

# Synthesis of Fe/TiO<sub>2</sub> photocatalyst with nanometer size by solvothermal method and the effect of H<sub>2</sub>O addition on structural stability and photodecomposition of methanol

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## Abstract

The nanometer particles of TiO<sub>2</sub> and Fe/TiO<sub>2</sub> with a high photo-catalytic activity were obtained by the solvothermal method. The TiO<sub>2</sub> and Fe/TiO<sub>2</sub> particles were characterized with XRD, SEM, DLS, TG–DSC, and UV-Vis spectroscopy. The TiO<sub>2</sub> and Fe/TiO<sub>2</sub> particles exhibited a uniform anatase structure with particle size below 50 nm after synthesis at 300 °C for 1 h without any treatments. Attained Fe/TiO<sub>2</sub> particles had a higher hydrophilic property compared with TiO<sub>2</sub>, and they absorbed wavelength above 350 nm. In photodecomposition of methanol, the methanol was decomposed to CO, HCHO, 2H<sub>2</sub>O, and H<sub>2</sub> as intermediates. Finally, these were transferred into 2CO<sub>2</sub>, 2H<sub>2</sub>O, and 2H<sub>2</sub>. While, when H<sub>2</sub>O was added as a reactant with methanol, the intermediates were CO<sub>2</sub>, HCOOH, H<sub>2</sub>O, and 3H<sub>2</sub>, and then these were converted to 2CO<sub>2</sub>, H<sub>2</sub>O, and 4H<sub>2</sub>. In particular, the methanol conversion enhanced about 20% with 10-mol% H<sub>2</sub>O addition over Fe/TiO<sub>2</sub> catalyst compared with pure TiO<sub>2</sub>. On the other hand, for Fe/TiO<sub>2</sub>, the anatase structure was stable in 10-mol% H<sub>2</sub>O addition as a reactant, but it was transferred into the rutile structure with an increase of added H<sub>2</sub>O amount. In particular, in this study, it was found that the anatase structural change is generated by H<sub>2</sub>O addition and, as the result, the partially structural change into rutile type could be better effected to photo-degradation for methanol over Fe/TiO<sub>2</sub>. In addition, we could confirm that the added H<sub>2</sub>O molecule on the photoreaction over Fe/TiO<sub>2</sub> plays a role of suppletion of OH radical.

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*Keywords:* Solvothermal method; Fe/Ti oxide; Structural change; Suppletion of OH radical

## 1. Introduction

In the mid 1990s, the solvothermal treatment was introduced in the field of synthesis of ceramic materials such as ZrO<sub>2</sub>, Ce<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> [1,2]. This method could be surprisingly employed as an alternative to calcinations for promoting crystallization

under mild temperature. Very recently, this process has been widely applied in the synthesis of zeolites and ceramic powders containing various metal oxides [3,4]. The solvothermal treatment could be used to control grain size, particle morphology, crystalline phase and surface chemistry by regulating sol composition, reaction temperature, pressure, nature of solvent, additives, and aging time [1–4]. In particular, the particles prepared by the solvothermal method were reported to have larger surface area, smaller particle size, and were more stable than those obtained by other methods such as the sol–gel one [5]. Among

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the oxides reported so far,  $\text{TiO}_2$  prepared by the solvothermal method has not, unexpectedly, appeared in the literature as far as we know.

On the other hand, the world has to manage a tremendous set of environmental problems and, thus extensive research activities are carried on advanced chemical, biochemical, and physicochemical methods for elimination of hazardous chemical compounds from air and water [6–8]. In this field, many works have been done on the photocatalytic treatment of environmental pollutants using semiconductors like  $\text{TiO}_2$ ,  $\text{Fe/TiO}_2$ , and  $\text{Zn/TiO}_2$ , etc. When a semiconductor made of  $\text{TiO}_2$  absorbs a photon and then is promoted to an excited state, an electron is transferred from valance band to the conduction band where it can function as a reducing moiety, leaving a hole in the valence band that is a strong oxidizing entity. The energy gap between valance and conduction bands in pure  $\text{TiO}_2$  is 3.2 eV: so UV-light is necessary to excite electrons on the  $\text{TiO}_2$  surface. Recently, in order to activate the photo-catalysts using UV-light with longer wavelengths, many works have focused on doping/mixing of other sulfides or oxides such as CdS,  $\text{Fe}_2\text{O}_3$ , ZnO, AgO, etc. [9–11] in the  $\text{TiO}_2$  anatase structure, which exhibit lower band gap energy. In particular, the introduction of Fe into the anatase structure of  $\text{TiO}_2$  has been often used in some studies [12,13].

In the case of surface reaction, the simple mechanisms of decomposition of pollutant were reported by many researchers [14–19]. However, some of them are still not clear, in particular, when the mixture of VOC with other compound, for example,  $\text{H}_2\text{O}$  was decomposed, analysis of the mechanism was very difficult. In addition, the deactivation of photo-catalyst made no mention until now, and the application is limited to photodecomposition because the performances observed were very low. Therefore, if the decomposition mechanism in mixture of VOC and other compounds could be resolved, the photo-catalyst could be extended to the other applications.

On the other hand, it was reported that the  $\text{H}_2\text{O}$  addition in methanol to olefin (MTO) process have good influenced on methanol conversion and olefin selectivity [20]. The  $\text{H}_2\text{O}$  has role as a Brönsted acid donor stability and continuously in reaction. In addition, it makes retardation of catalytic deactivation. However, too much  $\text{H}_2\text{O}$  addition rather generate the structural damage, which caused fast catalytic

deactivation [20]. While, in photoreaction, the role of  $\text{H}_2\text{O}$  was not cleared yet. Some papers reported that the addition of  $\text{H}_2\text{O}$  had not effected or badly effected to photo-degradation [21,22].

In this study,  $\text{Fe/TiO}_2$  having the anatase structure of nanometer size was synthesized as applying the solvothermal method, and the photodecomposition of methanol was carried out with the addition of  $\text{H}_2\text{O}$  to surely find out its role in photoreaction. In addition, we have also tried to change anatase to rutile structure as  $\text{H}_2\text{O}$  addition, and to find out the relationship between structural change and photocatalytic performance for methanol decomposition.

## 2. Experimental

### 2.1. Catalyst preparation

The preparation method of the  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$  catalysts is shown in Fig. 1. The comparison for physical properties and synthesized mechanisms between catalysts synthesized by solvothermal method and sol-gel method were already reported [23,24].

Reagents used for preparation of sol-mixtures were as follows; titanium tetra-isopropoxide (TTIP, 99.95%, Junsei Chemical, Japan) and ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Junsei Chemical, Japan) were used as the titanium and iron precursors. 1,4-Butanediol (Wako Pure Chem. Ltd.) was used as solvent. As shown in Fig. 1, the solvothermal method is considered as a synthesis method in this study. TTIP and iron precursor were mixed with the organic solvent in an autoclave (model R-211, Reaction Engineering Inc., Korea) as shown in Fig. 2, which was heated to 300 °C for 1 h with a rate of 5 °C/min. During thermal treatment, TTIP was hydrolyzed by the OH group in the alcoholic solvent and, finally crystallization of the  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$  occurred. The obtained powders were washed with acetone to eliminate the hydrolysis after solvothermal method and then dried at 100 °C for 24 h.

### 2.2. Characterizations of synthesized catalyst

The synthesized samples,  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$  catalysts, were identified by powder X-ray diffraction analysis (XRD, model PW 1830 from Philips) with nickel

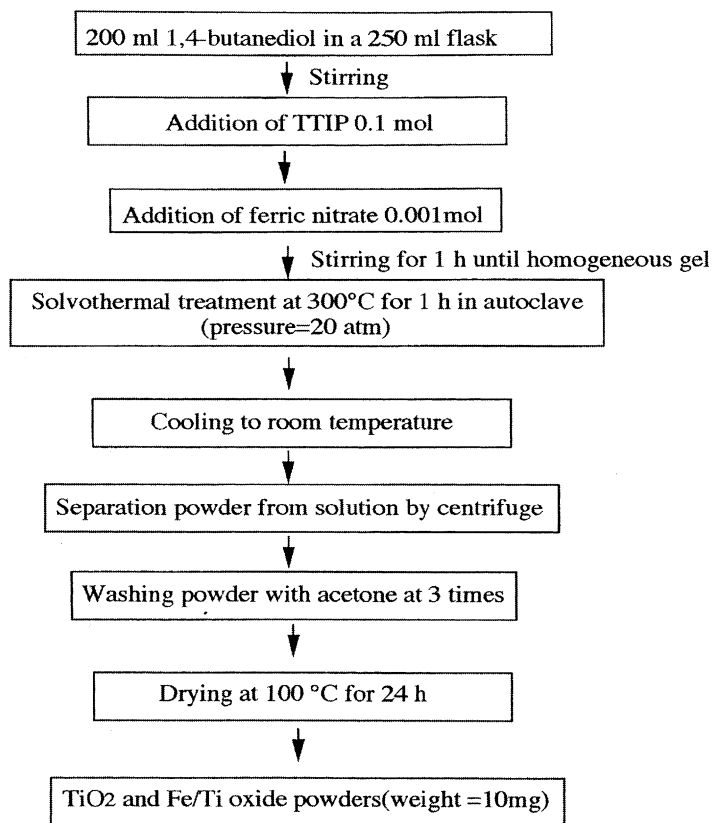


Fig. 1. Preparation of  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$  powders by the solvothermal method.

filtered  $\text{Cu K}\alpha$  radiation (30 kV, 30 mA) at  $2\theta$  angle from  $5$  to  $70^\circ$ . The scan speed was  $10^\circ/\text{min}$  and time constant was 1 s.

The particle size and shape of  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$  catalyst prepared were observed by scanning electron

microscope (SEM, model JEOL-JSM35CF). The power was set to 15 kV.

The BET surface area of the sample was measured by nitrogen gas adsorption with continuous flow method using chromatography equipped with a TCD detector at the liquid nitrogen temperature. A mixture of nitrogen and helium was flowed as the carrier gas with the GEMINI2375 model from Micrometrics. The sample was thermally treated at  $350^\circ\text{C}$  for 3 h before nitrogen adsorption.

The activation energies for  $\text{H}_2\text{O}$  decomposition in  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$  catalyst were determined by using a TG-DSC equipped with a micro thermo-differential and gravimetric analyzer (Perkin-Elmer Co., USA) using the Ozawa method [27]. A weight of 20 mg  $\alpha$ -alumina was used as reference sample. To keep the moisture condition identical, the sample was analyzed after contact with a saturated  $\text{NH}_3\text{OH}$  solution for 24 h.

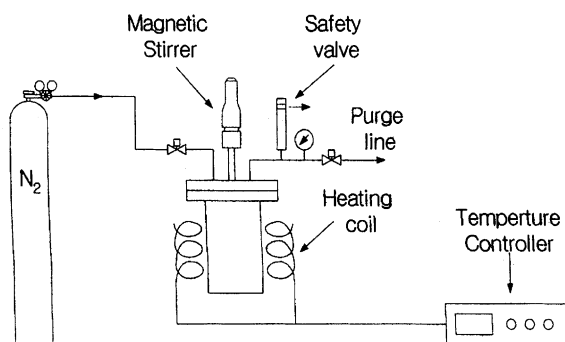


Fig. 2. Autoclave using for synthesis of  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$ .

The particle size distribution of the samples was obtained by dynamic light scattering (DLS) spectrophotometer (BI 9000AT) after ultrasonic wave treatment with 140 W in water for 2 min.

The zeta-potential value was obtained by Zetasizer 4000 at a 90° angle. Before measurement, the sample was treated by ultrasonic waves with 100 W in water for 10 s.

The UV-visible spectra were obtained by a Shimadzu MPS-2000 spectrometer equipped with a reflectance sphere. The special range was from 200 to 700 nm, and BaSO<sub>4</sub> was used as a reflectance standard.

### 2.3. Analysis of product for decomposition of methanol in photocatalytic systems

The decomposition of methanol was carried out using a flow reactor as shown in Fig. 3. Three grams catalysts were used. A quartz cylinder reactor with dimension of 65 cm in length and 0.8 cm in diameter was used and the UV-lamps (model BBL, 365 nm, 8 W × 3, 20 cm length × 1.5 cm diameter, Shinan Co., Korea) were used for photoreaction. The mixture of water and

methanol was used as a feed for methanol photodecomposition. The methanol concentration was fixed to 200 ppm. In methanol photodegradation, 5, 10, 20, 40, and 60 mol% H<sub>2</sub>O were added to confirm the influence of OH groups. The concentration of the mixture was determined from each mole-vapor enthalpy and the boiling point data of methanol–water mixture [20]. On the other hand, in continuous system for determination of catalytic lifetime, N<sub>2</sub> gas was used as a carrier gas, and the flow rate of O<sub>2</sub> gas was 300 ml/min. In addition, to confirm the effect of H<sub>2</sub>O addition on structural change in photocatalyst, it was then exposed to contain 5–60 mol% steam diluted by N<sub>2</sub> at 80 °C for 2 h.

The products in photo-catalytic decomposition were analyzed by a TCD-type gas chromatograph (GC). To determine exactly the products and intermediates, the GC was connected to the reactor of methanol decomposition, directly. The conditions of GC were as follows: detector, TCD; column, Chromosorb 102; injection temperature, 200 °C; initial temperature, 40 °C; final temperature, 200 °C; detector temperature, 200 °C.

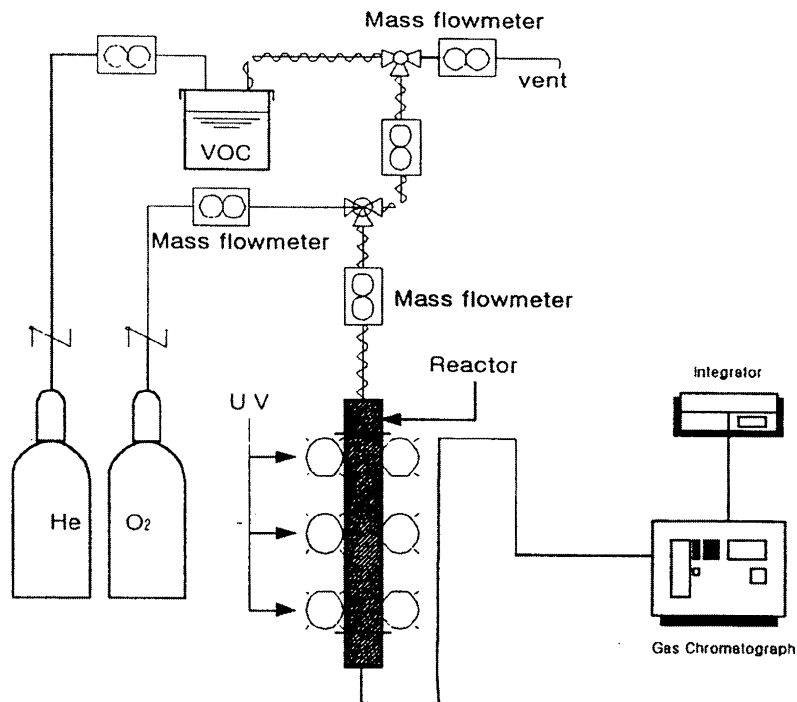


Fig. 3. Photo-reaction system for methanol decomposition.

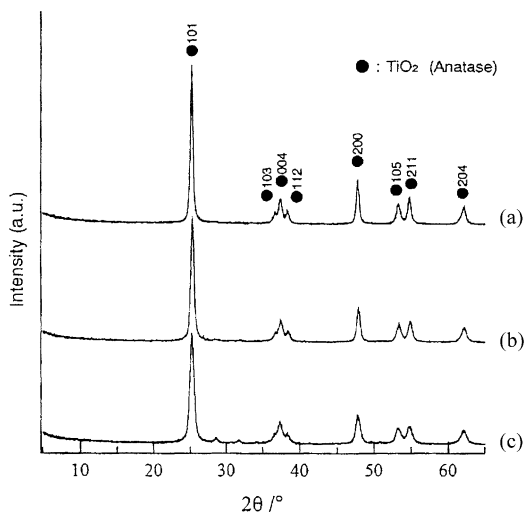


Fig. 4. The XRD patterns of synthesized  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$  by the solvothermal method. (a) Anatase structure [8], (b)  $\text{TiO}_2$  synthesized, and (c)  $\text{Fe/TiO}_2$  synthesized.

### 3. Results and discussion

#### 3.1. Characterization

Fig. 4 shows the XRD pattern of synthesized  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$  by the solvothermal method. In general, the  $\text{TiO}_2$  photocatalyst with anatase structure exhibited higher performance for VOC decomposition than that of other type, like rutile, brookite, and amorphous ones [6–8]. As shown in this figure, the

samples showed a well-developed anatase structure, although only a thermal treatment at  $300^\circ\text{C}$  for 1 h was done during the synthesis without further treatments. The width of peak was slightly broader in  $\text{Fe/TiO}_2$  compared with that of pure  $\text{TiO}_2$  particle. In general, the width of XRD peak corresponds to the crystallites sizes of porous materials. When the width was broad, the crystallites exhibited smaller size; in particular, the crystallites were smaller in the sample introducing transition metals like Ni and Fe.

The SEM photographs of samples were as shown in Fig. 5. The pure  $\text{TiO}_2$  sample showed relatively uniform and spherical particles with the size about 30 nm. In case of  $\text{Fe/TiO}_2$ , the particle size was smaller than pure  $\text{TiO}_2$ . However, the distribution was rather larger than that in pure  $\text{TiO}_2$ . This result is in accordance with the result of Fig. 4.

Physical properties for these catalysts are given in Table 1. The BET surface area of  $\text{TiO}_2$  was large ( $120\text{ m}^2/\text{g}$ ) compared with that of  $\text{Fe/TiO}_2$  ( $75\text{ m}^2/\text{g}$ ). In general, it is well known that  $\text{TiO}_2$  anatase particles synthesized by the sol–gel method possess a surface area of about  $60\text{ m}^2/\text{g}$ . The surface area of Degussa P-25, which is widely known as a commercial  $\text{TiO}_2$  photo-catalyst, was measured to be  $72\text{ m}^2/\text{g}$  in our laboratory. Therefore, this was a remarkable result. Of course, the surface areas of the samples prepared by sol–gel methods, in some of the papers, were much larger than that of the sample prepared by the solvothermal method [25,26]. However, the preparation methods, in these papers, were different with

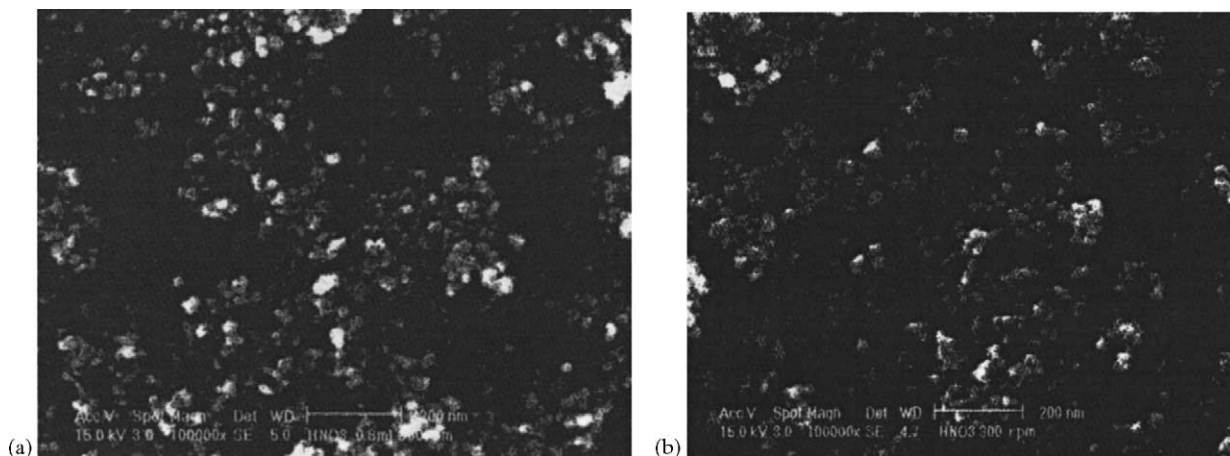


Fig. 5. SEM photographs of  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$  synthesized by the solvothermal method. (a)  $\text{TiO}_2$  and (b)  $\text{Fe/TiO}_2$ .

Table 1  
physical property of TiO<sub>2</sub> and Fe/TiO<sub>2</sub> photocatalysts

Catalyst	Preparation method	Structural type	Composition (Ti:Fe, at.%)	Surface area (m <sup>2</sup> /g)	Surface charge (mV)	Average particle size (nm)	Activation energy (kJ/mol)	
							First peak	Second peak
TiO <sub>2</sub>	Solvothermal method	Anatase	100:0	120	+24	30–50	60	69
Fe/Ti oxide	Solvothermal method	Anatase	90.01:10.11	75	+16	20–70	62	70
Characterization method	–	XRD	ICP	BET	Zeta-potential	DLS	DSC (Ozawa's method [27])	

our method, for example, different solvent and amount, and reaction temperature. On the other hand, 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 an increased stability. The TiO<sub>2</sub> and Fe/TiO<sub>2</sub> exhibited +24 mV and +16 mV, respectively. From this result, it could be suggested that pure TiO<sub>2</sub> particles were more stable compared to Fe/TiO<sub>2</sub> particles in water. On the other hand, concerning the particle size distribution, the particle size was smaller in Fe/TiO<sub>2</sub> than that in pure TiO<sub>2</sub>, however, the distribution rather larger than in pure TiO<sub>2</sub>. In general, the additions of nickel or iron also give smaller particle, while the addition of cobalt gives larger particle than pure sample in thermal catalysis. Maybe this is attributed that the crystallization rate is different as addition of Fe component, result in the crystallization rate decreased in Fe/TiO<sub>2</sub>. As shown, the TiO<sub>2</sub> particle sizes were sharply distributed from 30 to 50 nm, and the Fe/TiO<sub>2</sub> particles were broadly distributed from 20 to 70 nm. On the other hand, the activation energy was calculated by Ozawa method [27]. Ozawa has presented a useful equation to calculate the activation energy of various thermal reaction based on the shift of the maximum deflection temperature ( $T_m$ ) of DSC thermograms upon changing the heating rate.

$$\text{Log } \phi + 0.456 \frac{E_a}{RT_m} = \text{constant}$$

where  $\phi$  is heating rate (°C/min),  $T_m$  the maximum deflection temperature (K),  $E_a$  the activation energy,  $R$  the gas constant.

The activation energy can be derived from the slope,  $0.4567E_a/R$  from the plot of  $\log \phi$  versus  $1/T_m$ . From the first and second  $T_m$ , the activation energies for desorption of water molecules, which were adsorbed on and in particles, were calculated to be 60 and 69 kJ/mol in TiO<sub>2</sub>, respectively. While, for Fe/TiO<sub>2</sub>, the values increased as 62 and 70 kJ/mol. Generally, the activation energy for desorption of water molecules, which were adsorbed on single crystals, is usually below 40 kJ/mol. This result shows that the samples synthesized by solvothermal method have very hydrophilic property. In addition, in water, the rate of precipitation for particles synthesized by solvothermal method was slower than that of Degussa P-25. Although after 10 days, the particles were well dispersed in water. This result also shows that the particles synthesized by solvothermal method are very hydrophilic.

In Fig. 6, UV-Vis spectra are shown. In general, the absorption of Fe<sup>3+</sup> in octahedral symmetry is known to appear above 430 nm [28], whereas the absorption of Ti<sup>4+</sup> tetrahedral symmetry appears below 370 nm. In this result, obviously, the absorption band of Fe/TiO<sub>2</sub> was shifted to longer wavelength compared with that of pure TiO<sub>2</sub>. It is obvious that the catalyst included iron component absorbs longer wavelength. However, when the synthesis methods are different, for example, impregnation or sol-gel method, the absorption of Fe/TiO<sub>2</sub> and the tendency are different. The absorption of sample synthesized by impregnation appeared at two wavelengths, around 430 and 550 nm as small bands. On the other hand, it is observed broadly and weakly around 430 nm for the sample synthesized by sol-gel method. However, this is not illustrated in the influence of the absorption on catalytic performance. On the other hand, the absorption of Degussa P-25 was similar to that of the synthesized TiO<sub>2</sub> in this study.

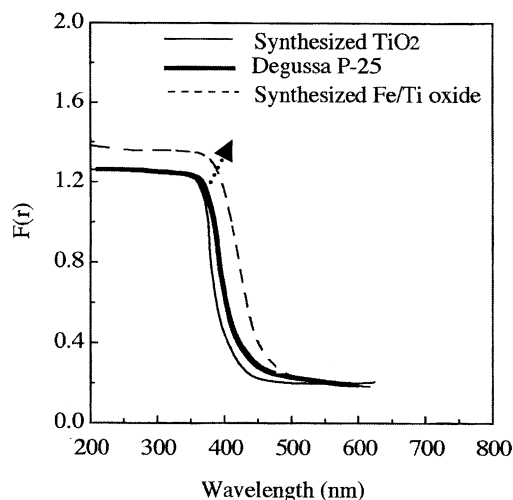


Fig. 6. UV-Vis spectra of  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$  synthesized by the solvothermal method.

### 3.2. Photodecomposition of methanol and structural stability with various vapor treatment over $\text{TiO}_2$ and $\text{Fe/TiO}_2$

Methanol is very useful in transportation, saving, and treatment compared with natural gas, like  $\text{CH}_4$ . Therefore, if it is economically considered, it is very

valuable that the methanol transferred into  $\text{CO/H}_2$ , and then these were recombined or produced new compounds. For example,  $\text{CO/H}_2$  can produce some compounds from Fisher-Tropsch, hydroformylation, and acetic acid with important value. Effectively, to use a method, which transferred methanol into valuable intermediates, it is very important to develop the catalyst with high methanol decomposition. As the catalysts, Cu, Cu-Ni, Zn, Fe, Al, Pt, and Pd were well known. These catalysts include formaldehyde and methoxy radical as the intermediates. If the intermediates were increased in reaction, the activated sites over catalysts were decreased. This resulted in the selectivity into  $\text{CO/H}_2$  decrease, finally. Therefore, to transfer methanol into  $\text{CO/H}_2$ , effectively, the catalyst used is very important. In this point, application of  $\text{TiO}_2$  is very valuable to transfer methanol into  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}$  in photo-reaction system. In this study, we tried to find out the best reaction condition with high selectivity into  $\text{CO/H}_2$  from methanol in photo-catalytic system.

In Fig. 7(a) and (b), the relation of methanol conversions and reaction time for photodecomposition without  $\text{H}_2\text{O}$  addition over  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$  are shown. In general, in thermal catalytic system, the methanol was decomposed to dimethylether,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and various hydrocarbons as products.

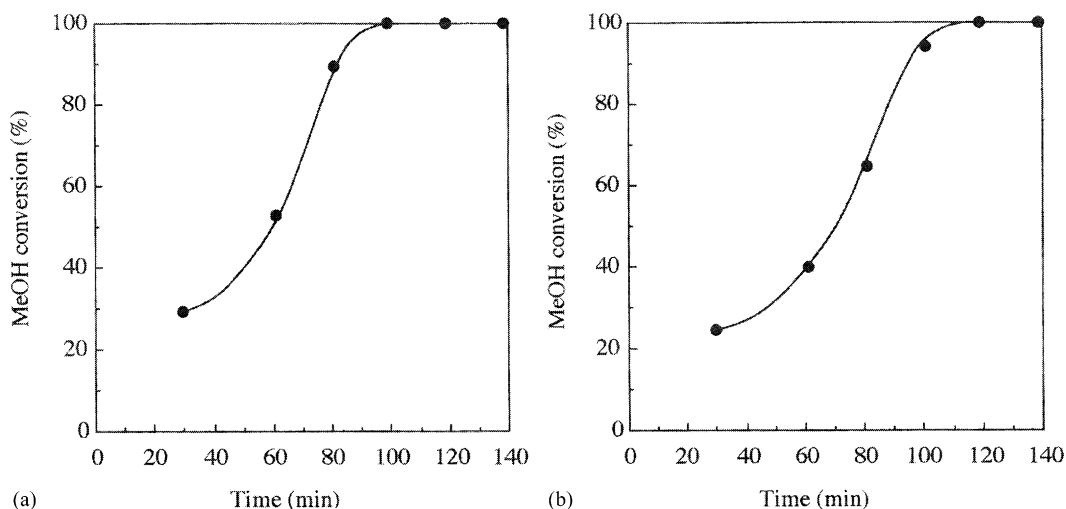
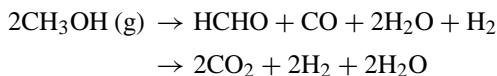


Fig. 7. Methanol conversion with reaction time for photocatalytic decomposition over  $\text{TiO}_2$  and  $\text{Fe/TiO}_2$  catalysts. (a) Over  $\text{TiO}_2$  catalyst, and (b) over  $\text{Fe/TiO}_2$  catalyst. Reaction conditions: methanol concentration, 200 ppm; catalyst weight, 3.0 g; UV-light intensity,  $365 \text{ nm}$ ;  $24 \text{ W/m}^2$ , batch system.

Contrary to thermal decomposition, as well known methanol decomposition mechanism follows the next in photo-reaction system.

Without H<sub>2</sub>O addition:

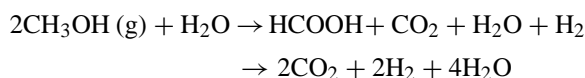


In this study, the selectivity to intermediates was not analyzed, and the methanol conversion was only determined for photo-catalytic performance. As shown in this figure, methanol was perfectly decomposed over TiO<sub>2</sub> after 100 min. But over the Fe/TiO<sub>2</sub>, the methanol conversion rather slightly decreased when compared with that over pure TiO<sub>2</sub> in spite of having longer wavelength in the result of UV-Vis spectra. The result means that the generation of OH radical, which was needed for oxidizing organic compound, was much over pure TiO<sub>2</sub> catalyst than over Fe/TiO<sub>2</sub> catalyst.

In order to enhance the generation of OH radical, H<sub>2</sub>O was added into the methanol in photodegradation reaction. Fig. 8 presents the methanol

conversion versus reaction time for photodecomposition of methanol over TiO<sub>2</sub> and Fe/TiO<sub>2</sub>, when H<sub>2</sub>O was added as a reactant. In this point, the mechanism for methanol photodegradation with H<sub>2</sub>O addition follows the next.

With H<sub>2</sub>O addition:



Contrary to without H<sub>2</sub>O addition, more oxidized HCOOH was produced as intermediates instead of HCHO. To begin with, over TiO<sub>2</sub>, the methanol conversion was not changed until 10-mol% of H<sub>2</sub>O addition. However, the conversion rather decreased above H<sub>2</sub>O addition of 10 mol%. This result was the same one as in other papers [21,22]. This result was ascribed that with an increase of H<sub>2</sub>O, the methanol decomposition reaction was reversed by Le Chatelier's principle. On the other hand, over Fe/TiO<sub>2</sub> catalyst, the methanol decomposition increased until 10-mol% H<sub>2</sub>O addition and, surprisingly, methanol was perfectly decomposed after 80 min. However, the

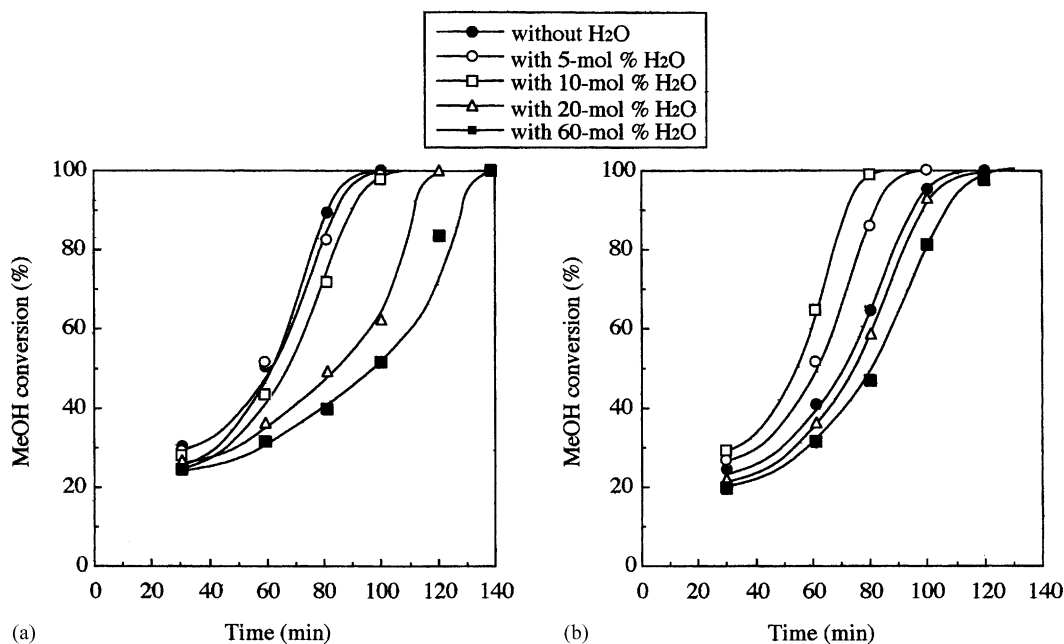


Fig. 8. Methanol decomposition with addition of H<sub>2</sub>O as a reactant in photoreaction over TiO<sub>2</sub> and Fe/TiO<sub>2</sub> catalysts. (a) Over TiO<sub>2</sub> catalyst, and (b) over Fe/Ti oxide catalyst. Reaction conditions: methanol concentration, 200 ppm; catalyst weight, 3.0 g; UV-light intensity, 365 nm, 24 W/m<sup>2</sup>, 5, 10, 20, 40, and 60 mol% H<sub>2</sub>O, batch system.



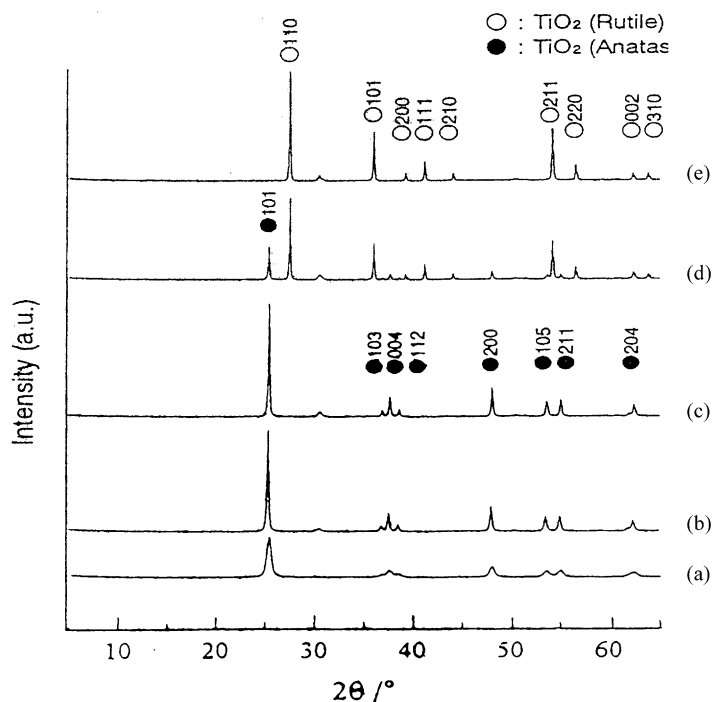


Fig. 9. The XRD patterns for TiO<sub>2</sub> and Fe/TiO<sub>2</sub> photocatalysts treated by 60 mol% steam at 80 °C for 2 h. (a) TiO<sub>2</sub> non-treated, (b) TiO<sub>2</sub> treated with 60 mol% steam diluted by N<sub>2</sub>, (c) Fe/TiO<sub>2</sub> non-treated, (d) Fe/TiO<sub>2</sub> treated with 60 mol% steam diluted by N<sub>2</sub>, and (e) TiO<sub>2</sub> rutile structure.

conversion decreased slightly above H<sub>2</sub>O addition of 20 mol.%. From these results, it was confirmed that the H<sub>2</sub>O addition as a reactant have better influenced on the methanol photo-degradation over Fe/TiO<sub>2</sub> catalyst compared with pure TiO<sub>2</sub>.

In order to find out the effect of H<sub>2</sub>O addition to photo-catalyst structure, TiO<sub>2</sub> and Fe/TiO<sub>2</sub> samples were treated with steam of 60 mol% at 80 °C for 2 h, and the XRD patterns are as shown in Fig. 9. As shown, the anatase structure in TiO<sub>2</sub> catalyst was not changed in condition of 60 mol% steam treatment as shown in Fig. 9(b). While, in Fe/TiO<sub>2</sub>, the structural change was scarcely found with 60 mol% steam treatment. The anatase structure was transferred into rutile structure, and the ratio of anatase/rutile was about 1/3. From the results of Figs. 8 and 9, it was confirmed that the reason of abruptly decreases of methanol decomposition in Fig. 8(b) over Fe/TiO<sub>2</sub> was attributed to the structural change in Fig. 9(d). In addition, it was identified that the anatase structure of Fe/TiO<sub>2</sub> was more affected by H<sub>2</sub>O than pure TiO<sub>2</sub> structure.

In Fig. 10, the photo-catalytic performance between the reactions with and without addition of 10-mol% H<sub>2</sub>O over Fe/TiO<sub>2</sub> catalyst in continuous photo-reaction system are shown. In case of H<sub>2</sub>O addition, the methanol conversion kept 60% for 10 h. While, the conversion slowly decreased after 8 h in reaction condition without H<sub>2</sub>O addition. Until now, the deactivation of photocatalyst has not been researched. The reason was attributed that the photoreaction was done in batch photo-reaction system, and so the reaction fast finished, therefore, the deactivation of photocatalyst could not be found. However, in this study, it was confirmed that the photocatalyst also have deactivation in continuous photo-reaction system as like a thermal catalytic reaction, due to disappearing of OH radical during reaction. In this result, we could suppose that the added H<sub>2</sub>O into the photoreaction over Fe/TiO<sub>2</sub> plays a role of the supplication of OH radical, which are responsible for the objective reactions.

In order to examine the structural stability during methanol decomposition over Fe/TiO<sub>2</sub>, XRD patterns

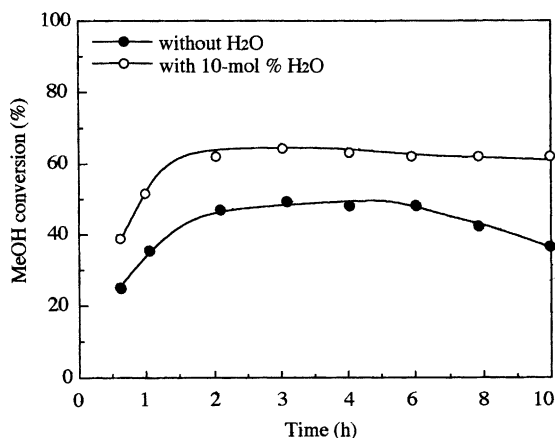


Fig. 10. Methanol decomposition with an increase of reaction time over Fe/TiO<sub>2</sub> catalyst. (a) Over Fe/TiO<sub>2</sub> catalyst without H<sub>2</sub>O addition, and (b) over Fe/TiO<sub>2</sub> catalyst with 10-mol% H<sub>2</sub>O addition as a reactant. Reaction conditions: methanol concentration, 200 ppm; catalyst weight, 3.0 g; UV-light intensity, 365 nm; 24 W/m<sup>2</sup>, 300 ml/min O<sub>2</sub>, continuous system.

of Fe/TiO<sub>2</sub> before and after reaction were measured, and the results are shown in Fig. 11. The specific peak of anatase structure was transferred into rutile structure with an increase of H<sub>2</sub>O addition. In particular, for 60 mol% H<sub>2</sub>O addition, the anatase structure was almost changed to rutile structure. From this result, we confirmed that the proper supplication of H<sub>2</sub>O into

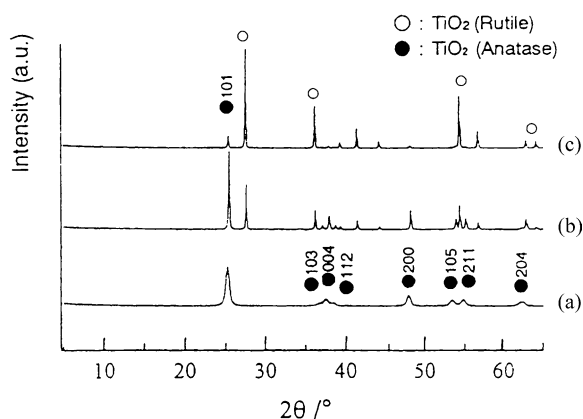


Fig. 11. The XRD patterns for Fe/TiO<sub>2</sub> used in Fig. 10 after photodecomposition of methanol. (a) TiO<sub>2</sub> anatase structure, (b) Fe/TiO<sub>2</sub> with 10-mol% H<sub>2</sub>O addition sample after 10 h, and (c) Fe/TiO<sub>2</sub> with 60 mol% H<sub>2</sub>O addition sample after 10 h.

methanol photodecomposition over Fe/TiO<sub>2</sub>, it could enhance the methanol decomposition.

#### 4. Conclusion

TiO<sub>2</sub> and Fe/TiO<sub>2</sub> particles with nanometer sizes were obtained by the solvothermal method: they exhibited a high photo-catalytic activity. Main conclusions are the following.

1. The TiO<sub>2</sub> and Fe/TiO<sub>2</sub> particles synthesized by solvothermal method exhibited uniform anatase structure with particle size below 50 nm after synthesis at 300 °C for 1 h without further treatments.
2. The Fe/TiO<sub>2</sub> particles prepared by solvothermal method have a higher hydrophilic property compared with TiO<sub>2</sub>.
3. The methanol conversion enhanced about 20% with H<sub>2</sub>O addition over Fe/TiO<sub>2</sub> oxide.
4. The anatase structure was stable in 10-mol% H<sub>2</sub>O addition as a reactant, but it was transferred into rutile structure with an increase of added H<sub>2</sub>O.

Therefore, in this study, it was found out that the structural change could be generated by H<sub>2</sub>O addition and, as the result, the partially structural change into rutile type could be better effected to photodegradation for methanol. In addition, we could reconfirm that the added H<sub>2</sub>O to the photoreaction over Fe/TiO<sub>2</sub> plays a role of the supplication of OH radical.

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