

# ELABORATION OF PHOTOACTIVE TiO<sub>2</sub> PARTICLES BY CVD: EFFECT OF OPERATIONAL PARAMETERS

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## ABSTRACT

*The TiO<sub>2</sub> photocatalyst is used for various purposes such as a cleanup of polluted air, antifouling, sterilization, deodorization, and so on. The purpose of this study is to synthesize the TiO<sub>2</sub> photocatalyst fines in the gas phase. We used TTIP (titanium tetraisopropoxide) as the precursor because gas phase processes using chlorine compounds cause serious operational problems such as corrosion. As TTIP has close boiling and thermal decomposition temperatures, liquid TTIP was directly (without vaporization) introduced through a water-cooled tube, while, H<sub>2</sub>O vaporized in a separate vaporizer was introduced from the lower part of the reactor. At the reactor temperature of 1000°C, the more Ar flow rate at the TTIP side increased without changing the flow rate of TTIP keeping the total flow rates of TTIP side and H<sub>2</sub>O side almost similar, the smaller particle size of TiO<sub>2</sub> was elaborated, the less the carbon content became, and the higher photocatalytic activity was observed. Then, the effect of reactor temperature between 800°C and 1100°C was examined under the optimum condition of flow rate. At the reactor temperature of 1000°C, small particle size of TiO<sub>2</sub> with the highest anatase content was elaborated, which showed the highest photocatalytic activity.*

**Keywords:** TiO<sub>2</sub>; photocatalyst; fine powder gas phase synthesis; TTIP.

## 1. INTRODUCTION

In recent years, photocatalysts have been used in various applications especially as self-cleaning materials. The main applications of photocatalyst are such as coating materials and architectural paints including the photocatalytic TiO<sub>2</sub> fines. The TiO<sub>2</sub> photocatalyst has been used for various purposes such as cleanup of polluted air, antifouling, sterilization, deodorization, and so on. When the sunlight energy is absorbed, the photocatalyst shows a strong oxidizing power and a super-hydrophilicity. The photocatalyst with both characteristics is a self-cleaning material. And, a poisonous organic material not broken by the other methods can be decomposed by the use of its strong oxidizing power (Fujishima & Segawa, 2005). However, because the wavelength that can be absorbed is limited to shorter wavelength than visible light, yield becomes several percent. Therefore, to improve the photocatalytic activity, the synthesis aiming at the TiO<sub>2</sub> with a high specific surface area and a few defects are performed. In general, gas phase synthesis with chlorine and liquid phase synthesis with

sulfuric acid are well known. The advantage of the liquid phase synthesis is the easiness to control particle size under various synthesis conditions without causing agglutination. The advantage of the gas phase synthesis is the possibility to obtain fine particles with high purity products (Fujishima & Segawa, 2005; Nosaka & Nosaka, 2004; Materials Science Society of Japan, 1993). In the case of sulfuric acid method, ilmenite is dissolved in concentrated sulfuric acid to remove iron impurities. Titanium hydroxide formed by hydrolysis, after being neutralized by washing, was dried and calcinated to obtain titanium dioxide. In the case of chlorine method, rutile ore is reacted with carbon and chlorine gas at 1000°C to form gaseous titanium tetrachloride. Then the produced gaseous titanium tetrachloride is reacted with oxygen to produce TiO<sub>2</sub> particle. P25 (the Evonik Degussa Japan Co., Ltd.) synthesized by chlorine method is well known to have high photocatalytic activity among the used photocatalysts commercially. However, this method generates harmful chlorine or the hydrochloric acid as a by-product material.

The authors focused on gas phase synthesis without using chlorine which often causes serious material selection and environmental problems. There are only a few reports on TiO<sub>2</sub> photocatalyst via gas phase synthesis, while most of them are from chlorine compounds (Jang, Kim & Kim, 2001). Besides, there are few reports of gas phase synthesis using TTIP (titanium tetraisopropoxide) as chlorine free raw materials, while liquid phase synthesis using TTIP has been reported (Qourzal, Assabbane & Ait-Ichou, 2004). Thus so far, we successfully obtained the know-how to control the particle size of silica fine particles from H<sub>2</sub>O and tetramethoxysilane by hydrolysis in the gas phase (Kojima, Tachi, Sakai, Kato & Satokawa, 2008). We tried to apply similar method to hydrolysis of H<sub>2</sub>O and TTIP in the gas phase. The gas phase synthesis by using TTIP is very difficult because the boiling point and the pyrolysis temperature of TTIP are very close to each other. Therefore, the papers regarding the gas phase synthesis of the TiO<sub>2</sub> particle by using TTIP are very limited (Chan, Porter, Li, Guo & Chan, 1999). Regardless of the above problem, we reported that the TiO<sub>2</sub> particles by the gas phase synthesis had photocatalytic activity which is possibly controlled by various operational parameters (Fukuhara, Yamakawa, Sakai, Yamasaki, Satokawa & Kojima, 2010). In this study, the same method as previously reported was partly modified to obtain finer particles with higher photocatalytic activity. As a result, we finally got the fine TiO<sub>2</sub> particles with high photocatalytic activity comparable to that of P25 (originally supplied by Evonik Degussa Japan Co., Ltd.).

## 2. METHODOLOGY

### 2.1 Experimental Flowchart and Apparatus

The present experimental flow sheet is shown in Figure 1. TTIP and H<sub>2</sub>O of the raw materials were introduced into the reactor by using a syringe pump with Ar as carrier gas. TTIP was introduced from the top of the reactor in liquid form by water cooling. The liquid TTIP was directly introduced in order to prevent the plugging of the supply pipe with the fines by pyrolysis of TTIP. On the other hand, H<sub>2</sub>O vaporized in a separate vaporizer with Ar as carrier gas was introduced from the lower part of the reactor. In such way as above, the cold liquid TTIP is mixed with heated steam; hence TTIP is vaporized and heated by the sensitive heat of H<sub>2</sub>O in the reactor. After both of TTIP and H<sub>2</sub>O were reacted together in the reactor, the synthesized TiO<sub>2</sub> was collected in a cylindrical glass filter mounted under the reactor. The reacted gas passed through a vessel filled with ethanol and then was exhausted.

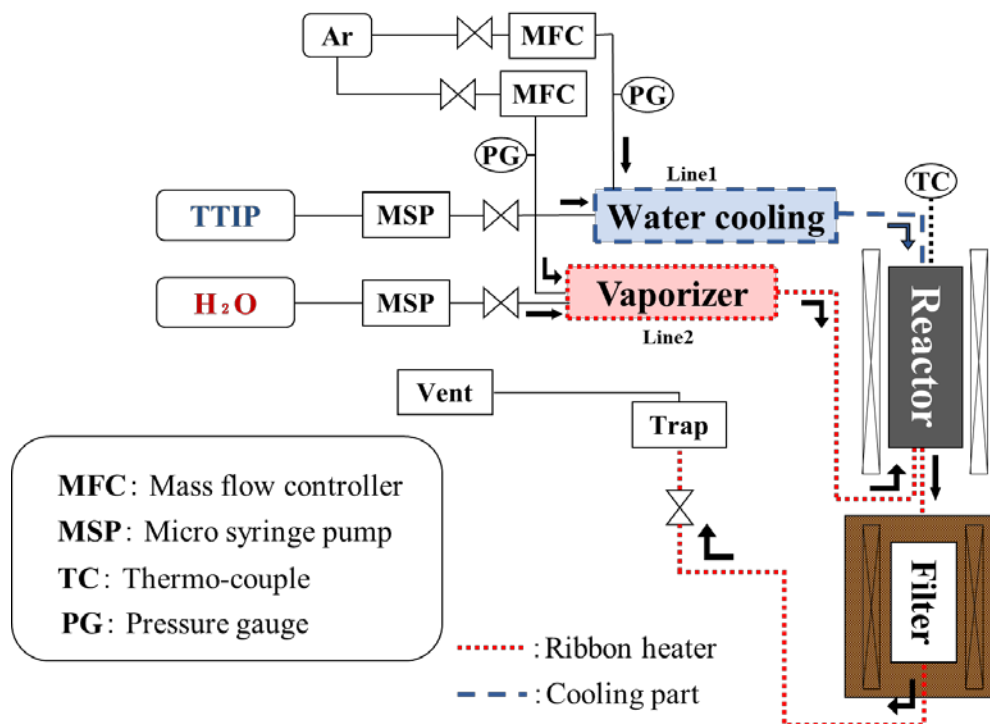


Figure 1: Experimental flow chart.

The detail structure of the reactor and temperature profile are shown in Figure 2. The reaction tube made of stainless steel has dual tubular structure, having outside diameter of 16 mm, inside diameter of 14 mm, and length of 430 mm, including a water-cooled tube with outside diameter of 10 mm to send liquid TTIP at the top of the reactor. The supply pipe of H<sub>2</sub>O was inserted at the bottom of the reactor. Thermocouple was mounted at the hottest part of the reaction tube.

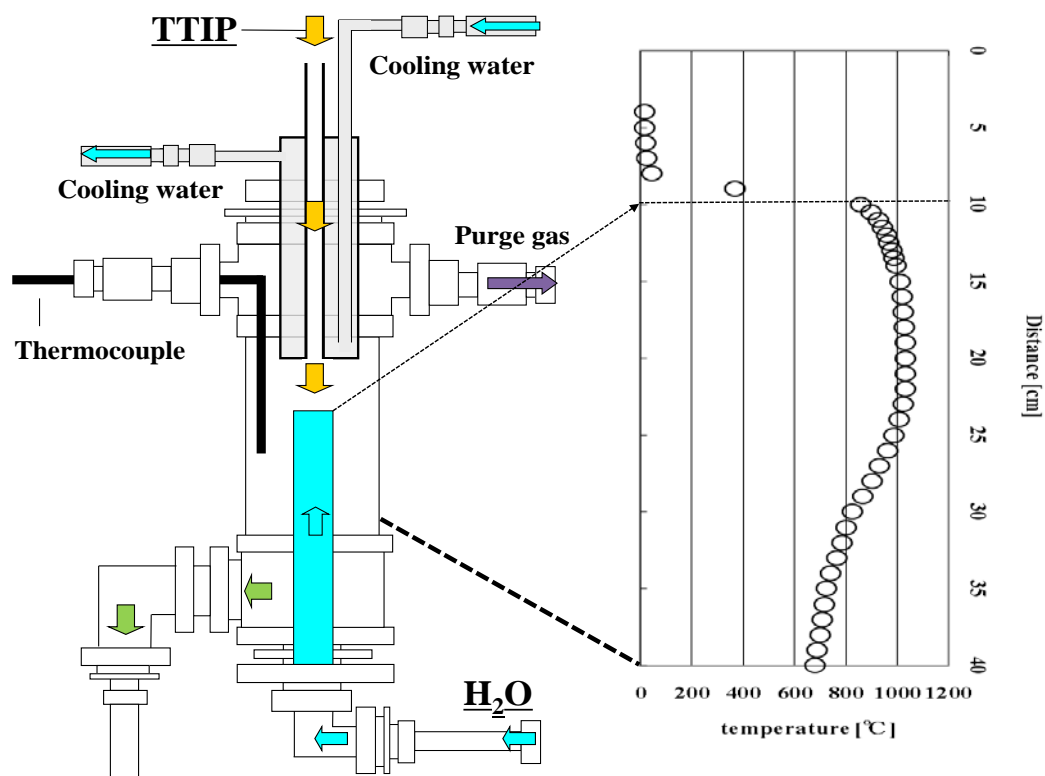


Figure 2: Reactor structure and temperature profile.

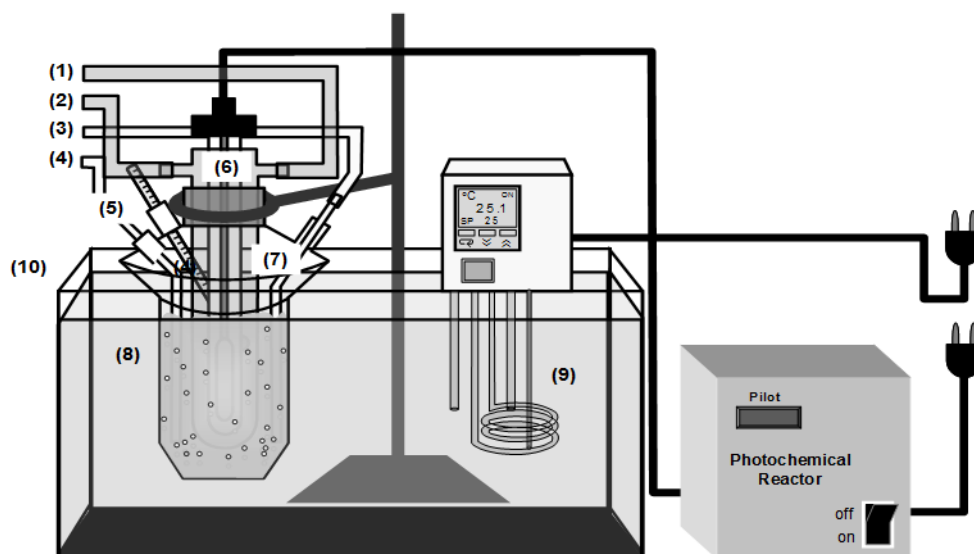
It has already demonstrated that it is possible to synthesize the TiO<sub>2</sub> with comparable activity to P25 in the previous research results by the present authors (Fukuhara et al., 2010), at the reaction temperature of 1000°C. At the temperature around 1000°C in the reactor, the synthesized TiO<sub>2</sub> contained the most amount of anatase phases, whereby its particle size was relatively small, and its photocatalytic activity was the highest. Hence in the present study, the reaction temperatures of the following experiments were kept at 1000°C.

However in the previous study (Fukuhara et al., 2010) the outlet position of H<sub>2</sub>O was not easy to be fixed and it changed slightly in each experiment because the H<sub>2</sub>O supply pipe was easily bent in the reactor. Therefore, it was difficult to confirm the reproducibility, which also suggests the importance of relative position between steam and TTIP outlet ports. In the present study the water vapor inlet tube with outlet diameter of 6 mm was used, which enables fixing the relative position between steam and TTIP outlet ports. Thus the synthesis of the TiO<sub>2</sub> with high photocatalytic activity was enabled by the structure with reproducibility. Furthermore, in the present study, we investigated the optimum condition of the photocatalyst synthesis to give the higher activity by varying operational parameters.

## 2.2 Analyses and Evaluation

The particle size was measured with a laser diffraction particle size analyzer (SALD-2100). The carbon content was measured with a CN analyzer (SUMIGRAPH NC-22A). The crystal phase rate (anatase rate) was calculated from the relative peak height from an X-Ray diffractometer (MINI-Flex). Their photocatalytic activity was evaluated and compared with that of P25 (supplied by Nippon Aerosil Co., Ltd., originally supplied by Evonik Degussa

Japan Co., Ltd.). The photocatalytic activity evaluation examination was carried out by the decomposition rate of 25 ppm methyl orange (MO) using the device shown in Figure 3.



(1) water inlet, (2) water outlet, (3,4) air inlet, (5) thermometer, (6) UV lamp, (7) water jacket, (8) reaction vessel, (9) heater, (10) water bath

Figure 3: Schematic diagram of the UV photochemical reactor.

The absorbance at 464 nm was measured with the UV-Visible Spectrophotometer (Shimadzu UV-1700). The value of  $\ln(\text{Abs}/\text{Abs}_0)$  was plotted against UV irradiation time, and the reaction rate constant  $k$  was calculated by the slope of plots.

### 3. RESULTS AND DISCUSSION

#### 3.1 Influence of Difference in $\text{H}_2\text{O}$ Flow Rate

Firstly, Table 1 shows the results when we changed the flow rate of  $\text{H}_2\text{O}$ .  $k$  is the first order reaction rate constant. The higher  $k$  means the higher photocatalytic activity. In order to get higher  $k$ , smaller particle size, more anatase rate and less carbon content are desirable. As a result, the more the  $\text{H}_2\text{O}$  flow rate increased, the less carbon content became and the smaller particle size of  $\text{TiO}_2$  was elaborated. However, the less the  $\text{H}_2\text{O}$  flow rate became, the more anatase rate increased, but when the  $\text{H}_2\text{O}$  flow rate was too small, anatase rate decreased. The highest photocatalytic activity was observed under the conditions of  $\text{HH}_2\text{O}_{100}$  and  $\text{HH}_2\text{O}_{150}$ .

Table 1: Influence of difference in H<sub>2</sub>O flow rate.

Run		HH <sub>2</sub> O <sub>400</sub>	HH <sub>2</sub> O <sub>250</sub>	HH <sub>2</sub> O <sub>200</sub>	HH <sub>2</sub> O <sub>150</sub>	HH <sub>2</sub> O <sub>100</sub>	HH <sub>2</sub> O <sub>50</sub>
Total flow rate [mL/min]		850	700	650	600	550	500
TTIP side [mL/min]	TTIP	5	5	5	5	5	5
	Ar	295	295	295	295	295	295
H <sub>2</sub> O side [mL/min]	H <sub>2</sub> O	400	250	200	150	100	50
	Ar	150	150	150	150	150	150

Run	<i>k</i> [min <sup>-1</sup> ]	particle size [nm]	carbon content[%]	anatase rate [%]
HH <sub>2</sub> O <sub>400</sub>	0.030	38.2	0.34	79.2
HH <sub>2</sub> O <sub>250</sub>	0.038	50.1	0.79	77
HH <sub>2</sub> O <sub>200</sub>	0.043	43.5	0.52	81.7
HH <sub>2</sub> O <sub>150</sub>	0.044	34.9	0.71	90.4
HH <sub>2</sub> O <sub>100</sub>	0.035	43.9	0.39	86.8
HH <sub>2</sub> O <sub>50</sub>	0.0029	70	11.3	70.1

### 3.2 Influence of Difference in Ar Flow Rate of the TTIP Side

Table 2: Influence of difference in Ar flow rate of the TTIP side.

Run		HH <sub>2</sub> O <sub>400</sub>	HH <sub>2</sub> O <sub>250</sub>	HH <sub>2</sub> O <sub>200</sub>	HH <sub>2</sub> O <sub>150</sub>	HH <sub>2</sub> O <sub>100</sub>	HH <sub>2</sub> O <sub>50</sub>
Total flow rate [mL/min]		850	700	650	600	550	500
TTIP side [mL/min]	TTIP	5	5	5	5	5	5
	Ar	295	295	295	295	295	295
H <sub>2</sub> O side [mL/min]	H <sub>2</sub> O	400	250	200	150	100	50
	Ar	150	150	150	150	150	150

Run	<i>k</i> [min <sup>-1</sup> ]	particle size [nm]	carbon content[%]	anatase rate [%]
HH <sub>2</sub> O <sub>400</sub>	0.030	38.2	0.34	79.2
HH <sub>2</sub> O <sub>250</sub>	0.038	50.1	0.79	77
HH <sub>2</sub> O <sub>200</sub>	0.043	43.5	0.52	81.7
HH <sub>2</sub> O <sub>150</sub>	0.044	34.9	0.71	90.4
HH <sub>2</sub> O <sub>100</sub>	0.035	43.9	0.39	86.8
HH <sub>2</sub> O <sub>50</sub>	0.0029	70	11.3	70.1

Secondly, Table 2 shows the results when we changed the flow rate of Ar at the TTIP side. As a result, the less the Ar flow rate of the TTIP side became, the less carbon content became. However, when the Ar flow rate of the TTIP side was too small, the synthesis failed because of plugging by fine deposit. The highest photocatalytic activity was observed under the conditions of TAr<sub>295</sub> and TAr<sub>395</sub>.

### 3.2 Influence of Difference in Ar Flow Rate of the H<sub>2</sub>O Side

Table 3: Influence of difference in Ar flow rate of the H<sub>2</sub>O side.

Run		HAr <sub>400</sub>	HAr <sub>350</sub>	HAr <sub>250</sub>	HAr <sub>150</sub>	HAr <sub>100</sub>	HAr <sub>50</sub>
Total flow rate [mL/min]		850	800	700	600	550	500
TTIP side [mL/min]	TTIP	5	5	5	5	5	5
	Ar	295	295	295	295	295	295
H <sub>2</sub> O side [mL/min]	H <sub>2</sub> O	150	150	150	150	150	150
	Ar	<b>400</b>	<b>350</b>	<b>250</b>	<b>150</b>	<b>100</b>	<b>50</b>

Run	$k$ [min <sup>-1</sup> ]	particle size [nm]	carbon content[%]	anatase rate [%]
HAr <sub>400</sub>	0.0092	45.5	3.46	75.1
HAr <sub>350</sub>	0.042	38.3	0.58	72
HAr <sub>250</sub>	0.043	29.8	0.31	86
HAr <sub>150</sub>	0.044	34.9	0.71	90.4
HAr <sub>100</sub>	0.044	33.9	0.36	80.2
HAr <sub>50</sub>	0.0010	76.2	15.3	75.2

Thirdly, Table 3 shows the results when we changed flow rate of Ar at the H<sub>2</sub>O side. When the flow rate of Ar at the H<sub>2</sub>O side was too large or too small, carbon content in the powder increased. When Ar flow rate of the H<sub>2</sub>O side is too small, it is thought that TTIP pyrolysis before hydrolysis causes the formation of larger particles and higher carbon content. On the other hand, when Ar flow rate of the H<sub>2</sub>O side is too large, it is thought that poor supply of the heat by less H<sub>2</sub>O concentration causes delay of reaction leading to increased particle size with agglomeration. It is also pointed out that the less H<sub>2</sub>O concentration also causes the prior carbonization which increased carbon contents in the produced powder. It was found that the sufficient supply of H<sub>2</sub>O and total flow rate comparable to the TTIP side are desirable.

### 3.3 Influence of Difference in Total Flow Rate

Next, Table 4 shows the results when we changed total flow rate keeping TTIP flow rate constant. As a result, the more total flow rate increased, the smaller particle size of TiO<sub>2</sub> was elaborated. The more Ar flow rate at the TTIP side increased without changing flow rate of TTIP keeping the total flow rates of TTIP side and H<sub>2</sub>O side almost same, the smaller particle size of TiO<sub>2</sub> was elaborated, the less the carbon content became, and the higher photocatalytic activity was observed.



Table 4: Influence of difference in total flow rate and comparison with P25.

Run		TF <sub>2400</sub>	TF <sub>1800</sub>	TF <sub>1200</sub>	TF <sub>600</sub>	TF <sub>300</sub>
Total flow rate [mL/min]		2400	1800	1200	600	300
TTIP side [mL/min]	TTIP	5	5	5	5	5
	Ar	1195	895	595	295	145
H <sub>2</sub> O side [mL/min]	H <sub>2</sub> O	600	450	300	150	75
	Ar	600	450	300	150	75
Run		<i>k</i> [min <sup>-1</sup> ]	particle size [nm]	carbon content[%]	anatase rate [%]	
TF <sub>2400</sub>		0.068	21	0.50	54.8	
TF <sub>1800</sub>		0.080	24.9	0.46	84.8	
TF <sub>1200</sub>		0.056	27.6	0.43	75.5	
TF <sub>600</sub>		0.044	34.9	0.71	90.4	
TF <sub>300</sub>		0.037	49.3	4.64	84.7	
P25		0.081	25.9	0.04	92.8	

### 3.4 Influence of Difference in reaction temperature

Table 5: Influence of difference in reaction temperature and comparison with P25.

Run		T <sub>1100</sub>	T <sub>1050</sub>	T <sub>1000</sub>	T <sub>950</sub>	T <sub>900</sub>	T <sub>800</sub>
Temperature [°C]		1100	1050	1000	950	900	800
TTIP side [mL/min]	TTIP	5	5	5	5	5	5
	Ar	895	895	895	895	895	895
H <sub>2</sub> O side [mL/min]	H <sub>2</sub> O	450	450	450	450	450	450
	Ar	450	450	450	450	450	450
Run		<i>k</i> [min <sup>-1</sup> ]	particle size [nm]	carbon content[%]	anatase rate [%]		
T <sub>1100</sub>		0.053	34.6	0.34	51.2		
T <sub>1050</sub>		0.054	32.3	0.54	70.5		
T <sub>1000</sub>		0.080	24.9	0.46	84.8		
T <sub>950</sub>		0.062	27.7	0.41	78.0		
T <sub>900</sub>		0.071	17.2	0.76	86.0		
T <sub>800</sub>		0.049	15.2	0.73	89.0		
P25		0.081	25.9	0.04	92.8		



Lastly, Table 5 shows the results when we changed reaction temperature. Reaction temperature changed between 800°C and 1100°C under the optimum conditions of flow rates. As a result, the more reaction temperature increased, the less carbon content became, the less anatase rate became, and the bigger particle size of TiO<sub>2</sub> was elaborated. At the reactor temperature of 1000°C, small particle size of TiO<sub>2</sub> with the highest anatase content was elaborated, which showed the highest photocatalytic activity.

### 3.5 Comparison with Reference Materials

The TiO<sub>2</sub> synthesized under the optimum conditions showed photocatalytic activity as high as that of P25.

## 4. CONCLUSION

The more Ar flow rate at the TTIP side increased without changing flow rate of TTIP keeping the total flow rates of TTIP side and H<sub>2</sub>O side almost similar, the smaller particle size of TiO<sub>2</sub> was elaborated, the less the carbon content became, and the higher photocatalytic activity was observed. At the reactor temperature of 1000°C, small particle size of TiO<sub>2</sub> with the highest anatase content was elaborated, which showed the highest photocatalytic activity. The TiO<sub>2</sub> synthesized under the optimum condition showed photocatalytic activity as high as that of P25.

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