



Preparation of decahedral anatase titania particles with high-level photocatalytic activity

Noriyuki Sugishita^{a,*}, Yasushi Kuroda^a, Bunsho Ohtani^b

^a Showa Titanium Co. Ltd., Toyama 931-8577, Japan

^b Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

ARTICLE INFO

Article history:

Received 28 June 2010

Received in revised form 3 November 2010

Accepted 3 November 2010

Available online 4 December 2010

Keywords:

Photocatalyst

Decahedral particles

Anatase

ABSTRACT

Anatase titania (TiO₂) particles were synthesized from titanium(IV) chloride (TiCl₄) and oxygen (O₂) through an improved gas-phase reaction process under rapid heating and rapid quenching conditions. The obtained particles were decahedral-shaped highly crystalline particles with specific surface area of 5–40 m² g^{−1}. These particles exhibited a level of photocatalytic activity higher than the representative commercial TiO₂ photocatalysts for oxidative decomposition of acetic acid in an aqueous solution and acetaldehyde in air. Their higher level of activity is considered to be due to a combination of their moderate specific surface area and high crystallinity.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

It has been reported recently that decahedral-shaped anatase TiO₂ particles have been prepared from TiCl₄ and O₂ through a gas-phase reaction using a hydrogen–oxygen flame burner as the heat source, and have exhibited a high level of photocatalytic activity [1,2].

It has been reported also that a liquid-phase reaction process added to the above gas-phase reaction produces decahedral TiO₂ particles [3], but the mean particle size of those produced by this latter method is larger than 1 μm. Furthermore, the liquid-phase reaction process is a hydrothermal reaction of titanium(IV) fluoride (TiF₄) with hydrofluoric acid and seems not suitable for industrial production. In this study, the former gas-phase reaction which is applicable to industrial processes was improved, precise control of the reaction conditions was achieved, and attempts were made to enhance their photocatalytic activity.

2. Experimental

2.1. Methods for synthesis

An infrared furnace (ULVAC-Riko) was used as a heating instrument (Fig. 1) [4]. A quartz reactor tube was placed in the infrared

furnace. A portion of the quartz reactor tube was wrapped with a platinum foil and this portion only was heated. The temperature of the platinum foil was set at 1200 °C. Mixed gas of TiCl₄ and O₂ preheated to a fixed temperature was introduced into the quartz reactor tube, passed through the heating zone and then quenched rapidly.

2.2. Photocatalytic decomposition of acetic acid (AcOH) in an aqueous solution

A 5.0 vol.% aqueous AcOH solution (5.0 mL) and TiO₂ powder (50 mg) were put in a test tube which was then sealed off with a rubber septum and irradiated with the light of a high-pressure mercury lamp under vigorous stirring. The amount of carbon dioxide (CO₂) produced was measured by using a TCD gas chromatograph (GC) (Shimadzu GC-8A).

2.3. Photocatalytic decomposition of acetaldehyde in air (Fig. 4, Fig. 7)

TiO₂ powder (10 mg) was dispersed in water in a glass dish of 27-mm inner diameter and dried at 110 °C. The glass dish was placed in a glass chamber of 500 mL volume. Acetaldehyde (500 ppm) and water (5.8 μL, corresponding to 50% RH at 25 °C) were injected into the chamber, which was then irradiated with light at the intensity of 0.2 mW cm^{−2} from a xenon lamp. The amount of CO₂ produced was measured by TCD-GC.

* Corresponding author. Tel.: +81 76 437 9201; fax: +81 76 437 6600.
E-mail address: Noriyuki.Sugishita@sdk.co.jp (N. Sugishita).

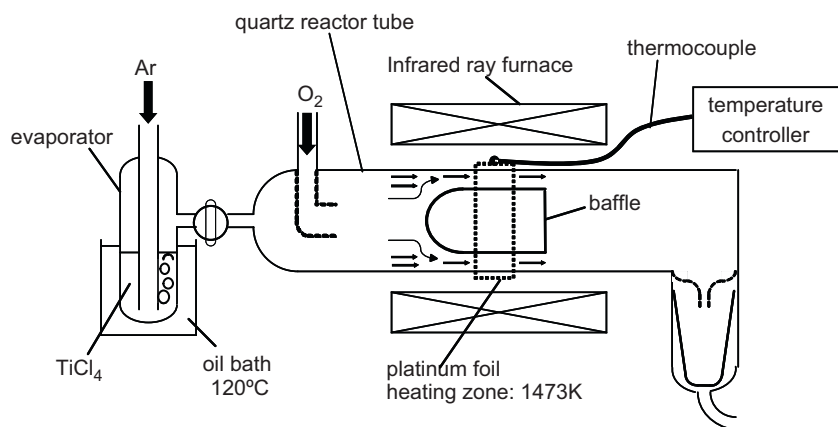


Fig. 1. Gas-phase reaction apparatus for the preparation of decahedral anatase titania particles.

3. Results and discussion

3.1. Improvement of the apparatus for synthesis

The previously reported method for synthesizing decahedral TiO_2 particles by a gas-phase reaction using a hydrogen–oxygen flame burner heated the raw material gas locally from the outside of the reactor tube. Since the temperature of the burner was controlled by the mixing ratio of oxygen and hydrogen, it was difficult to regulate the temperature of the heating zone precisely.

On the other hand, the apparatus used in the present study had a heating system in which only a platinum foil is heated by absorption of the infrared light irradiated from an infrared furnace. Accordingly, the part of the reactor tube which is in contact with the platinum foil is heated locally. In addition, as shown in Fig. 1, a thermocouple was set on the platinum foil and the intensity of an infrared light was controlled by a temperature controller so as to regulate the temperature on the platinum plate itself to a given temperature. Thus, the heating zone and the heating temperature of the reactor could be controlled precisely by a combination of platinum foil and an infrared furnace. This apparatus is suitable for realizing the rapid heating and rapid quenching conditions suited to synthesis of the decahedral-shaped particles.

Additionally, a baffle was set in the inside of the quartz reactor tube to make the raw material gas pass near the platinum foil where the highest temperature would be attained. By installing this baffle, the yield of the decahedral-shaped particles was increased and the uniformity of particle size was also improved. It is considered that these improvements were achieved by facilitation of generation of homogeneous cores due to uniform heating of the raw material gas in the heating zone. Fig. 2 shows SEM images of the decahedral-shaped anatase TiO_2 particles (Particles A) with specific surface area of $25 \text{ m}^2 \text{ g}^{-1}$ prepared with the apparatus shown in Fig. 1. These results indicate that the decahedral-shaped anatase particles can be prepared by using either a burner or an electric furnace in a gas-phase reaction process comprising rapid heating and rapid quenching of the raw materials.

3.2. Photocatalytic activity of decahedral anatase TiO_2 particles

Fig. 3 shows the relationship between the acetic-acid decomposition activity in a liquid-phase and the specific surface area of the decahedral particles prepared with the use of an apparatus indicated in Fig. 1. Generally photocatalytic TiO_2 particles with the larger specific surface area tend to have the higher activity, because the larger surface area facilitates more adsorption of a reaction substrate [5]. Similarly, there was a trend toward higher activity in the

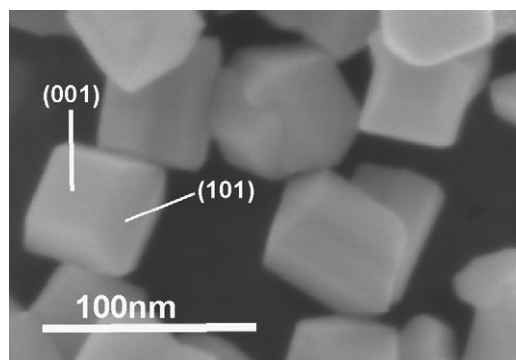


Fig. 2. SEM image of decahedral anatase titania particles prepared through gas-phase process. Particles A (ca 70-nm primary particle size and $25 \text{ m}^2 \text{ g}^{-1}$ specific surface area).

decahedral anatase TiO_2 particles with the larger specific surface area with the highest activity being 2 times higher than that of P25 (Nippon Aerosil; $40 \text{ m}^2 \text{ g}^{-1}$).

On the other hand, there is a local maximum of photocatalytic activity at around $12 \text{ m}^2 \text{ g}^{-1}$ of surface area in Fig. 3. The activity at this local maximum does not differ so much from that at $40 \text{ m}^2 \text{ g}^{-1}$. Surface area is one possible factor to affect photocatalytic activity, but it is not the only factor. The specific surface area of the particles was controlled by varying concentration of TiCl_4 in the feed gas. And the concentration of TiCl_4 was controlled by varying the

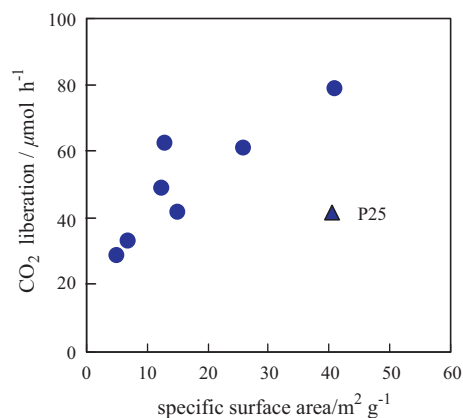


Fig. 3. Relationship between specific surface area and photocatalytic CO_2 production from an aqueous solution of 5 vol.% acetic acid. Circles: decahedral anatase titania particles. Triangle: P25.

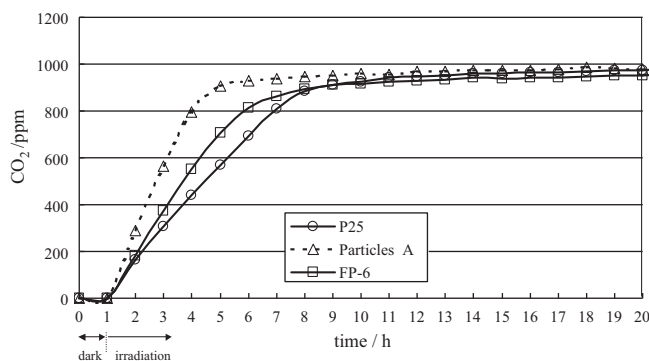
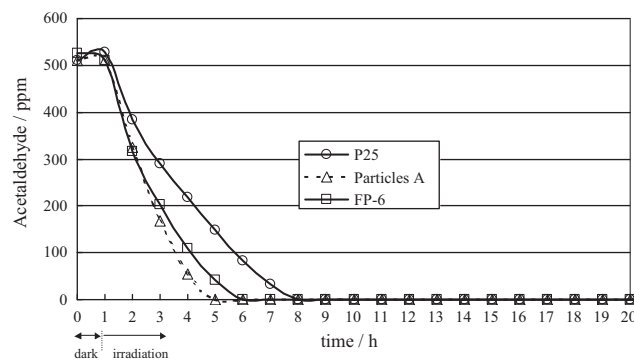


Fig. 4. Photocatalytic activity for mineralization of acetaldehyde in air.



volume of the raw material gas (Ar and O₂). Thus in addition to the concentration of TiCl₄, the time during when the reaction gas stayed at the main heating zone were also changed. The difference of the staying time may have changed another variable factor (e.g. crystal structure) to affect photocatalytic activity.

High photocatalytic activity of the decahedral-shaped anatase TiO₂ particles was also observed in decomposition of acetaldehyde in a gas-phase. In Fig. 4 are shown the results of evaluation of the activity of photocatalytic anatase TiO₂ particles prepared by industrialized gas-phase processes and that of *Particles A*. Both particles had sufficient activity to decompose 500 ppm of acetaldehyde entirely. Rate of CO₂ liberation by *Particles A* was 1.8 times higher than that by P25 and 1.5 times higher than that by FP-6 (Showa Titanium; 100 m² g⁻¹).

3.3. Discussion on activity of decahedral anatase TiO₂ particles

The XRD pattern of each particle, shown in Fig. 5, indicates that *Particles A* and FP-6 primarily consist of an anatase crystal-phase.

By comparing the SEM image of *Particles A* (with a 70 nm mean primary particle size) shown in Fig. 2 and that of FP-6 (with a 15 nm mean primary particle size) provided in Fig. 6, the difference in specific surface areas between these 2 types of particles are visually understandable. *Particles A* have a higher activity than those of active commercial titania products, even though it have a crystal-phase comparable to those of the latter but noticeably smaller specific surface area than those of the latter. Those results suggest that decahedral TiO₂ particles have high potential as a material for photocatalysts.

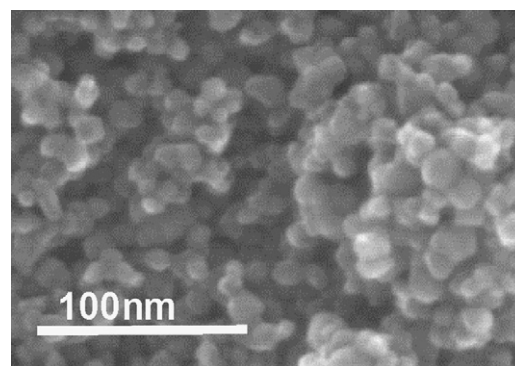


Fig. 6. SEM image of FP-6 (Showa Titanium; ca 15-nm primary particle size and 100 m² g⁻¹ specific surface area).

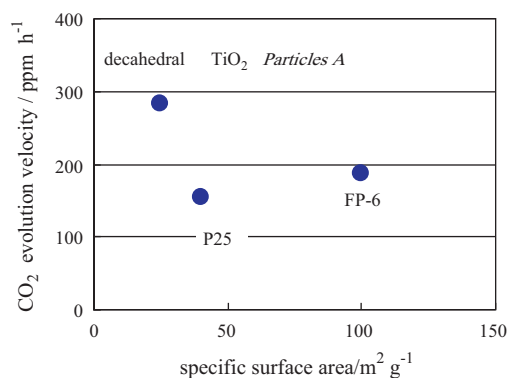


Fig. 7. Relationship between specific surface area and photocatalytic activity for mineralization of acetaldehyde in air.

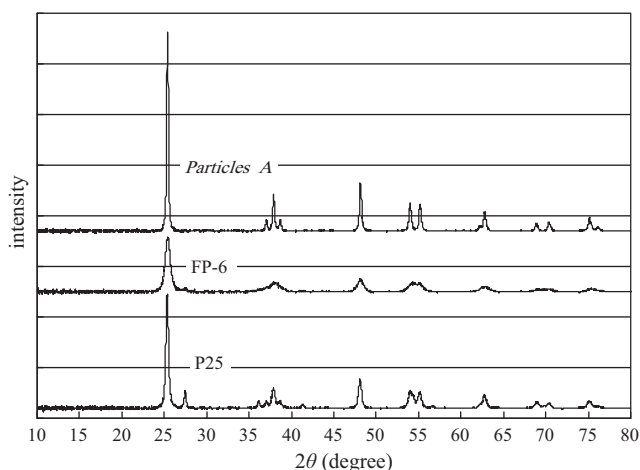


Fig. 5. XRD patterns of titania samples. Baselines were shifted for clarity.

This suggestion can be deduced also from the relationship between specific surface area of particles and their acetaldehyde decomposition activity in a gas-phase, as shown in Fig. 7.

4. Conclusions

Highly active decahedral anatase titania particles were fabricated with high reproducibility and efficiency through a gas-phase reaction process with improved heating by an infrared furnace that allowed precise control of heating temperature, residence time and other conditions.

In assessments in a liquid-phase and a gas-phase, the decahedral anatase titania particles that were prepared with this improved apparatus were found to have high activity. Since decahedral particles with 70-nm primary particle size were found to have higher activity than those of FP-6 with 15 nm primary particle size, it sug-

gests that decahedral particles have high potential as a material for photocatalysts. After this study, we have started to establish techniques for mass production of the decahedral anatase titania particles.

Acknowledgements

This study was partly supported by the “Project to Create Photocatalyst Industry for Recycling-Oriented Society” supported by the New Energy and Industrial Technology Development Organization (NEDO).

References

- [1] F. Amano, O.O. Prieto-Mahaney, Y. Terada, T. Yasumoto, T. Shibayama, B. Ohtani, *Chem. Mater.* 21 (2009) 2601.
- [2] B. Ohtani, F. Amano, T. Yasumoto, O.O. Prieto-Mahaney, S. Uchida, T. Shibayama, Y. Terada, *Top. Catal.* 53 (2010) 455.
- [3] H.G. Yang, C.H. Sun, S.Z. Qiao, J. Zou, G. Liu, S.S. Smith, H.M. Cheng, G.Q. Lu, *Nature* 453 (2008) 638.
- [4] N. Sugishita, Y. Kuroda, B. Ohtani, Abstracts for The 15th Symposium “Recent Developments on Photocatalysis”, December 2, 2008, Kanagawa, 2008, pp. 64–65.
- [5] O.O. Prieto-Mahaney, N. Murakami, R. Abe, B. Ohtani, *Chem. Lett.* 38 (2009) 238.