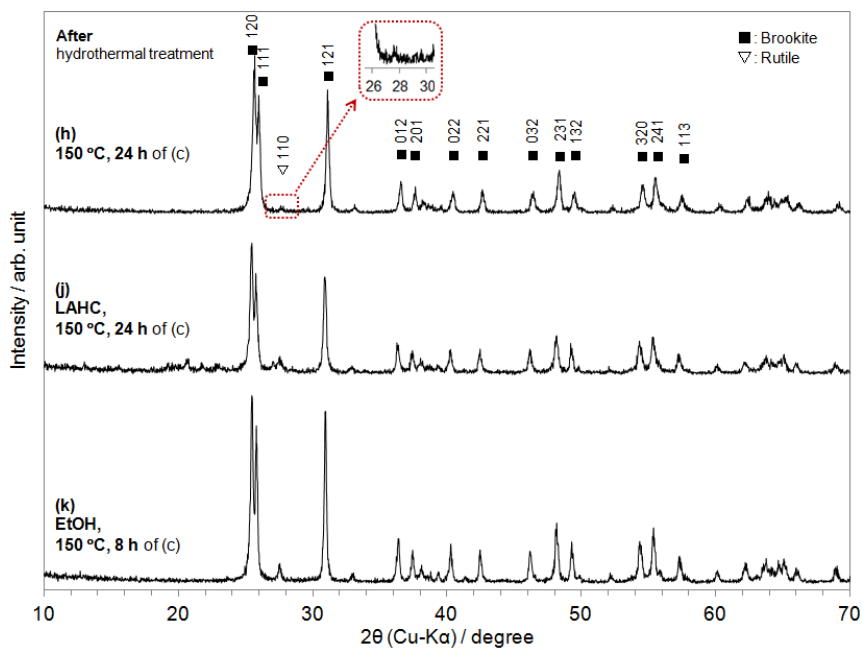


Fig. 3 XRD patterns of the samples after the hydrothermal treatment using sample (c): (h) at 150 °C for 24 h, (j) at 150 °C for 24 h with LAHC, and (k) at 150 °C for 8h with EtOH.

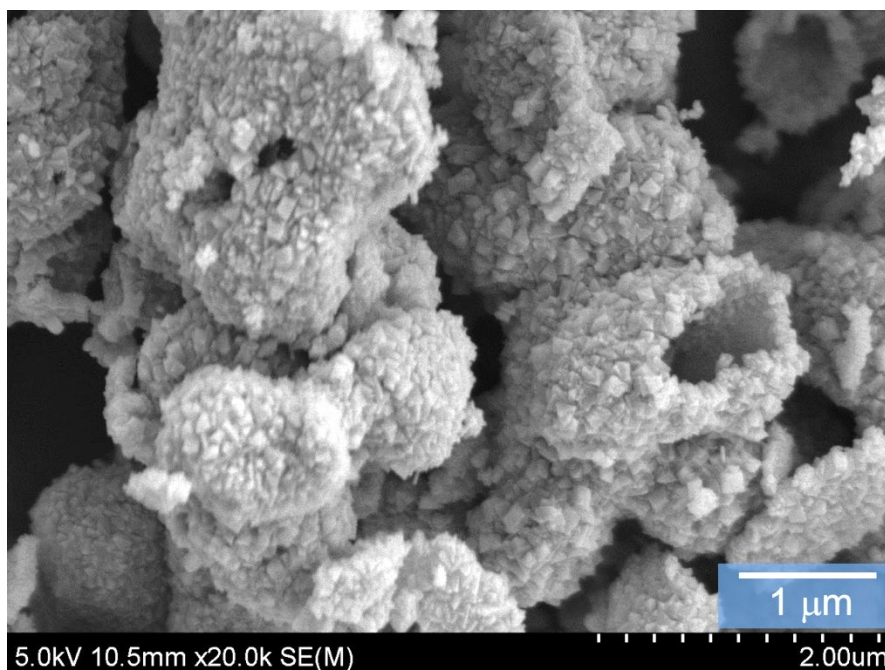


Fig. 4 SEM micrograph of the brookite powder, sample (h), with the surface area of 27.7 m²/g.