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Thermogravimetric study of the sulfurization of TiO_2 nanoparticles using CS_2 and the decomposition of their sulfurized product

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1. Introduction

Titanium dioxide (TiO_2, titania) powder is one of the most important particulate materials, such as ceramic materials, pigments, cosmetics, medicines and catalysts [1]. In addition, TiO_2 nanocrystals are well known as semiconductor materials for a wide variety of photocatalytic applications, being different from its bulk materials in physicochemical properties, such as morphology, surface area, and reactivity. On the contrary, titanium sulfides absorbing visible light exhibits little stability against photodissolution and then become the loss of the photocatalytic activity during their use. On the other hand, transition metals sulfides exhibit unique properties, in comparison with commercial oxide catalysts as can be seen in the results obtained over ruthenium, niobium and titanium after their sulfurization [2–5]. Some attempts have been carried out for the partial sulfurization of TiO_2, because partially sulfurized TiO_2 is expected to have higher photocatalytic activity due to efficient absorption of visible light. Namely, the partial sulfurization of TiO_2 would enhance their photocatalytic activity, which is in accordance to early studies made by Ziolek et al. on TiO_2 granulates [6]. Furthermore, it was reported that photoelectrochemical property was improved by a partial sulfurization of TiO_2 [7]. In addition to the sulfurization of TiO_2, the oxidation process of TiS_2 enhanced the photocurrent density due to the replacement of S by O [8].

In this regard, the sulfurization behavior of TiO_2 should be identified, in order to prepare chemically and physically stable TiO_2 sulfurized partially. However, very few studies have been published about the sulfurization of TiO_2 using CS_2 and are more associated with the hydrolysis process [9–11]. In this paper, the sulfurization of TiO_2 nanoparticles in the presence of CS_2 was studied by thermogravimetric (TG) method using a quartz spring-type thermobalance in comparison with other powders of anatase, rutile and $Ti(OH)_4$. As a complement to the sulfurization, the decomposition of the partially sulfurized TiO_2 and the TiS_2 were also studied by the same method.

2. Experimental

2.1. Materials

TiO_2 nanoparticles (Ishihara Ind., ST01), as shown in Fig. 1(a), were used as-received or dried at 110 °C in an oven for 10 days. The anatase-type TiO_2 particles shown in Fig. 1(b) (Wako Pure Chemicals Co. Ltd.) were used as-received. The rutile-type TiO_2 particles (Fig. 1(c)) were prepared by calcining the anatase-type ones in air at 900 °C for 1 h. $Ti(OH)_4$ was prepared by mixing titanium tetra-*iso*-propoxide (Wako Pure Chemicals Co. Ltd.) with distilled water in a proportion of 1:5 [12]. The mixing apparatus was kept at ca. 0 °C to avoid the formation of TiO_2

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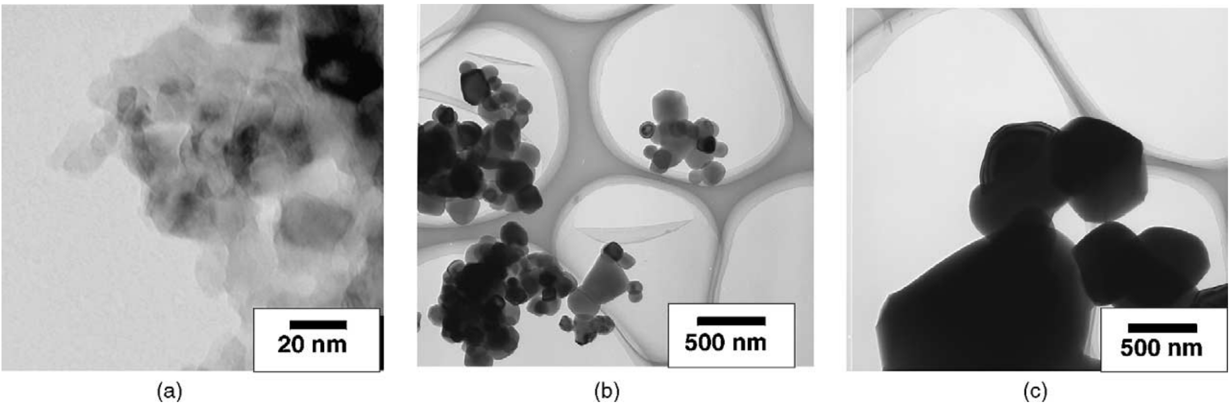

Fig. 1. TEM micrographs of (a) as-received ST01; (b) anatase and (c) rutile.

via hydrolysis of $Ti(OH)_4$. Then, as-prepared suspension was dried under vacuum for 10 h using a rotary evaporator.

TiS_2 powder was prepared by heating of TiO_2 nanoparticles (ST01) in a flow of CS_2 and N_2 gas mixture at 550 °C and maintained for 20 h. In order to eliminate the free sulfur as an impurity, as-prepared TiS_2 was purified by washing with toluene and then dried at 100 °C under vacuum. Partially sulfurized ST01 samples were prepared by heating them in a flow of CS_2 and N_2 gas mixture at temperatures of 250 and 500 °C.

Analytical grade CS_2 with a boiling point of 46–47 °C and maximum water content of 0.02% (Wako Pure Chemicals Co. Ltd.) was used as-received. Nitrogen gas of 99.99% purity (Nippon Sanso Co. Ltd.) was used as-received.

2.2. Thermogravimetric analysis (TG)

The experimental setup was reported elsewhere [13]. TG profiles were obtained in a vertical resistance tube furnace equipped with a quartz spring. A quartz crucible containing the weighed sample, approximately 100 mg, was suspended from quartz spring at the center of the uniform temperature zone of the furnace. The sample was heated at constant rate from room temperature to 1000 °C. Before heating, the reaction tube was evacuated to approximately 100 Pa for 30 min and then refilled with N_2 up to ambient pressure. After that, CS_2 in N_2 carrier gas obtained by passing N_2 gas flow through a bubbler containing liquid CS_2 was introduced. The N_2 gas flow rate was measured using a digital mass flow meter (Kofloc Model DPM-2A). The change in length of the quartz spring caused by the weight change during heating was measured by a level meter (Mitsutoyo) with an accuracy of 0.001 mm. The change in length was calibrated by using a standard weight. The sensitivity of the spring was 6.7 mg mm^{-1}.

The sulfurization experiments were carried out at a heating rate of 1 °C min^{-1} with a CS_2/N_2 gas flow rate of 5/50 ml min^{-1} and the decomposition of TiS_2 and partially sulfurized TiO_2 samples were also examined at a rate of 5 °C min^{-1}, in a stream of N_2 gas of 50 ml min^{-1}.

In addition, TG curves for as-received ST01 and $Ti(OH)_4$ particles were obtained using TG-DTA equipment (Rigaku Thermoplus TG 8120) at a heating rate of 5 °C min^{-1} in argon gas flow and the gases liberated during the heating rate were analyzed by gas chromatograph mass spectrometer (Shimadzu GC-MS QP5050).

2.3. Characterization

The identification of the products was performed by X-ray diffraction analysis using a Rigaku Type RAD-IC diffractometer with a Ni filtered Cu Kα radiation (40 kV and 20 mA) equipped by a curved pyrolitic carbon. The average size of initial materials was estimated using transmission electron microscopy (TEM) in a JEOL JEM 2000EX Electron Microscope operating at 200 kV. The specific surface area (BET) for as-received ST01 sample was performed using Micromeritics ASAP 2010 equipment.

3. Results and discussion

3.1. Sulfurization of ST01

TiO_2 nanoparticles, ST01, were characterized as 7 nm in average diameter with a narrow size distribution, 300 $m^2\,g^{-1}$ of specific surface area, and anatase-type TiO_2 in bulk structure, as their transmission electron micrograph was shown in Fig. 1(a). In contrast, larger particles were observed in commercial powders, as larger as 400 nm for anatase-type TiO_2 (Fig. 1(b)) and 1 μm for rutile-type TiO_2 powders (Fig. 1(c)), approximately.

Hence, we first focused on the sulfurization behavior of TiO_2 nanoparticles in the present study. Thermogravimetric analyses for the sulfurization of as-received and dried ST01 were made at heating rates of 1 °C min^{-1}, as shown in Fig. 2. The curve of the as-received ST01 (Fig. 2(a)) showed a weight decrease of 3.1% at around 140 °C followed by a slight weight increase and became flattened up to 420 °C. Then, the weight gradually increased and it attained

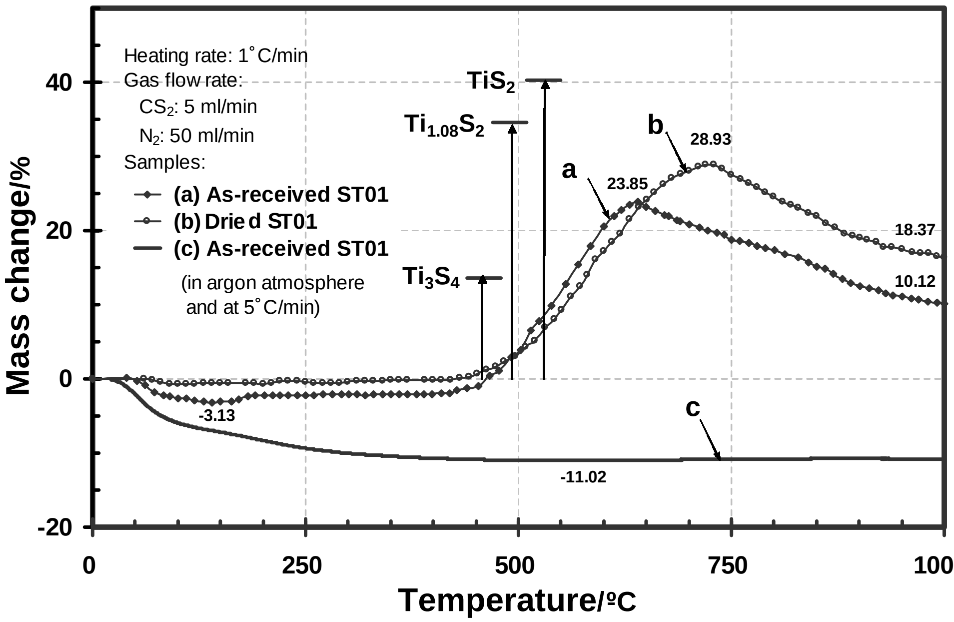

Fig. 2. TG curves (a–c) of sulfurization of ST01 samples.

to 23.9% at 640 °C. Finally, the weight decreased to 10.1% at 1000 °C.

Fig. 2(c) represents TG curve of as-received sample in the absence of CS_2. An initial decrease in the weight of 6.3% was observed up to 170 °C that was assigned to the vaporization of adsorbed water. The second weight decrease of 4.7%, from 170 to 540 °C, would be due to dehydration of amorphous $Ti(OH)_4$ contained in as-received ST01 sample, since amorphous $Ti(OH)_4$ synthesized independently showed the similar trend of the weight decrease in the same temperature range (Fig. 4(d)). However, no weight change was recorded in further increase in temperature in Fig. 2. Products other than water, such as organic compounds, were not detected in this TG measurement of ST01.

XRD patterns for ST01 sulfurized at 250, 500, 700 and 1000 °C are shown in Fig. 3. Since the 250 °C-sulfurized sample (curve (b)) did not give any peaks corresponding to titanium sulfide, sulfur may be adsorbed on the sample. On the contrary, the 500 °C-sulfurized sample (curve (d)) showed a mixture of anatase and TiS_2. The intensity of TiO_2

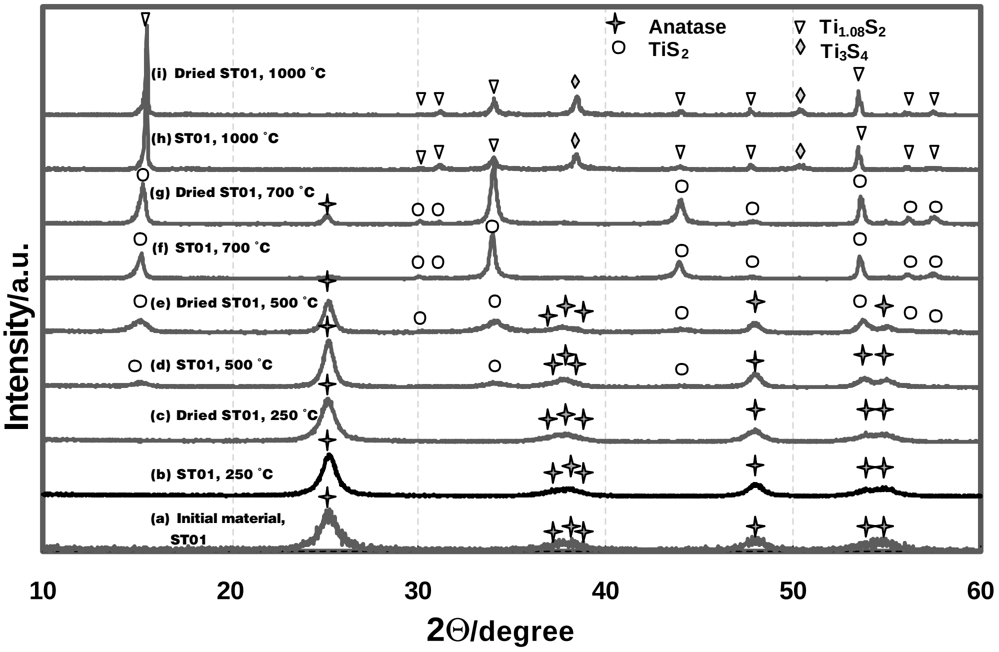

Fig. 3. XRD patterns (a–i) of sulfurized ST01 samples.

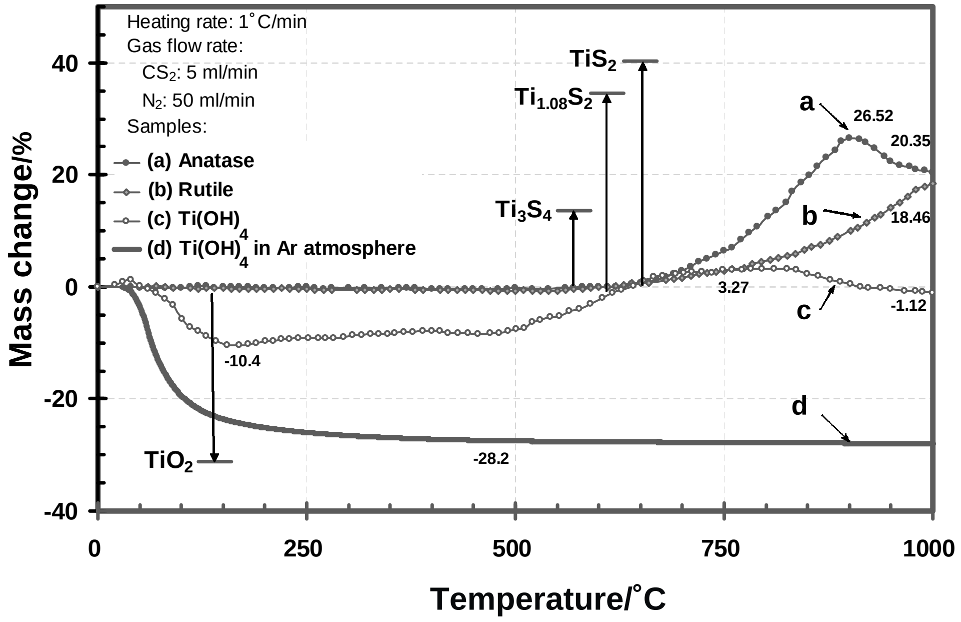

Fig. 4. TG curves (a–d) of sulfurization of anatase, rutile and $Ti(OH)_4$ powders.

peaks gradually decreased, in favor of TiS_2 peaks, with increasing temperature. Thus, at 700 °C (curve (f)), only TiS_2 peaks were observed. The final products (curve (h)) were found to be a mixture of $Ti_{1.08}S_2$ and Ti_3S_4, while no peaks corresponding to titanium oxides were observed.

From these results, we could discuss the phenomena during the sulfurization. It can be summarized as follows. For as-received sample, the weight loss below 200 °C was associated to the removal of absorbed water from the sample, while the weight increase starting from 200 °C was due to adsorption of CS_2 on TiO_2 [14], which avoided or delayed the condensation of OH groups. TiO_2 bulk started to be sulfurized at around 420 °C up to 640 °C, in accordance with the Eq. (1). Finally, the decomposition of obtained TiS_2 to lower sulfides compounds occurred above 650 °C.

$$TiO_2+CS_2 \rightarrow TiS_2+CO_2 \qquad (1)$$

In the case of dried ST01 (Fig. 2(b)), almost no weight change was observed up to 420 °C, since no absorbed water was present. In this temperature range, CS_2 was adsorbed on TiO_2 surface and gradually the surface is sulfurized by direct reaction between CS_2 and TiO_2 [14]. During the sulfurization of TiO_2 to TiS_2, the weight gradually increased and reached 28.9% at around 720 °C. Then, TG curve turned to weight decrease to 16.4% at 1000 °C because of decomposition of TiS_2 to lower sulfides. With respect to the XRD patterns (Fig. 3(c), (e), (g) and (i)), at low temperatures, negligible difference for as-received ST01 and dried ST01 was found. However, at 700 °C, a complete sulfurization was observed in as-received ST01, while dried ST01 still contained oxide phase. It seems that the presence of OH groups also makes the sulfurization easier.

3.2. Effect of initial materials

In order to compare the sulfurization behavior between initial materials, the TG for the sulfurization of anatase, rutile, and $Ti(OH)_4$ was measured, as shown in Fig. 4. The flow rate of nitrogen, which passed through CS_2 solvent, was fixed at 5 ml min^{-1} and the heating rate was 1 °C min^{-1}.

As mentioned above, the sulfurization started at around 420 °C for both samples of the as-received and dried ST01. In contrast, as shown in Fig. 4(a), anatase showed a similar TG curve to that of dried ST01, but the sulfurization started at around 630 °C, which is remarkably higher than that for ST01. As the result of rutile is shown in Fig. 4(b), the rutile seemed to be less reactive than anatase. Namely, the increase in weight from around 630 °C is rather gradual but a clear peak top is not found. On the other hand, in the case of $Ti(OH)_4$ (Fig. 4(c)), the TG curve showed the first weight decrease until 170 °C and then slight increase, indicating the sulfurization. The weight increased rapidly up to 8%, at 410 °C, with further increase in temperature, followed by the gradual decrease. The first drop may correspond to the dehydration reaction of $Ti(OH)_4$ (Eq. (2)), where the observed weight loss was only 10.4%. However, the theoretical value of the weight loss due to the dehydration is calculated to be 31.2%, which is three times higher than the above weight loss. When the TG analysis was carried out for $Ti(OH)_4$ independently in the absence of CS_2 (Fig. 4(d)), the experimental weight loss due to the dehydration process was 28.2%, which is in good agreement with the theoretical one. As a result, it is suggested that not only a part of $Ti(OH)_4$ was dehydrated but also some interaction and/or reaction between $Ti(OH)_4$ and CS_2 occurred.

$$Ti(OH)_4 \rightarrow TiO_2+2H_2O \qquad (2)$$

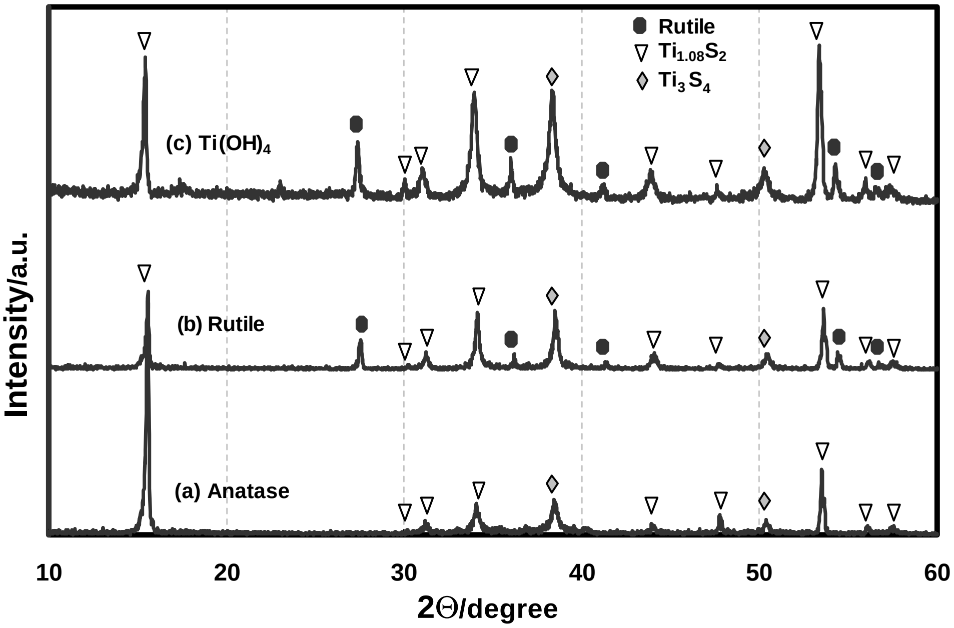

Fig. 5. XRD patterns (a–c) of sulfurized anatase, rutile and $Ti(OH)_4$ powders.

The maximum weight change (curve (c)) is around 3.8%. If the theoretical weight loss, 31.2%, by the dehydration is considered, the total weight gain could be 34.5%, which is comparable with that for the dried ST01 (Fig. 2(b)).

XRD patterns for the final products treated in CS_2 as mentioned above are shown in Fig. 5. Anatase-type powders (curve (a)) were completely sulfurized to $Ti_{1.08}S_2$ and Ti_3S_4, in accordance with the sulfurized product of ST01. In contrast, the product from rutile sample was found to be the mixture of rutile and the above sulfides (curve (b)). Thus, rutile is more difficult to be sulfurized than anatase because of the thermal stability of the structure and larger particle size. In the case of $Ti(OH)_4$ (curve (c)), a similar XRD pattern to the rutile case was observed. Namely, the product was a mixture of rutile and sulfides ($Ti_{1.08}S_2$ and Ti_3S_4). It could be considered that a part of $Ti(OH)_4$ was converted to sulfide via direct reaction of $Ti(OH)_4$ and CS_2, in parallel with the dehydration and phase transformation into rutile. As-formed rutile remained even after sulfurization at 1000 °C because of its difficulty as mentioned above.

It can be summarized that ST01 nanoparticles were sulfurized more easily than powders in the same structure, that rutile was rather stable against the sulfurization, and the starting temperature of the sulfurization of $Ti(OH)_4$ was almost similar to that of ST01. As a result, the unique behavior of sulfurization of ST01 can be explained by the Ti–OH structure located in the surface and/or bulk, which may be highly reactive with CS_2 to give sulfides, as well as by the large surface area and unsaturated active surface.

3.3. Decomposition of TiS_2 nanoparticles

For identifying the thermal behavior of TiO_2 sulfurized completely or partially, the decomposition of titanium sulfides was also investigated by TG method. Fig. 6 shows the TG profiles of the decomposition behavior of TiS_2 samples prepared by the complete sulfurization of ST01 nanoparticles at 550 °C and anatase-type powders at 900 °C with CS_2, named as TiS_2 nanoparticles and TiS_2 particles, respectively. The purified samples were obtained by washing the above sulfide particles with toluene for the removal of elemental sulfur from the products. The curve (a) for TiS_2 particles shows a weight decrease of 6.1% up to 350 °C and then flatness to ca. 700 °C, followed by the rapid decrease till 1000 °C. The final product was identified as a mixture of $Ti_{1.08}S_2$ and Ti_3S_4 from XRD analysis, as shown in Fig. 7 (curve (c)). By washing the sample with toluene to remove adsorbed sulfur, the curve (c) was obtained, where the amount of the first weight loss was reduced, suggesting that this weight loss was caused by the removal of absorbed elemental sulfur from the surfaces. The thermal behavior of TiS_2 nanoparticles, prepared by sulfurizing ST01 completely, were basically the same as the TiS_2 particles, as shown in Fig. 6(b). However, the cleaned TiS_2 nanoparticles (curve (d)) shows a very slight weight loss at 550 °C, similar to the curve (c). Namely, the sulfurized ST01 contains around 20% of the absorbed sulfur which was much larger than 6% of TiS_2 particles, since the specific surface area was remarkably larger.

The XRD patterns for the decomposed product of TiS_2 nanoparticles (Fig. 7(d) and (f)) indicate a mixture of rutile, $Ti_{1.08}S_2$ and Ti_3S_4 with a small amount of unidentified

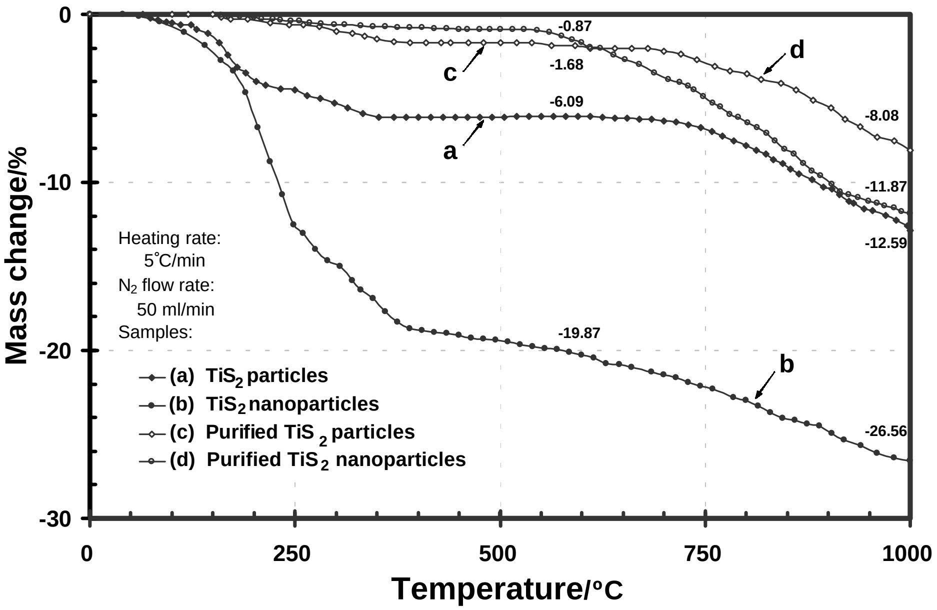

Fig. 6. TG curves (a–d) of thermal decomposition of TiS_2 of different sizes.

phase, while those of TiS_2 particles show $Ti_{1.08}S_2$ and Ti_3S_4 with a little rutile. As the initial particles were pure TiS_2 for both cases (Fig. 7(a) and (b)), water adsorbed on TiS_2 nanoparticles in atmospheric conditions could be concerned with the formation of oxide as an impurity in the resultant sulfide.

3.4. Decomposition of partially sulfurized TiO_2 nanoparticles

A partially sulfurized TiO_2 was prepared by the sulfurization of ST01 at 250 and 500 °C using a CS_2/N_2 mixture gas whose XRD patterns were shown in Fig. 2. The TG curves for the all samples, as shown in Fig. 8, indicate a large weight loss until 500 °C and then constant level over further increase in temperature. Considering the result of Fig. 6(b), as mentioned above, in the case of 250 °C-sulfurized sample, the weight loss may be ascribed to the removal of absorbed sulfur mainly. Virtually, there are no peaks corresponding to sulfides before and after the partial sulfurization treatment (Fig. 2(b) and (c), and Fig. 9(a) and (b)). The curve of ST01 sulfurized at 500 °C shows a similar trend to the other samples, but the considerable weight loss over 500 °C. This is caused by the decomposition of TiS_2 to lower sulfides as

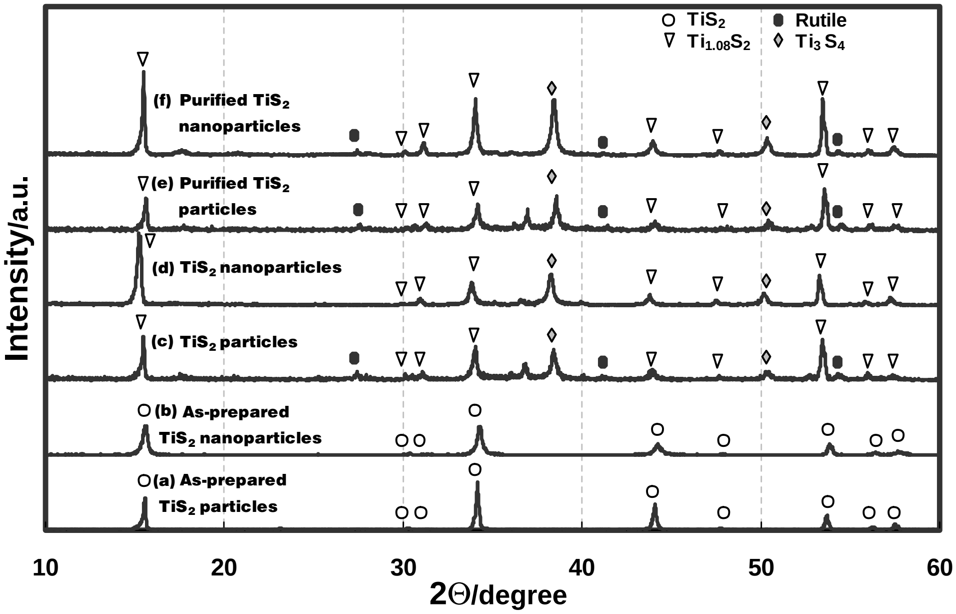

Fig. 7. XRD patterns (a–f) of thermally decomposed TiS_2 of different sizes.

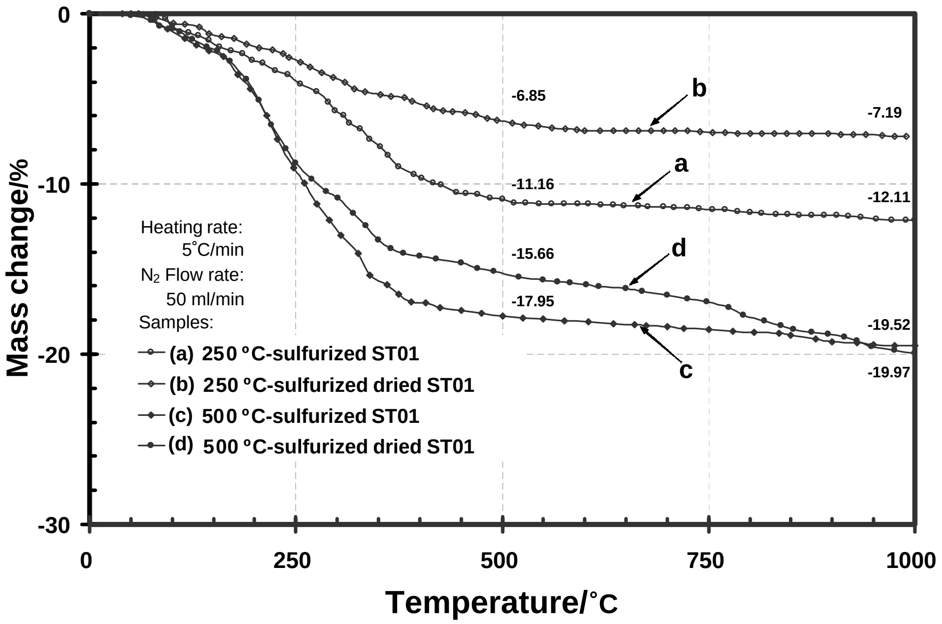

Fig. 8. TG curves (a–d) of decomposition of partially sulfurized ST01 samples.

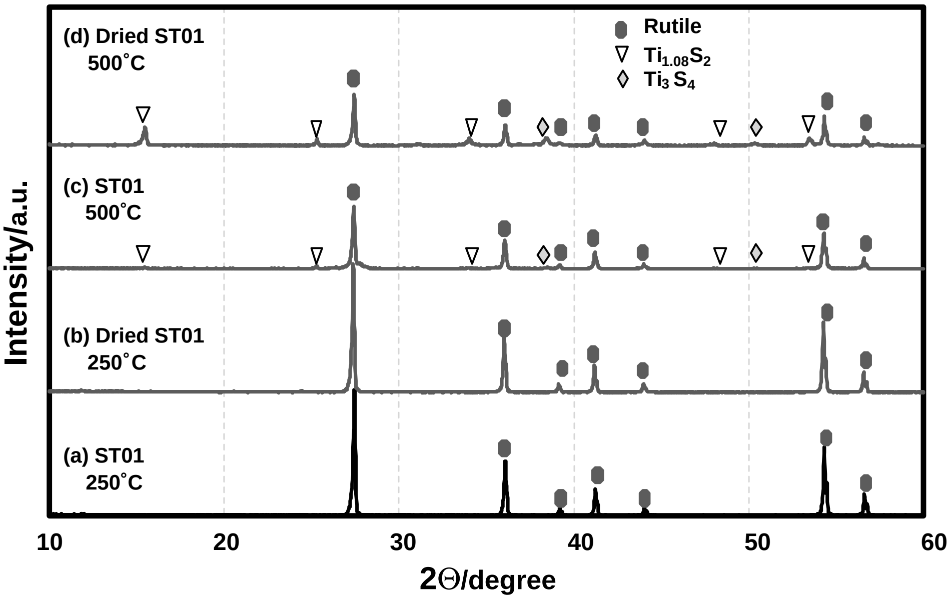

Fig. 9. XRD patterns (a–d) of decomposition of partially sulfurized ST01 samples.

seen in Fig. 9(c). The amount of the adsorbed sulfur in partially sulfurized TiO_2 was calculated from the first weight loss of TG curves (Fig. 9) and listed in the Table 1. It seems that the sample prepared from the as-received ST01 contains larger amounts of sulfur than that of dried ST01. Moreover, the amount of the absorbed sulfur was increased on increasing the temperature of partial sulfurization. Hence, it can be concluded that the sulfurization progresses via CS_2 adsorption and its decomposition to form free sulfur on the surface of ST01.

Table 1
Amount of absorbed sulfur in partially sulfurized TiO_2

Sample	Sulfur content in ST01 samples (%)	
	Sulfurized at 250 °C	Sulfurized at 500 °C
As-received ST01	11.16	17.95
Dried ST01	6.85	15.66

4. Conclusion

The sulfurization behavior of ST01 using CS_2 was determined by TG method and summarized as follows. At temperature lower than 420 °C the removal of absorbed water and condensation of OH groups occurred and the adsorption of CS_2 on TiO_2 surface without a fixed temperature that defined each phenomenon. The sulfurization of TiO_2 bulk was developed between 420 and 640 °C. Finally, above 640 °C, the TiS_2 obtained decomposed to give $Ti_{1.08}S_2$ and Ti_3S_4 compounds.

The starting temperature of sulfurization for ST01 was found to be lower than those for TiO_2 (anatase or rutile) and $Ti(OH)_4$ particles. It was in most part due to the smaller particle size and larger specific surface area of ST01 so the sulfurization of it was made easier.

In contrast, the thermal behavior of TiS_2 produced from nanoparticles was unstable and decomposed at lower temperatures than those produced from nanoparticles. Moreover, the sulfur content on the samples increased on increasing the temperature of sulfurization and it was observed that the OH groups present in the as-received ST01 sample provided a better adsorption of it and as a consequence it produced an easier sulfurization in comparison with dried ST01 samples.

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