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Original Research Paper

The synthesis of a porous-type of TiO_2 with rutile structure

Yukiya Yamashita [a,b], Kei Ishiguro [a], Daisuke Nakai [a], Masayoshi Fuji [b,*]

[a] Nippon AEROSIL Co. Ltd., 3 Mita-cho, Yokkaichi, Mie 510-0841, Japan
[b] Advanced Ceramics Research Center, Nagoya Institute of Technology 3-101-1, Honmachi, Tajimi, Gifu 507-0033, Japan

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ABSTRACT

The synthesis of a porous-type of TiO_2 with rutile structure was studied. The focuses were on the thermal treatment temperature and time. AEROXIDE® TiO_2 P 25, as a fumed TiO_2, was thermally treated in a vertical-type tubular furnace by the natural dropping method. Even though the thermal treatment time was less than 1 s, a drastic increase of polymorphism from anatase structure to rutile structure was observed. The relationships between the rutile structure transformation ratio and surface area of obtained porous type of TiO_2 were investigated depending on the thermal treatment temperature. The porous-type of fumed TiO_2 showed high dispersibility in the sedimentation test although is showed large particle size.

1. Introduction

Titanium dioxide (TiO_2) has a wide variety of applications in industrial fields, such as white pigment, ultraviolet cutting and photocatalytic material such as coating, paint, cosmetics, paper, resin, photocatalytic material and others. Recently, TiO_2 nanomaterials were extensively investigated for their special properties especially focusing on their photocatalytic activities [1].

TiO_2 has three typical crystalline polymorphs, i.e., anatase, brookite and rutile. For industrial purposes, the anatase and rutile structures are mainly used. There are several production processes for industrial applied TiO_2 such as the sulfate process, chloride process, sol-gel process and fumed process. Among these production processes, the fumed process is unique in its production which can produce very fine TiO_2 powders directly from a hydrogen and oxygen burner using the same process as fumed silica [2]. This fumed TiO_2 is composed of weak agglomerated particles like a 3-dimendional network structure and this agglomerate is easily destroyed by the addition of mechanical agitation when it is dispersed in media such as water, organic solvent, resin and others. Due to this unique property, fumed TiO_2 is used as an UV cutting material for cosmetics having a high transparency due to its fine primary particle size. Fumed TiO_2 is a mixture of the anatase and rutile type crystal structures and the main phase being the anatase structure [2]. This material shows excellent photocatalytic activities. Recently, it has been used as a reference material to evaluate photocatalytic activities [3]. However, this excellent photocatalytic activity can also be a disadvantage of fumed TiO_2 in cosmetic applications. Normally, the rutile structure is preferred for this application.

It is well known that anatase transforms into the rutile structure by thermal treatment at a high temperature. Actually, there are many studies about TiO_2 to prevent or accelerate this transformation. For example, metal oxide additives [4,5], the addition of SiO_2 [6], the addition of carbon [7], non-metal doping [8] and ultrasonic irradiation as a special processing [9]. However, in general cases, sintering and grain growth of the TiO_2 occur by a thermal treatment, caused a decrease in a dispersibility of the fumed TiO_2. The control of the thermal treatment conditions is very important factor to prevent the sintering and grain growth for the additional thermal treatment.

There are also several studies about sintering of TiO_2 such as microwave irradiation [12], sintering temperature [13], and O_2 pressure [14]. As another approach, the photocatalytic activities have been investigated for the sintered TiO_2 [15]. However, these investigations focused on the production of sintered TiO_2 with a high density. Regarding the fumed TiO2, the increase of the primary particle size depended on the increase of the content of rutile structure was shown depended on rising the thermal treatment temperature to 1000 °C for 3 h [16].

In this current study, it was desired to synthesize a new type of fumed TiO_2 having a high content of rutile and keeping the high dispersibility by controlling with a partial sintering by the additional thermal treatment at high temperature for very short time. The experimental results suggested that the newly-fumed TiO_2

* Corresponding author.
E-mail address: fuji@nitech.ac.jp (M. Fuji).

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has a higher porosity in the agglomerate and acts as a porous-type of fumed TiO_2.

2. Experimental details

2.1. Materials and preparation

As fumed TiO_2, commercially produced TiO_2 with different surface areas and primary particle sizes, (AEROXIDE® TiO_2 P 25: 50 m^2/g; 21 nm; (P25), AEROXIDE® TiO_2 P 90: 90 m^2/g; 14 nm; (P90) and sample A: 65 m^2/g; 18 nm; produced by Nippon AEROSIL Co., Ltd.) were used. An electric tubular furnace (OSK 55DB125B Ogawa Seiki Co., Ltd.) was vertically placed and equipped with a 2 L glass conical beaker at the bottom with a wrapped opening by oven cloth to protect the upstream inserted air. A sample of TiO_2 was directly dropped from top of the furnace to the bottom by a natural dropping method without a sieve or through several mesh sizes of sieves (0.5 mm, 1.0 mm and 1.4 mm) fixed on the top of the electric furnace. The sieve was vibrated by a vibration device (THRIVE HandyVibe MD-01 Daito Electric Machine Industry Co., Ltd.). The electric furnace was heated at several temperatures from 800 °C to 1450 °C. The thermal treatment time was measured by checking the dropping time of the fumed TiO_2 from the top to the bottom by visual inspection. A schematic outline of experimental apparatus for thermal treatment is illustrated in Fig. 1.

2.2. Characterization

The crystalline phases were analyzed by an X-ray diffractometer (XRD-6100 Shimazu Corp.) using Cu-Kα radiation to identify the content of rutile and anatase of the thermally-treated fumed TiO_2. The content of rutile (f rutile) was calculated by using the following equation [17].

$$f\ rutile = 1 - f\ anatase;$$

$$f\ anatase = 1/(1 + 1.26\ (I rutile\ /I anatase))$$

Irutile, Ianatase: XRD peak intensity of rutile (1 1 0) and anatase (1 0 1) structure

The particle size distribution was measured by a MT3300EX2 from the MicrotracBEL Corp. The surface area was measured by the BET technique (Macsorb HM-1200S Mountech Co., Ltd.) using the one point measurement method [18].

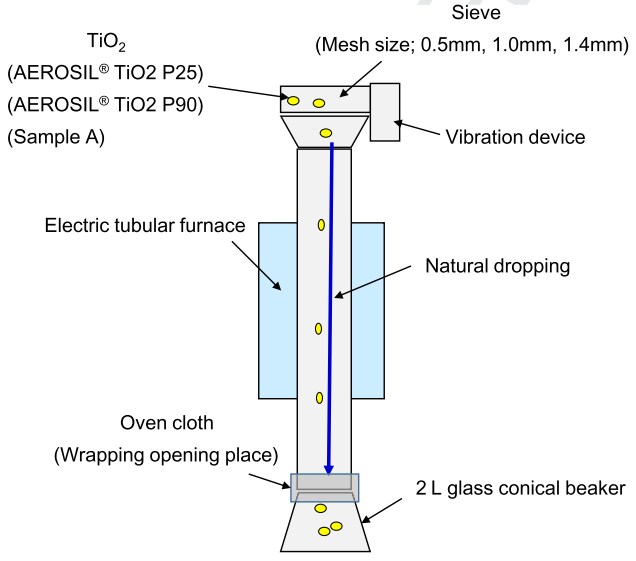

Fig. 1. Schematic outline of experimental apparatus for thermal treatment.

For the sedimentation test, 0.5 wt% of a TiO_2 water dispersion was prepared by an ultrasonic homogenizer (US-300CCVP Nihon Seiki Kaisha, Ltd.,) at 300 W for 5 min. The resulting dispersion was poured into a 15 ml sedimentation tube graduated on the outside of the wall. One ml of the dispersion was taken from the 8-ml point of the sedimentation tube and the absorbance of the water dispersion was measured by a spectrophotometer (V-670 JASCO Corp.) at a 700 nm light wavelength. The appearance of the water dispersion in the sedimentation tube was also visually observed. The water vapor adsorption-desorption isotherms were measured by a BELSOP-max (MicrotracBEL Corp.). The nanostructure and morphology were observed by a transmission electron microscope (TEM, JEM-1010 JEOL Ltd.).

3. Results and discussion

3.1. Conversion ratio from anatase to rutile structure

Table 1 is a summary of the results of the thermal treatment of P25 at 1450 °C without the sieve and through the 0.5 mm mesh sieve. The original P25 has the content of rutile (15%). After the thermal treatment at 1450 °C without the sieve, P25 showed a slight increase in the content of rutile (from 14% to 16%). However, by passing the sample through the 0.5 mm mesh sieve, there was a drastic increase in the content of rutile (from 14% to 94%). The thermal treatment time was measured at less than 1 s in both cases.

Fig. 2 shows the X-ray diffraction (XRD) peaks of the anatase (1 0 1) and rutile (1 1 0) for the P25 treated at several temperatures through the 0.5 mm mesh sieve. In all cases, the thermal treatment time was less than 1 s. The XRD data indicated that the content from anatase to rutile (%) was significantly affected by the temperature rise. The anatase gradually decreased depending on the increase in the thermal treatment temperature and the content of rutile (%) increased relative to the anatase.

Fig. 3 confirms the content of rutile for three fumed TiO_2 samples with different surface areas treated at several temperatures from 800 °C to 1450 °C through the 0.5 mm mesh sieve. P90 and Sample A indicated higher content of rutile than P25 for the same thermal treatment temperature and they showed the content of

Table 1
Physical properties of P25 after thermal treatment.

Temperature (°C)	Mesh size of sieve (μm)	Rutile ratio (%)	S_{BET} (m^2/g)
Room temperature	–	16	51
1450	–	18	49
1450	500	94	9

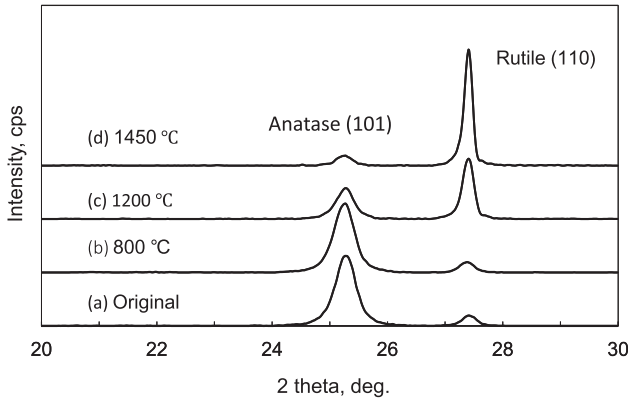

Fig. 2. XRD patterns of thermal treated P25.