Pressure Effect on Low-Temperature TiO\textsubscript{2} Synthesis

J. Ida, T. Honma, S. Hayashi, K. Nakajima, E. Wada, A. Shimizu
Dept. of Environmental Engineering for Symbiosis, Soka Univ.1-326, Tangi-cho, Hachioji, Tokyo, 192-8577, Japan
ida@soka.ac.jp

Abstract. In this study, the effect of wide range of pressure (0.1~100 MPa) on low temperature synthesis of crystalline TiO\textsubscript{2} was investigated. Three different synthesis methods using acid catalyst, base catalyst and no catalyst were tried under three different pressure conditions such as atmospheric pressure, hydrothermal condition (about 0.27 MPa) and high pressure (10~100 MPa) at various temperature conditions (45~130 ºC). The results showed that under atmospheric pressure, nanocrystalline anatase or rutile phase TiO\textsubscript{2} particles were obtained under the temperature below 100 ºC for all the synthesis methods. Hydrothermal condition resulted in higher crystallinity anatase or rutile TiO\textsubscript{2} depending on the methods, however, slight reduction of specific surface area was observed. Applying higher pressure up to 100 MPa for the method using acid catalyst did not affect the resulting crystallite structure, however, slight decrease of crystallite size was observed with the increase of pressure.

1. Introduction
Titanium dioxide, TiO\textsubscript{2} has been attracted considerable interest because of its versatile applicability such as photoconductors, sensors and especially as photocatalysts. In the conventional synthesis methods, amorphous TiO\textsubscript{2} is prepared first and then high temperature treatment is applied to obtain desired crystalline structure. In these processes, however, although high crystallinity is achieved, specific surface area becomes lower due to sintering effect at high temperature. Since it is considered that high crystallinity and high specific surface area are the two important properties to obtain high photocatalytic activity TiO\textsubscript{2}, the reduction of specific surface area is undesirable. In order to prevent surface area reduction during heat treatment, direct synthesis of crystalline TiO\textsubscript{2} at low temperature without requiring subsequent sintering procedure was developed recently. Various procedures have been reported including sol-gel method, hydrothermal method and solvothermal method, etc., and the effect of solvents, catalyst (acid or base), synthesis temperature, ramping rate, aging time and so on were investigated in their report. However, the effect of wide range of pressure during synthesis process has not examined and reported so far. Therefore, in this study, the effect of wide range of pressure on low temperature synthesis of crystalline TiO\textsubscript{2} was investigated.

2. Experimental
In the experiment, for three different synthesis methods using acid catalyst[1], base catalyst[2] and no catalyst[3], three different pressure conditions such as atmospheric pressure, hydrothermal condition (about 0.27 MPa) and high pressure (10~100 MPa) were applied under various temperature conditions.
2.1. Synthesis method

2.1.1. Synthesis method using acid catalyst. The synthesis method using acid catalyst reported by Gopal et al. [1] was modified and used. First, 10 ml of 5.0 M nitric acid, 72 ml of ultra pure water, and 5 ml of 2-propanol were mixed at room temperature, and then 2.96 ml of TTIP (Kanto Chemical) was added into the solution slowly. After agitated ultrasonically for about 10 min at 30 W, reaction was carried out for 24 h at 45 ºC or 90 ºC under atmospheric pressure. Although white precipitates were formed immediately when the TTIP was added to the solution, the suspension became clear and transparent after ultrasonic agitation.

By using the same starting solution, hydrothermal synthesis was tried as follows; after the same starting solution was mixed and agitated ultrasonically, the solution was transferred to an autoclave and reacted at 130 ºC for 24 h. The pressure inside the autoclave was about 0.27 MPa. In addition, to apply much higher pressure, a high pressure system shown in Fig. 1 was used. The starting solution was prepared as mentioned above, and transferred to a high pressure tube (container) after ultrasonic agitation. Then the reaction was proceeded at 45 ºC under 10 ~ 100 MPa for 24 h. It should be noted that because of the system restriction, the maximum reaction temperature for high pressure experiments (above 10 MPa) was 45 ºC.

2.1.2. Synthesis method using base catalyst. The synthesis method using base catalyst reported by Jiu et al. was modified and used. Although the original method was using surfactant of cetyltrimethylammonium bromide (CTAB), we did not use it, since it was added to change the morphology of the TiO₂ into rod like structure. First, 0.25 M of ethylenediamine (EDA) 0.1 ml and 0.25 M of TTIP 6 ml were added to 80 ml of ultra pure water, and mixed at room temperature. After agitated ultrasonically for about 10 min at 30 W, reaction was carried out for 24 h at 45 ºC or 90 ºC under atmospheric pressure. Similar to the synthesis experiment using acid catalyst, the hydrothermal condition (0.27 MPa, 30 ºC) and high pressure conditions (10 MPa at 45 ºC) were applied to the same starting solution in the case of using base catalyst.

2.1.3. Synthesis method using no catalyst. In this method, TiO₂ was synthesized by modifying the procedure reported by Zeng et al [3], in which only TTIP and water were used without using any catalyst or other additional reagents. In the experiment, 0.01 mol of TTIP was added to 100 ml of ultra pure water and reacted for 24 h at 45 ºC or 90 ºC under atmospheric pressure. Similar to the synthesis experiment using acid or base catalyst, the hydrothermal condition (0.27 MPa, 30 ºC) and high pressure conditions (10 MPa at 45 ºC) were applied to the same starting solution in the case of using no catalyst. For all the synthesis methods, the resulting white precipitates were recovered by centrifugation at 5000 rpm for 5 min. after the reaction was finished. In table 1, all the synthesis conditions were summarized.

![Figure 1. Schematic diagram of the hi pressure system used for TiO₂ synthesis](image-url)
Table 1 Synthesis conditions and characteristics of the obtained TiO₂

| No. | catalyst | Temp. °C | Pressure Mpa | BET surface area m²/g | Specific diameter nm | Crystallite size nm |
|-----|----------|----------|-------------|-----------------------|---------------------|---------------------|
| 1   |          | 45       | 0.1         | 111                   | 13.9                | 9.3                 |
| 2   | HNO₃     | 45       | 10          | -                     | -                   | 9.9                 |
| 3   |          | 45       | 15          | -                     | -                   | 7.2                 |
| 4   |          | 45       | 100         | -                     | -                   | 5.7                 |
| 5   |          | 90       | 0.1         | 282                   | 5.5                 | 5.1                 |
| 6   |          | 130      | 0.27        | 66                    | 23.3                | 12.5                |
| 7   | EDA      | 45       | 0.1         | 447                   | 3.4                 | -                   |
| 8   |          | 45       | 10          | 525                   | 2.9                 | -                   |
| 9   |          | 90       | 0.1         | 366                   | 2.4                 | 1.4                 |
| 10  |          | 130      | 0.27        | 53                    | 29                  | 16.6                |
| 11  |          | 45       | 0.1         | 291                   | 5.3                 | 4.3                 |
| 12  | No catalyst | 45      | 10          | -                     | -                   | -                   |
| 13  |          | 90       | 0.1         | 221                   | 7                   | 5.5                 |
| 14  |          | 130      | 0.27        | 118                   | 13.1                | 6.7                 |

2.2. Characterization

The crystalline structure of all the prepared samples was characterized by X-ray diffraction (XRD) (Rigaku RINT 2000). Crystallite size of the samples was estimated using Scherrer’s equation and the half-width of the diffraction peak of the anatase TiO₂ (101) plane:

\[ D = \frac{0.9\lambda}{\beta\cos\theta} \]

where D is the average crystallite size, λ is the X-ray wavelength employed, θ is the diffraction angle of the (101) peak, and β is defined as the half-width after subtracting for the instrumental broadening. Specific BET surface area measurements were carried out using a Micromeritics ASAP 2000. Prior to the surface area measurement, the samples were dried at 200 °C for 2 h under N₂. Particle size of the samples was calculated based on the measured specific BET surface area and called as BET diameter.

3. Results and discussion

Figures 2~4 show the X-ray diffraction patterns of the TiO₂ samples synthesized under atmospheric pressure conditions and hydrothermal condition using acid catalyst (HNO₃), base catalyst (EDA) and no catalyst, respectively. The results showed that in the case of using acid catalyst (Fig.2), rutile phase TiO₂ was obtained at 45 °C, 0.1 MPa and also under hydrothermal condition (130 °C, 0.27 MPa). However, even under the same 0.1 MPa, anatase phase TiO₂ was obtained when the temperature was 90 °C. In the case of using acid catalyst under atmospheric pressure, the mechanism can be explained as follows: the white precipitates obtained after all the reagents were mixed together were considered to be amorphous phase according to Aruna et al. [4]. Then, after ultrasonication, the precipitates were dissolved as [TiO₆] octahedra by protonation in the case of using acid. It is known that both rutile and anatase can grow from [TiO₆] octahedra, and the phase formation proceeds through the structural rearrangement of the octahedra, i.e., arrangement of octahedral by face-sharing results in anatase and that by edge-sharing results in rutile phase.
Gopal et al. reported that ramping rate and synthesis temperature during the rearrangement determine the crystalline phase and higher ramping rate and/or synthesis temperature result in anatase since rutile is thermodynamically stable phase and anatase is metastable phase. This agrees well to our experimental results obtained under atmospheric pressure at 45 and 90 ºC. However, the reason why rutile phase was obtained even at higher temperature under hydrothermal condition is still not known.

In the case of base catalyst (Fig.3), crystalline TiO2 was not obtained under atmospheric condition. However, highly crystalline anatase phase TiO2 was obtained under hydrothermal condition. Figure 4 indicates that anatase phase TiO2 can be obtained only from water and TTIP without using catalyst and also even at very low temperature of 45 ºC under 0.1 MPa. The result also showed that the crystallinity and crystallite size seemed to increase when the temperature and pressure increased. However, in this method, small amount of brookite phase was also observed for all the obtained samples. In table 1, specific surface areas and crystallite sizes estimated using Scherrer’s equation for all the samples were summarized. The results demonstrate that regardless of the used methods, the samples prepared at 45 ºC and 90 ºC have a large specific surface area of more than 100 m²/g, which is probably due to low synthesis temperature. BET diameters which was calculated based on the surface area indicates the particle sizes were in the range from several to ten nm. Crystallite sizes of the samples were also in the same range and both values agreed well in each sample. This indicates that the obtained TiO2 exists in single nano crystal. On the other hand, the specific surface area of the samples decreased because of higher reaction temperature of 130 ºC in the case of hydrothermal condition at the expense of higher crystallinity.

Figure 5 shows the XRD patterns of the sample prepared under relatively high pressure of 10 MPa (45 ºC) using three different synthesis methods. Broad peak indicating amorphous is attributed to sample holder because of small sample amount in the case of high pressure experiments, which is due to low reaction yield at low temperature and small reactor volume of the equipment. In this case, only the method using acid catalyst resulted in crystalline TiO2 (rutile) probably due to too low reaction temperature of 45 ºC for other methods as shown in the results at 45 ºC, 0.1 MPa. Therefore, to examine the effect of pressure on TiO2 synthesis in more detail, much higher pressures of 15 and 100 MPa were applied for the method using acid catalyst at the reaction temperature of 45 ºC. The result was shown in Fig.6. The result showed that even pressure changed 0.1~100 MPa during synthesis, crystallite structure of the obtained TiO2 was not affected and was rutile phase. However, since the crystallite size decreased slightly when the pressure increased, there may be an effect of crystalline growth depression. In table 2, polymorphs of the obtained TiO2 under all the conditions were summarized. Applying high pressure during TiO2 synthesis at higher temperature of 90 to 130 ºC would be interesting. However, it requires the improvement of the high pressure equipment. Therefore, it will be future work. Also to understand the mechanism of nucleation and crystallization process in more detail, analysis of morphology and size distribution of all the obtained samples by TEM is required.

4. Conclusion
In this study, to examine the effect of wide range of pressure on the low temperature synthesis of crystalline TiO2, three different pressure conditions were applied for the three different TiO2 synthesis methods using acid or base catalyst or using nocatalyst. The results can be summarized as follows;

1. Under atmospheric pressure, nano sized anatase phase TiO2 particles were obtained in the acid catalyst case at 90 ºC and no catalyst case at 45 and 90 ºC. However, in the no catalyst case, small amount of brookite phase was also observed. Nano sized rutile phase TiO2 particles were also obtained in the acid catalyst case at 45 ºC. However, crystalline TiO2 was not obtained in the case of base catalyst under atmospheric condition.
(2) Under hydrothermal condition, rutile TiO$_2$ was obtained in the acid catalyst case and anatase TiO$_2$ was obtained in the base catalyst and no catalyst case. In spite of attaining high crystallinity under the hydrothermal condition, the reduction of specific surface area was also observed.

(3) In the case of applying high pressure of 10 MPa, only the method using acid catalyst resulted in crystalline TiO$_2$ (rutile) probably due to too low reaction temperature as 45 °C (because of equipment restriction).

(4) Applying higher pressure up to 100 MPa for the method using acid catalyst did not affect the resulting crystallite structure, however, slight decrease of crystallite size was observed when the applied pressure increased.

References
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Table 2 Effects of synthesis conditions on polymorphs of obtained TiO$_2$

| Catalyst | Atmospheric pressure (0.1 MPa) | Hydrothermal (0.27 MPa) | High pressure (10 MPa) (15 MPa) (100 MPa) |
|----------|--------------------------------|------------------------|------------------------------------------|
|          | 45°C  | 90°C  | 130°C | R       | A + r   | R + a  | R    | R    | 45°C   |
| HNO$_3$  |       |       |       | R      | A + r   | R + a  | R    | R    | 45°C   |
| EDA      | amorphous | A    | A     | amorphous | -       | -      |      |      |
| no catalyst | A + b | A + b | A + b | amorphous | -       | -      |      |      |

A: anatase, R: rutile, b: brookite. Capital letter: predominant polymorph, small letter: secondary phase

Figure 2. XRD patterns of TiO$_2$ nanoparticles synthesized with HNO$_3$: (a) at 45°C, 0.1 MPa, (b) at 90°C, 0.1 MPa, (c) at 130°C, 0.27 MPa.

Figure 3. XRD patterns of TiO$_2$ nanoparticles synthesized with EDA: (a) at 45°C, 0.1 MPa, (b) at 90°C, 0.1 MPa, (c) at 130°C, 0.27 MPa.

Figure 4. XRD patterns of TiO$_2$ nanoparticles synthesized without catalyst: (a) at 45°C, 0.1 MPa, (b) at 90°C, 0.1 MPa, (c) at 130°C, 0.27 MPa.
**Figure 5.** XRD patterns of TiO$_2$ nanoparticles synthesized at 45°C under 10 MPa: (a) with HNO$_3$ (b) with EDA, (c) without catalyst.

**Figure 6.** XRD patterns of TiO$_2$ nanoparticles synthesized at 45°C with HNO$_3$: (a) under 0.1 MPa (b) under 15 MPa, (c) under 100 MPa.