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Characterization of a TiO_2 photocatalyst synthesized by the solvothermal method and its catalytic performance for $CHCl_3$ decomposition

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Abstract

It is considered that the solvothermal method in this study renders a reliable synthesis procedure of the TiO_2 photocatalyst having the anatase structure of nano size. Two kinds of TiO_2 photocatalysts were synthesized by using the sol–gel and solvothermal methods, and then their physical properties and catalytic performances were compared. The TiO_2 powder (Cat. 2) obtained by the solvothermal method at 300°C exhibited a pure anatase structure without any further treatment, while the TiO_2 powder (Cat. 1) prepared by the sol–gel method was transformed to the anatase structure after thermal treatment at 500°C for 3 h. Cat. 2 had higher surface area (121 m^2/g) and surface charge (+24.1 mV) than Cat. 1 (51 m^2/g, +16.4 mV). In addition, the activation energy for H_2O desorption over Cat. 2 was very high. These results show that the surface of Cat. 2 is very hydrophilic. In chloroform ($CHCl_3$) decomposition under the UV-light (254 nm, 24 W/m^2) with O_2 bubbling (500 ml/min), the catalytic performance of Cat. 2 was considerably higher than that of Cat. 1. More than 95% of the chloroform was decomposed in 2 h over Cat. 2. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: TiO_2 photocatalyst; Anatase structure; Sol–gel method; Solvothermal method; Activation energy; Chloroform decomposition

1. Introduction

By 1990s the world was assembled with tremendous sets of environment problems, and thus extensive research activities are underway on advanced chemical, biochemical, and physicochemical methods for elimination of hazardous chemical compounds from air and water [1–3]. In particular, the search for the solution to this problem has involved extensive examinations in the field of advanced oxidation processes (AOPs) [4–6]. In this field, many works have been done on the photocatalytic treatment of environmental pollutants using semiconductors [7–9]. The photocatalysis on semiconductor particles, especially titanium dioxide, has been attracting much attention because of the possible applications to elimination of pollutants in water and air. When a semiconductor of TiO_2 absorbs a photon and then was promoted to an excited state, an electron is transferred from the valence band to the conduction band where it can function as a reducing entity, leaving a hole behind in the valence band that is a strong oxidizing entity. The mechanism is simply given as follows in Scheme 1 [10].

On the other hand, in the semiconductor synthesis, the sol–gel method has been widely used and applied. However, the typical sol–gel method [11,12] involves some problems such as irregular particle size, necessity of calcination for crystallization, inclusion of impure phases, and others. Generally, it has been well known that important variables deciding the catalytic performance are the properties of a catalyst such as particle size, surface charge, surface area, degree of crystallization, crystal structure, impurities in particles, and metal species added. It is desirable that these variables could be controlled by the synthesis method itself. However, tantalizingly, the improvement for these variables has not been well established in a file of catalyst synthesis methods yet. Until now, the photoactivity has just been measured by observing the kinds and quantities of reaction products in most of studies [13–15].

In the latter half of 1990, the solvothermal treatment was introduced in field of synthesis of ceramic materials such as ZrO_2, CeO_2, and Al_2O_3 [16,17]. This method surprisingly could be employed as an alternative to calcination for promoting crystallization under mild temperatures. Very recently, this processing has been widely applied in the synthesis of zeolites and ceramic powders containing various

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$$\text{charge-carrier generation}: TiO_2 + h\nu \text{ ---> } h^+ + e^-$$

$$\text{charge-carrier trapping}: h^+ + Ti^{4+}OH \text{ ---> } \{Ti^{4+}OH\cdot\}^+ ;\ \text{oxidation}$$

$$e^- + Ti^{4+}OH \text{ ---> } \{Ti^{3+}OH\} ;\ \text{reduction}$$

$$\text{charge-carrier recombination}: e^- + \{Ti^{4+}OH\cdot\}^+ \text{ ---> } Ti^{4+}OH$$

$$h^+ + \{Ti^{3+}OH\} \text{ ---> } Ti^{4+}OH$$

$$\text{interfacial charge transfer}: \{Ti^{4+}OH\cdot\}^+ + Red \text{ ---> } Ti^{4+}OH + Red\cdot^+$$

$$e^- + Ox \text{ ---> } Ti^{4+}OH + Ox\cdot^-$$

Scheme 1. Photo-electrochemical mechanism on TiO_2 particle.

metal oxides [18,19]. The solvothermal treatment could control grain size, particle morphology, crystalline phase and surface chemistry by regulating sol composition, reaction temperature, pressure, nature of solvent, additives, and aging time [16–18]. In particular, the particles prepared by the solvothermal method were reported to have larger surface area and smaller particle size and was more stable than those by other methods such as the sol–gel method. Among the oxides reported so far, TiO_2 prepared by the solvothermal method has not, unexpectedly, appeared in the literature as far as we know.

Against this background, we attempted to synthesize TiO_2 having the anatase structure of nano size by applying the solvothermal method, and then compared its physical properties and catalytic performance with those of another TiO_2 which was synthesized by the sol–gel method.

2. Experimental

2.1. Catalyst preparation

In Fig. 1, the two preparation procedures of TiO_2 are shown. Reagents used for preparation of the gel mixture were as follows: titanium–tetraisopropoxide (99.99% TTIP, Junsei Chemical Co. Ltd., Japan) and 1,4-butanediol (Fluka Co. Ltd.) were used as the TiO_2 source and the solvent, respectively.

The first one was the typical sol–gel method, and the sample obtained was designated as Cat. 1. From the other method, another kind of TiO_2 particles was synthesized by the solvolysis of TTIP in 1,4-butanediol under the synthesis temperature of 300°C and the autogeneous pressure of 40 atm. This method was named to be the solvothermal method in this paper, and this method could be repeated reproducibly and hence reliably. TTIP mixed with the organic solvent in an autoclave was heated to 300°C with the rate of 5°C/min, and then the temperature was kept for 50 min. During this thermal treatment, TTIP was decomposed by the OH group in the organic solvent, and finally crystallization of the TiO_2 occurred. The obtained TiO_2 powders were washed with acetone repeatedly, and then dried at 100°C for 5 h. The product was designated as Cat. 2.

2.2. Characterization of catalyst

The synthesized samples were analyzed by the powder X-ray diffraction analysis (XRD) using Shimazu XD-DI with nickel filtered Cu Kα radiation (30 kV, 30 mA) and with the 2θ range from 20 to 80°. The scan speed was 10°/min and the time constant was 1 s. The diffraction angle of 25.0° was selected to discuss the crystallinity of synthesized samples.

The particle size and shape of the acquired samples were observed by a scanning electron microscope (SEM) of Hitachi–Akashi.

The activation energy for H_2O desorption was determined by using a TG-DSC equipped with a microthermo-differential and gravimetric analyzer (Shimadzu DT-40) and the Ozawa method [20]. A 20 mg of α-alumina was used as the reference sample. To keep the moisture condition in the TiO_2 particles all the same, the sample was analyzed after kept in saturated NH_4OH solution for 24 h. The detail experimental conditions were as follows: DSC range: 10 mcal/F.S.; TGA range: 10 mg/F.S.; heating rate: 5, 7, 10, and 15 K/min; and environment: in air.

The BET surface areas of the samples were measured by nitrogen gas adsorption with continuous flow method using a gas chromatography equipped with a TCD detector at the liquid nitrogen temperature. A mixed gas of nitrogen and helium was flowed as the carrier gas with model GEMINI2375 from Micromeritics. The samples were thermally treated at 300°C for 30 min before nitrogen adsorption.

The particle size distribution of the samples was obtained by dynamic light scattering (DLS) spectrophotometer of Photal Otsuka Electronics after ultrasonic wave treatment with 140 W in water for 2 min.

The zeta potential value was attained by ELS-8000SA at a 90° angle. Before measurement, the sample was treated by ultrasonic wave with 140 W in water for 1 min.

2.3. $CHCl_3$ decomposition and analysis

The decomposition of $CHCl_3$ was carried out by using a stationary closed apparatus as shown in Fig. 2. A 0.1 g of the TiO_2 photocatalyst was added into a stainless steel square reactor with the dimension of 21 cm × 15 cm × 7 cm, and the reaction mixture was 1000 ppm $CHCl_3$ in 600 ml of

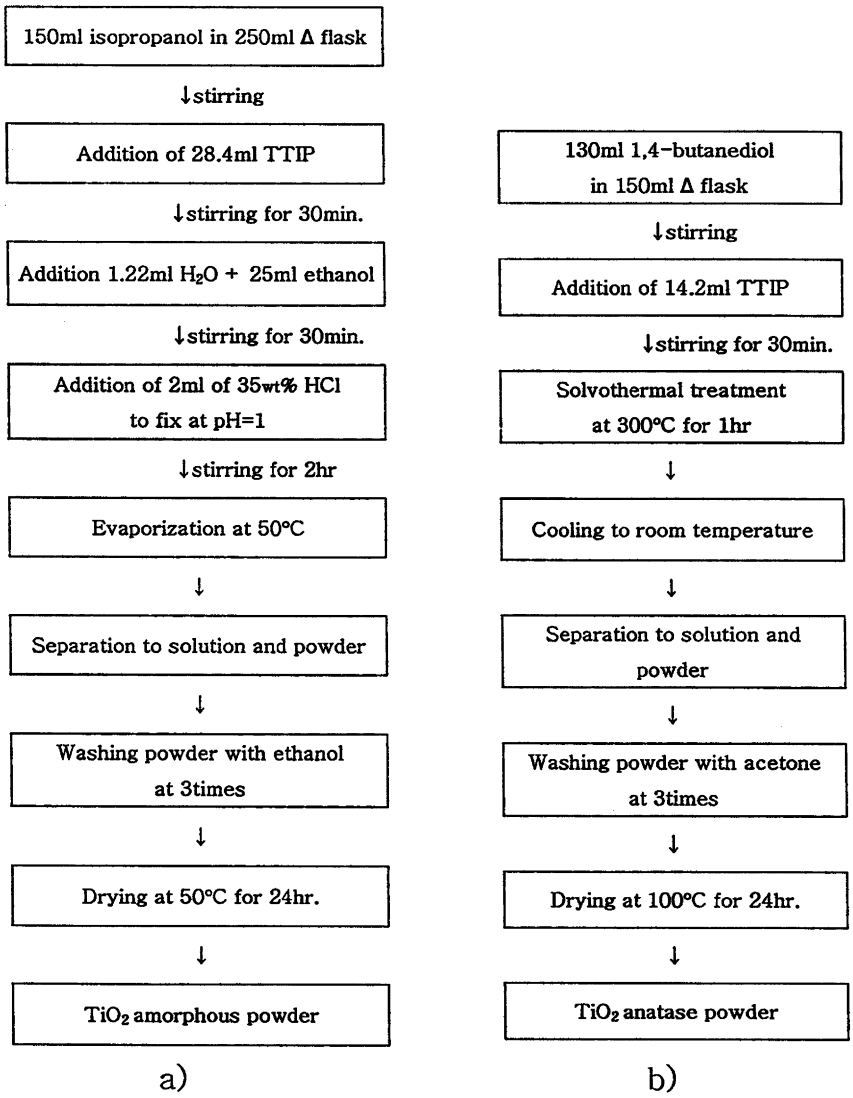

Fig. 1. Preparation of TiO_2 photocatalysts by two kinds of the synthesis method. (a) Sol–gel method (Cat. 1) and (b) solvothermal method (Cat. 2).

distilled water. The UV-lamps (model BBL, 254 nm, 8 W × 3, 20 cm length × 1.5 cm diameter, Shinan Co., Korea) and air bubbling of 500 ml/min were used in the dark condition.

The reaction solution was analyzed by a FID-type gas chromatograph (GC). A HP-624 column was used for the analysis of $CHCl_3$ remaining in the reaction solution. The GC operating conditions were as follows: injection temperature 150°C, split ratio 10:1, initial oven temperature 70°C, final oven temperature 150°C, and detector temperature 250°C.

3. Results and discussion

3.1. Properties of catalysts

XRD patterns of the TiO_2 photocatalyst crystals are shown in Fig. 3. Cat. 1 as-synthesized by the sol–gel method was amorphous, and heat treatment at 500°C for 3 h was needed to acquire the anatase structure. On the contrary, the sample (Cat. 2 as-synthesized) prepared by the solvothermal method showed a well-developed anatase structure although only the thermal treatment at 300°C for 50 min was employed during the synthesis.

Physical properties for these catalysts are shown in Table 1. The surface area of Cat. 2 was very large (121.92 m^2/g) compared with that of Cat. 1 (51.36 m^2/g). In general, it is well known that TiO_2 anatase particles synthesized by the sol–gel method possess the surface area below 100 m^2/g. The surface area of Degussa P-25, which is a widely known commercial TiO_2 photocatalyst, was measured to be 72 m^2/g in our laboratory. Therefore, the surface area of Cat. 2 was a remarkable result. In fact, it has been reported that ZrO_2 crystalline powders synthesized by the solvothermal method have the surface area of around 150 m^2/g [21].

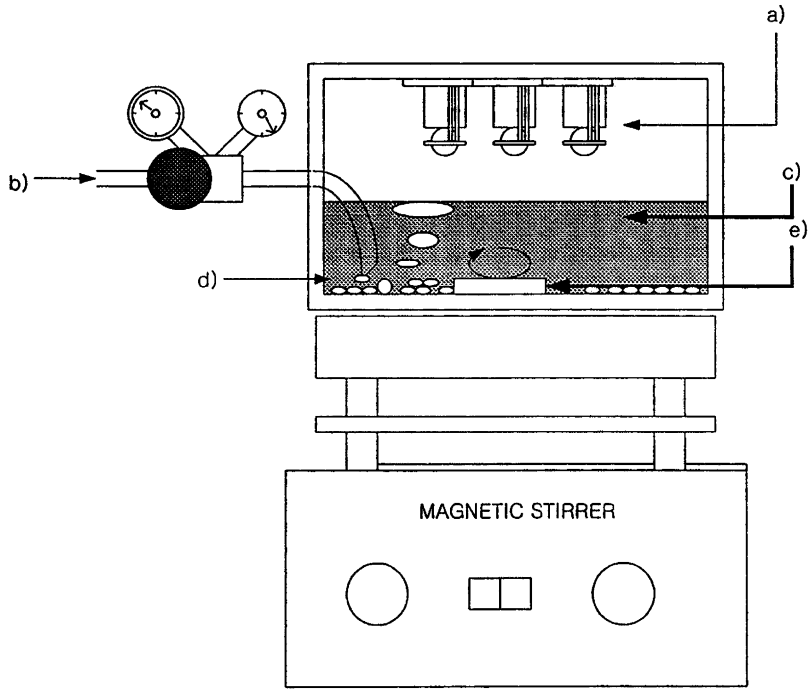

Fig. 2. Stationary closed apparatus for $CHCl_3$ decomposition. (a) UV-lamp (8 W × 3, 350–400 nm); (b) air bubbling (500 ml/min); (c) $CHCl_3$ solution (1000 ppm, 600 ml); (d) Cat. (0.1 g/l); and (e) stirrer.

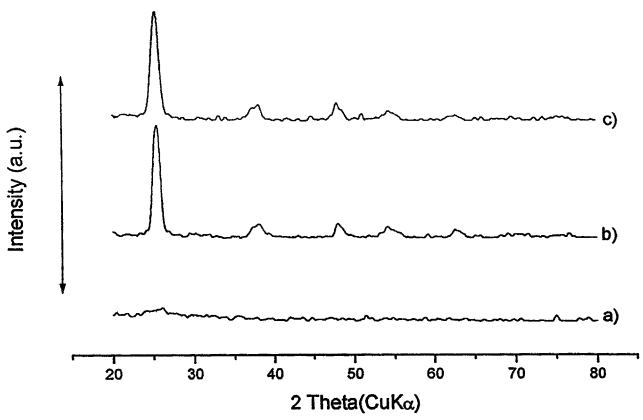

Fig. 3. XRD patterns of as-synthesized TiO_2 photocatalysts. (a) Cat. 1 as-synthesized; (b) Cat. 1 calcined at 500°C for 3 h; and (c) Cat. 2 as-synthesized.

The surface charge of the catalysts in water was measured by the electrophoresis or the zeta-potential, which was attained from electronic light scattering (ELS) equipment. Generally, the value is a measure of stability of a surface against agglomeration, and an increase of the zeta-potential value indicates that the stability increases. Cat. 1 and Cat. 2 exhibited +16.4 and +24.1 mV, respectively. From this result, it was confirmed that the surface of Cat. 2 in water was more stable than Cat. 1.

Fig. 4 shows the morphology of the TiO_2 photocatalysts observed by SEM. Cat. 2 was shown to consist of relatively uniform and spherical particles with the size of 20–50 nm. On the other hand, Cat. 1 after calcination was quite irregular; the particle size was larger and widely distributed from less than 100 nm to about 3 μm.

The distribution of the particle size was also measured by DLS, as shown in Fig. 5. This value was measured over 5 min after ultrasonic treatment. The particles in Cat. 1 were distributed from 400 to 800 nm. The particles in Cat. 2 were bimodally distributed in the ranges of 50–60 nm and 110–150 nm, but the size of single particles is believed to belong to the former range. It was observed that the particle size distribution became wider and the mean particle size became larger with the elapsed time after the ultrasonic wave treatment. This is certainly due to agglomeration of particles, as is usually observed. The group of larger particles in

Table 1
Physical properties of TiO_2 photocatalysts

Catalysts	Preparation method	Structure type	Surface area (m^2/g)	Surface charge (mV)	Average particle size (nm)
Cat. 1 (500°C, 3 h calcination)	Sol–gel method	Anatase	51.36	+16.4	400–800
Cat. 2 (as-synthesized)	Solvothermal method	Anatase	121.92	+24.1	50–60, 110–150
Characterization method	–	XRD	BET	Zeta-potential	DLS

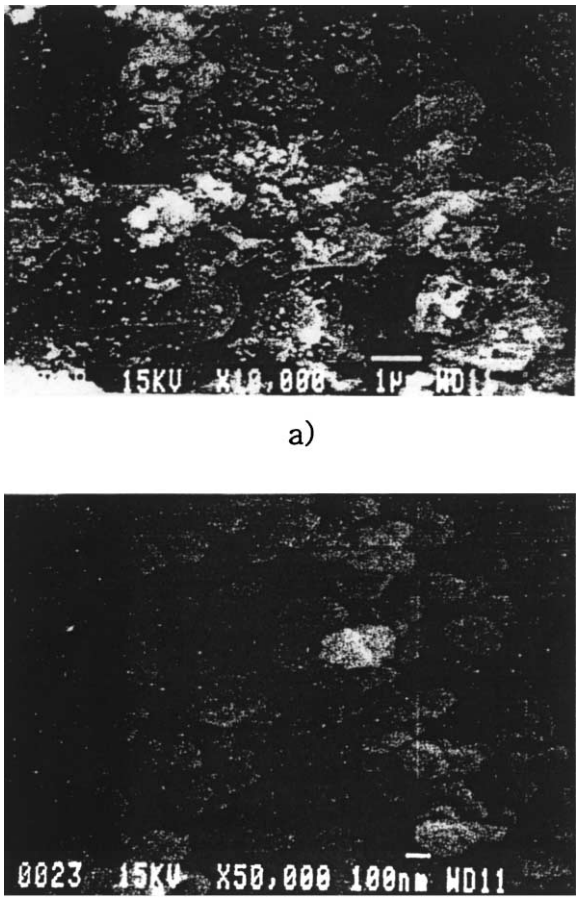

Fig. 4. SEM photographs of as-synthesized TiO_2 photocatalysts. (a) Cat. 1 calcined and (b) Cat. 2 as-synthesized.

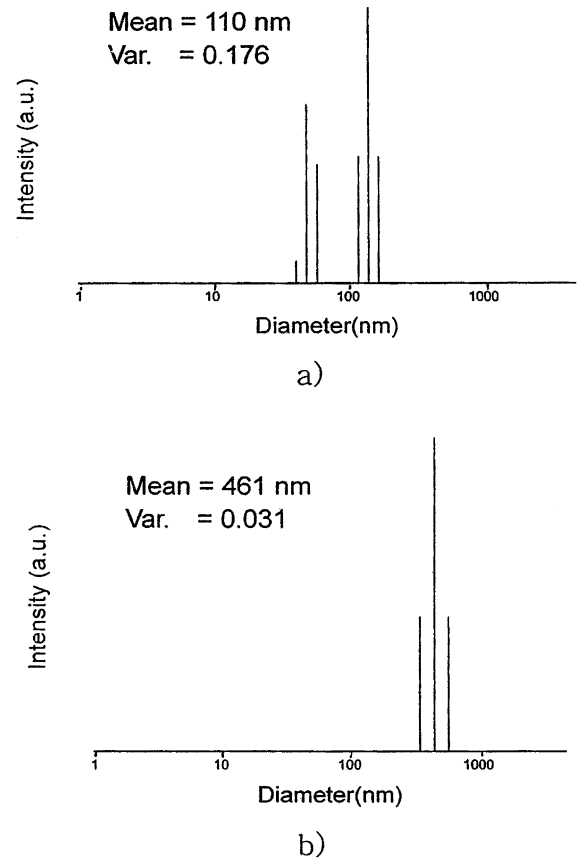

Fig. 5. Distribution in TiO_2 particle size measured by DLS. (a) Cat. 1 calcined and (b) Cat. 2 as-synthesized.

Fig. 5(a) is considered to mainly consist of two particles agglomerated. One hour after the sonification, the mean particle size was measured to be 220 nm, indicating that three to four particles were conglomerated. The agglomeration tendency was observed to be more pronounced, or occur faster for Cat. 1.

Fig. 6 shows the DSC thermogram results for Cat. 2. Two endothermic peaks of 80–100 and 180–210°C, which were assigned to desorption of water adsorbed on crystal surface and in crystal cavity, respectively, were observed [22]. Using the results in Fig. 6, Table 2 summarizes the activation energy calculated by the Ozawa method [20]. Ozawa has presented a useful equation to calculate the activation energy of various thermal reactions based on the shift of the maximum deflection temperatures (T_m) of DSC thermograms upon changing the heating rate:

$$\log\phi + \frac{0.456E}{RT_m} = \text{constant}$$

where ϕ is the heating rate (°C/min); T_m the maximum deflection temperature (K); E the activation energy; R the gas constant.

The activation energy can be derived from the slope, $0.456E/R$ from the plot of $\log\phi$ versus $1/T_m$. From the first and second T_m's, the activation energies for desorption of water molecules which were adsorbed on and in TiO_2 particles were calculated to be 14.4 and 16.5 kcal/mol, respectively. The activation energy for desorption of water

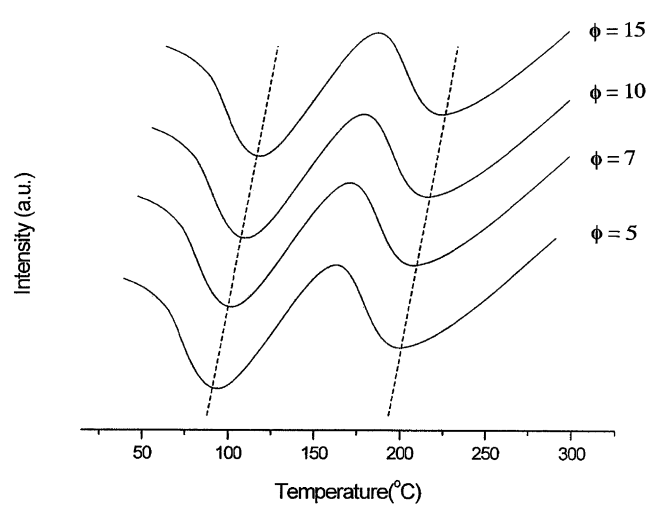

Fig. 6. TG-DSC profiles for Cat. 2 with varying ϕ.

Table 2
Activation energy on H_2O desorption by Ozawa's equation[a] for Cat. 2

Peak[b]	ϕ	$\log\phi$	T_m (°C)	T_m (K)	Activation energy E (kcal/mol)
First	5	0.6990	84.90	358.05	
	7	0.8451	86.76	359.91	14.4
	10	1.0000	94.12	367.27	
	15	1.1760	103.23	376.38	
Second	5	0.6990	186.53	459.68	
	7	0.8451	189.10	462.25	16.5
	10	1.0000	196.45	469.60	
	15	1.1760	212.68	485.83	

[a] Ozawa's equation: $\log\phi + 0.456E/RT_m = \text{constant}$.
[b] ϕ: heating rate (°C/min), T_m (°C or K): maximum deflection temperature, R: gas constant.

molecules, which was adsorbed on single crystal molecules, was usually below 10 kcal/mol [20]. Therefore, this result shows that the Cat. 2 is very hydrophilic.

3.2. Photocatalytic performance on chloroform decomposition

Photocatalytic oxidation of organic compounds is of considerable interest for environmental applications. In particular, chlorine-containing compounds, such as 4-chlorophenol, pentachlorophenol, trichloroethylene (TCE), perchloroethylene (PCE), CCl_4, $CHCl_3$, CH_2Cl_2, vinyl chloride, and *p*-chlorobenzene, are of greater interest because of its hazardness. These are widespread in soils and ground waters. Among these, $CHCl_3$ was selected in this study as a model compound.

In Fig. 7, $CHCl_3$ decomposition in only UV-light, air bubbling, and UV-light/air bubbling systems were compared. By only air bubbling or UV-light, the conversions of $CHCl_3$ increased very slowly with time, and then these reached about

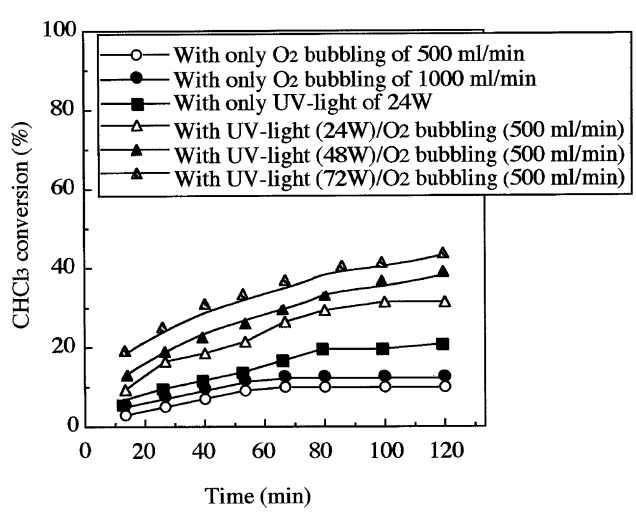

Fig. 7. Photo-catalytic decomposition of $CHCl_3$ in various conditions. Reaction condition: $CHCl_3$ concentration; 1000 ppm/min.

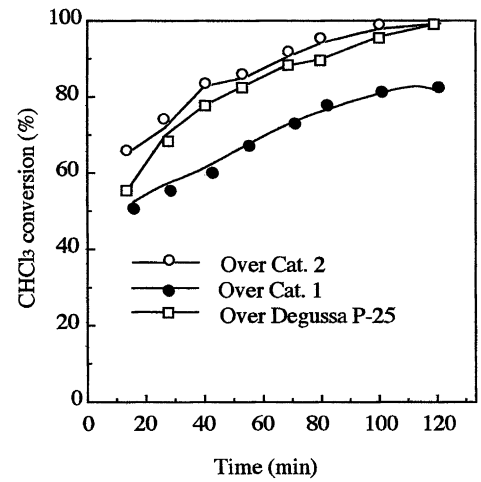

Fig. 8. Performance of $CHCl_3$ decomposition over the photocatalysts. Reaction conditions: UV-lamp: 24 W/m^2; air bubbling: 500 ml/min; initial $CHCl_3$ concentration: 1000 ppm (600 ml in water); Cat.: 0.1 g/l.

10 and 15% after 120 min, respectively. On the other hand, with an increase of intensity of UV-light in UV-light/air bubbling system, $CHCl_3$ decomposition increased. However, the decomposition of $CHCl_3$ was not increased largely with an increase of air bubbling compared with that with an increase of UV-light intensity. From result, it was confirmed that the UV-light was more affected to $CHCl_3$ decomposition compared with air bubbling.

Fig. 8 showed the conversions of $CHCl_3$ with time over various catalysts. As shown, Cat. 2 exhibited higher performance than Cat. 1, and more than 95% of the $CHCl_3$ was decomposed after 2 h. In particular, a remarkable result was that the performance for $CHCl_3$ photo-decomposition over Cat. 2 was higher that over Degussa P-25, which be well-known as a photocatalyst with high photo-activity. This result could be ascribed to the smaller particle size and larger surface area of Cat. 2.

4. Conclusion

This study showed that TiO_2 particles with the anatase structure of nano size could be synthesized by the solvothermal method, which is a reproducible and reliable method. The results are as follows.

1. The TiO_2 powder (Cat. 2) acquired by the solvothermal method exhibited well-developed anatase structure without additional heat treatment.
2. Cat. 2 displayed higher surface area and surface charge than Cat. 1 which was prepared by the sol–gel method.
3. The activation energy for H_2O desorption over Cat. 2 was very high, higher than 14 kcal/mol.
4. In the chloroform ($CHCl_3$) decomposition, the catalytic performance of Cat. 2 was distinguishably higher than those of Cat. 1 and Degussa P-25.

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