Synthesis of Fumed Titanium Dioxide with a High Content of Rutile Structure by Novel Natural Dropping Thermal Treatment

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A natural dropping thermal treatment is an effective method to calcine materials with very short heating time. It has been applied to the transformation of titanium dioxide from anatase to rutile structure. In particular, the novel thermal treatment is an indispensable method for the fumed titanium dioxide (Fumed TiO_2) to give high rutile structure content inhibiting the sintering / grain growth. Meanwhile, the relationships between conversion ratio of the rutile structure content and the morphology of the agglomerate before the thermal treatment (Precursor) has been investigated.

Keywords: Natural dropping thermal treatment, Fumed TiO_2, Agglomerate

1. Introduction

A novel thermal treatment method; natural dropping thermal treatment has been reported as one of very simplified calcination process. It has advanced as part of thermal treatment process with very short heating time around 1 second. It has been applying to synthesize the new fumed TiO_2 with high rutile structure content maintaining the high dispersibility. The fumed TiO_2 is applied to various application fields such as a reference of photocatalytic materials, TiO_2 electrode of a dye sensitive solar cell and UV cutting agent for cosmetics by the unique properties; high purity, fine primary particle size, high anatase contents and excellent dispersibility [1]-[7]. Comparatively, it is reported that the anatase structure is not preferred to use for the cosmetics because of the high photocatalytic activities [8]. It is well known that the anatase structure transforms to the rutile structure at high temperature and long heating time. Some studies are reported for the additional thermal treatment for the fumed TiO_2. However, in these investigations, the drastic increase of the primary particle size and rapid decrease of the surface area are observed [9]-[10]. In generally, the sintering of the fumed TiO_2 are not affordable by the conventional thermal treatment method by using a muffle furnace and results a loose of the high dispersibility.

The natural dropping thermal treatment has been investigating to improve this issue by reducing the thermal treatment time as short as possible. In the investigations, the effect of the morphology for the fumed TiO_2 before the thermal treatment (Precursor) was investigated. This paper introduces examples of the novel natural dropping thermal treatment applying to the fumed TiO_2 as the new calcination method.

2. Novel natural dropping thermal treatment

The natural dropping thermal treatment is consisted from very simple thermal treatment method and applied to the fumed TiO_2. In this process, the fumed TiO_2 is directly dropped without a sieve or through sieves from top to the bottom of the electric furnace at several temperature under air atmosphere. The heating time is very short around 1 second. Fig.1 shows typical experimental apparatus for the thermal treatment.

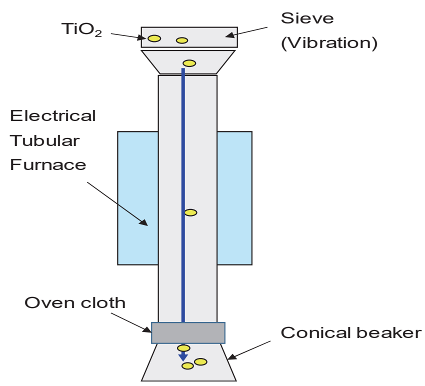

Fig. 1 Outline of the natural dropping thermal treatment

3. Thermal treatment of the fumed TiO_2

The natural dropping thermal treatment has been applied to the pure fumed TiO_2 (P25) to increase the rutile structure content inhibiting the sintering / the grain growth [11]. It is reported that just passing 0.5 mm mesh sieve, the rutile structure content drastically increases to 94%, although only very slight change of the rutile structure content; from 16 % to 18 %. without the sieve were observed.

Fig. 2 shows X-ray diffraction (XRD) patterns of the thermally-treated P25 at several temperatures through the 0.5 mm mesh sieve. The XRD data indicates that the content of the rutile structure (%) from the anatase is significantly affected by the temperature rise.

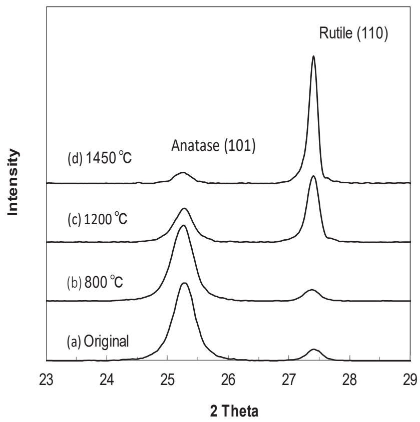

Fig. 2 XRD patterns of thermally-treated P25

Fig. 3 confirms the content of the rutile structure of the thermally-treated P25 at several temperatures using several mm mesh sieves. The same contents of the rutile structure; 94 % are obtained by passing through from 0.5 mm and 1.0 mm mesh sieves at 1450 ℃.

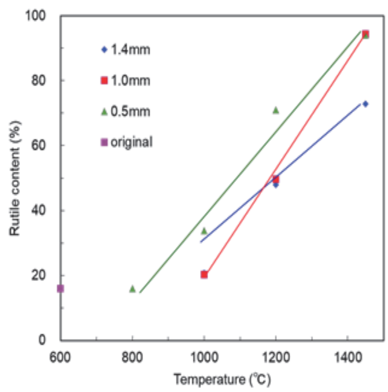

Fig. 3 Rutile conversion ratio for P25

Comparatively, the content of the rutile structure is stayed at 73 % with through 1.4 mm sieve.

The thermally-treated P25 showed good dispersibility due to many pores in the agglomerate, sponge-like agglomerate although it demonstrates large particle in the particle size distribution analysis. The particle residence time during the heating unit in the electrical furnace are examined by using the terminal velocity of the powder calculated with Stokes's equation. The relationship between rutile structure content and particle residence time at 1450 ℃ is appeared in Fig. 4.

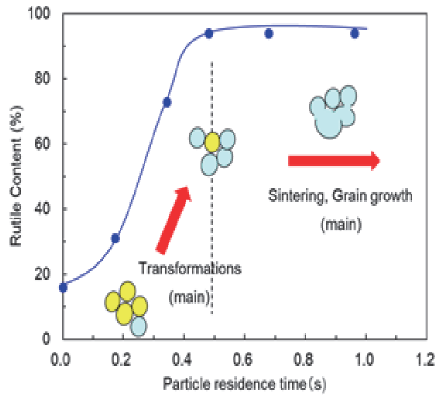

Fig. 4 Illustration of thermal treatment based on particle residence time

From 0.00 to 0.48 seconds of residence time, the rutile structure content is increased related to the prolonging the residence time. After 0.48 seconds, the rutile structure contents sustained at 94% up to around 1.00 seconds. This result suggests that the crystal transformation from the anatase to the rutile structure of P25 is mainly proceeded before 0.48 seconds and after 0.48 seconds the applying heat energy is not mainly used to the transformation but sintering or grain growth.

This result is caused from the deviations of agglomerate density of P25. When some small agglomerates have higher bulk densities than whole original P25, the terminal velocity of the densified agglomerates become higher than the normal ones and the residence time also becomes too short to the crystal transformation.

As described above, the novel natural dropping thermal treatment is very effective method for transformation from anatase to rutile structure of fumed TiO_2 (P25) with very short heating time. It is confirmed it is difficult to achieve 100% of rutile structure for a pure P25 due to existing small portion of densified agglomerates.

4. Dry-type of surface modification with metallic alkoxide

For the synthesis of the fumed TiO_2 (P25) with 100% rutile structure content, surface modification of P25 with metallic alkoxides has been reported before the natural dropping thermal treatment as other approach [12]. In this study, P25 precursors are produced by the surface modification with metallic alkoxides; Tetraethoxysilane (TEOS; TE(2); 2wt% and TE(5); 5wt%), and Titaniumtetraisopropoxyde (TTIP; TT(2); 2wt% and TT(5); 5wt%) by a dry-type of surface modification process. Next the produced precursors are thermally-treated by the natural dropping method. P25 modified with TE(2), TT(2) and TT(5)) by the dry-type of modification process achieves 100% of rutile structure at 1400℃ although TE(5) maintains low rutile structure content. A precursor modified with TEOS by the wet-type process; W-TE(2) shows low content of rutile structure. The results are shown in Fig. 5.

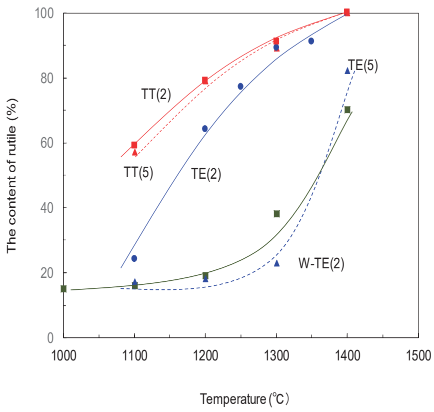

Fig. 5 Rutile conversion rate for thermally-treated P25

It is confirmed that the results are caused from the agglomerate conditions of the precursors.

The precusor TE(2) shows smaller agglomerate than precursors TE(5) and W-TE(2). The precursor W-TE(2) seems to make rigid and densified agglomerate. The SEM photos of precursors are demonstrated in Fig. 6.

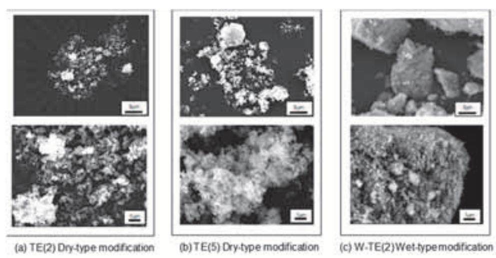

Fig. 6 SEM photos of precursors

The terminal velocity of W-TE(2) becomes faster than the others due to the high densified small agglomerate. These agglomerate conditions are relatively well fit to the results of the conversion ratio from the anatase to the rutile structure. The thermally-treated TE(2) with 100% rutile structure showed very excellent dispersibility in the water dispersion due to strong negative zeta potential, -42.0mV. The high dispersibility of the thermally-treated TE(2) is cased from both the porous agglomerate structure; sponge-like agglomerate and the electro charge repellence of the SiO_2 layer coated on the P25 surface.

As described above, the dry-type of the surface modification with small portion of TOES is very useful method to synthesize 100% of rutile structure content controlling the agglomerate of the precursor for the natural dropping thermal treatment

5. Mixing of external additive

As another approach to synthesize 100% rutile structure content for P25, mixing with solid stated external additive has been reported [13]. In this investigation, P25 is mixed with fumed SiO_2 modified with dimethylsilyl group (R972), fumed Al_2O_3 (AluC) and Calcium stearate to synthesize the suitable precursors improving the agglomerate conditions and then the precursors are thermally-treated by the natural dropping method. The rutile structure conversation ratio is demonstrated in Fig. 7.

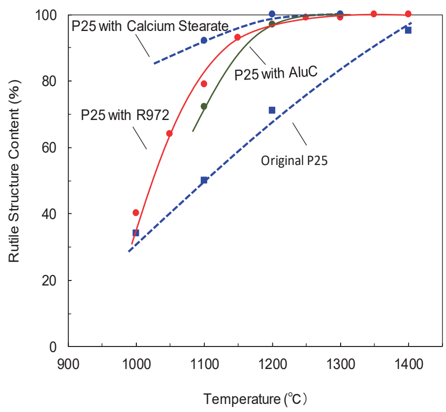

Fig. 7 Rutile conversion ratio for thermally-treated P25 mixed with external additive

The thermally-treated P25 with R972 and AluC show 100 % of rutile structure at 1350 ℃ and 1300 ℃ respectively. These temperatures are lower than that of metallic alkoxides modified ones, TE(2), TT(2) and TT(5). The thermally-treated P25 with calcium stearate shows 100 % rutile content at 1200 ℃. This temperature is more than 100 ℃ lower than the addition of R972 and AluC, and more than 250 ℃ lower than the thermally-treated original P25.

Fig. 8 indicates the sedimentation test results of the dispersion in water versus storage time for these thermally-treated P25 having 100 % of the rutile structure. The other types (Chloride process) of TiO_2 (CR-EL (7 m^2/g) Ishihara Sangyo Co. Ltd.) with the rutile structure and similar surface area, and the original P25 without thermal treatment are also illustrated.

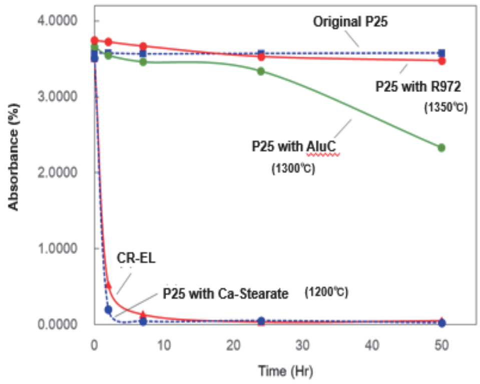

Fig. 8 Sedimentation results of TiO_2 dispersion

The thermally-treated P25 with R972 demonstrates an excellent dispersibility with very similar to the original P25. Regarding the thermally-treated P25 with calcium stearate, it demonstrates low dispersibility similar to CR-EL even though the thermal treatment temperature is the lowest; 1200℃. All thermally-treated P25 show larger particle size distribution patterns than CR-EL. The sedimentation results are very different from particle size distribution results. For the estimation of the sedimentation velocity, the result of CR-EL is relatively good consistency with one of the particle size distribution. Comparatively, the results of the thermally-treated P25 are quite different from the sedimentation results. This difference suggests that the thermally-treated P25 have much lower powder densities than CR-EL. Additionally, the thermally-treated P25 with R972 at 1350℃ shows -47.8mV of zeta potential although original P25 at 1400℃ demonstrates -18mV. This strong negative charge seems to result to high dispersibility of thermally-treated P25 with R972 due to electros charge repellence of the SiO_2 on P25 surface similar to the surface coating with TEOS TE(2). TEM photos of the thermally-treated P25 with the external additives are illustrated in Fig. 9.

The thermally-treated P25 with R972 and AluC contain small particle and many pores in the agglomerate. The thermally-treated P25 with calcium stearate shows no small particles and supports the sintering / grain growth.

The Carr Cohesion values is applied as an index of the powder agglomerate [14]. The Carr Cohesion tendency of these precursors are as follows; P25 with calcium stearate (28) < P25 with AluC (49) < P25 with R972 (55) < original P25 (69). The Carr Cohesion values show relatively good relationships between the temperature achieve 100 % rutile structure. The agglomerate with the low Carr Cohesion value passes through the sieve as smaller agglomerate than the agglomerate with high Carr Cohesion value. The remarkable sintering / grain growth of the thermally-treated P25 with calcium stearate would be resulted from an additional heat source by the burning of an alkyl-group of the calcium stearate under air atmosphere.

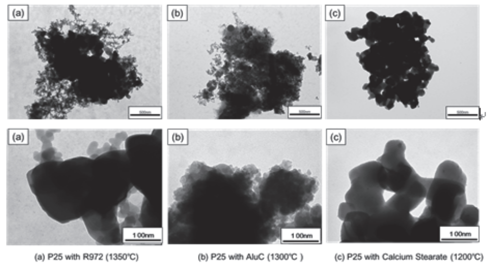

Fig. 9 TEM images of the thermally-treated P25 with the external additives

As described in this section, the mixing with external additive is quite effective method to synthesis the new fumed TiO_2 (P25) with 100% of rutile structure maintaining the high dispersibility for the natural dropping thermal treatment. Additionally, a new possibility is also reported that the sintering / grain growth of the fumed TiO_2 by burning of calcium stearate with very short thermal treatment time.

6. Extended application of the natural dropping thermal treatment

The natural dropping thermal treatment has been applying to not only fumed TiO_2 but also other fumed oxides; fumed SiO_2 and fumed Al_2O_3. There are no changed of the crystal structure at 1450℃ and made slightly large agglomerate due to partial sintering in both fumed oxides.

It is confirmed that the natural dropping thermal treatment is only applied to the fumed TiO_2 for the crystal transformation. Otherwise, the morphology change maintaining the original crystalline polymorphs is possible to not only fumed TiO_2 but also fumed SiO_2 and fumed Al_2O_3.

7. Conclusion

We introduced examples of applying the novel natural dropping thermal treatment to fumed TiO_2 (P25). It is a very effective method for the crystal transformation from anatase to rutile structure inhibiting the sintering / grain growth to maintain the high dispersibility. The preferable agglomerate conditions have been investigated by controlling the morphology of P25 precursors. The preferable P25 precursors are produced with the dry-type of surface modification and mixing with the external additives. The precursors modified with TEOS and mixing with fumed SiO_2 (R972) achieve 100 % of rutile structure content maintaining the high dispersibility with the sponge-like structure and the static electricity repellence of SiO_2 on the P25 surface.

We anticipate future application of the natural dropping thermal treatment to not only fumed TiO_2 but also various other materials.

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