Surface Fluorination of Titanium Oxides and Applications

* Jae-Ho Kim1, Takashi Kimura2, Susumu Yonezawa3 and Masayuki Takashima4

1), 2), 3), 4) Department of Materials Science & Engineering, University of Fukui, Fukui 910-8507, Japan
1) kim@matse.u-fukui.ac.jp

ABSTRACT

The dispersion stability and photocatalytic activity of TiO2 particles were improved by the surface fluorination using fluorine gas (F2) at a pressure less than 50.5 kPa at 25°C. Average particle sizes and zeta potentials of fluorinated TiO2 (F-TiO2) particles in all solvents were approximately 11 times smaller and 1.5 times larger, respectively, than those of untreated TiO2 particles (2.5×10^3 nm and −19 mV). In the photocatalytic activity of TiO2, the UV–Vis absorption range of F3-TiO2 with Ti3+ and Ti2+ valences expanded to about 500 nm. Also, the degradation ratio of methylene blue (73%) with F-TiO2 was much higher than that (18%) with untreated TiO2 at 4 h. However, TiOF2 in F4-TiO2 synthesized at 200°C severely affected the dispersion stability and the photocatalysis of TiO2. To optimize the beneficial effects of surface fluorination considering the dispersion stability and photocatalytic activity, it is necessary to control the fluorine content (x), 0 < x < 0.5 in TiO2−xF2x.

1. INTRODUCTION

Nanosized TiO2 is one of the most promising photocatalysts currently available. To achieve high activities in solution-phase catalysis, it is important to facilitate good dispersion of the catalyst. [1–3]. However, small particles tend to aggregate, resulting in low or complete absence of photocatalytic activity. Many studies have focused on the dispersion stability of TiO2 particles in water [4–6]. Surface modification of TiO2 nanoparticles is an effective method to minimize the agglomeration of TiO2 particles [7–9]. Silane alkoxides with organic functional groups also have been widely used for this purpose. It is important to consider the high cost of surfactants required and the residues generated in the particles. Al2O3 and TiO2 metal oxide particles tend to disperse in a highly polar solvent; in contrast, they tend to flocculate in a low dielectric solvent because the Hamaker constant between the particles is high in such a solvent [10, 11]. TiO2 particles generally disperse well in water but not in other solutions such as acetone and ethanol. Many researchers have reported that the photocatalytic activity of TiO2 can be improved using various fluorinating agents other than F2 gas [12–14]. Park and Choi [15] reported that surface fluorination results in enhanced photocatalytic degradation of certain substrates because of the formation of electron trapping sites. Li et al. [16–18] attributed the enhanced photocatalytic activity of F-doped powders mainly...
to the creation of surface oxygen vacancies and the beneficial effects of F-doping. Yu et al. [19] also reported the incorporation of fluoride ions into a TiO$_2$ lattice using an NH$_4$F source. However, the surface fluorination of TiO$_2$ could have either a positive or negative effect depending on the fluorine contents in TiO$_2$ particles. The relationship between the photocatalytic activity and fluorine contents in TiO$_2$ using F$_2$ gas has not been reported. Our previous work proved that surface fluorination using F$_2$ gas is beneficial to the dispersion stability of TiO$_2$ particles in water [20]. F-TiO$_2$ particles with good dispersion stability were synthesized at a temperature lower than 100°C using fluorine gas. The idea was to stabilize the TiO$_2$ particles by enabling their surfaces to carry an electric charge to create electrostatic repulsive forces that repel each other.

In this paper, we report the effects of surface fluorination on the dispersion stability of TiO$_2$ in various organic solvents and also investigate the relationship between fluorine contents in TiO$_2$ and the photocatalytic activity of TiO$_2$.

2. EXPERIMENTAL DETAILS

2.1 Preparation of fluorinated TiO$_2$ samples

TiO$_2$ particles (ST-21, anatase; 98% purity) were obtained from Ishihara Sangyou Kaisha, Ltd. Fluorine gas (99.5% purity) was supplied by Daikin Industries Ltd. Details of the fluorination apparatus have been given in our previous paper [21, 22]. Fluorinated TiO$_2$ (F-TiO$_2$) particles were prepared by direct fluorination using F$_2$ gas under various reaction conditions. Reaction temperature, fluorine pressure, and reaction time were set at 25–200°C, 1–50 kPa, and 1 h, respectively.

2.2 Catalysts characterization

The structural and electronic properties of the samples were investigated using powder X-ray diffraction (XRD, XD-6100) and X-ray photoelectron spectroscopy (XPS, XPS-9010). The surface morphology of various samples was observed using a scanning electron microscope (SEM, s-2400; Hitachi Ltd.). The BET surface area was determined using a Micromeritics ASAP 2000 nitrogen adsorption apparatus.

2.3 Dispersion stability measurements

Particle size distribution and zeta potential profiles were measured using a zeta-potential/particle-size measurement device (Otsuka Electronics Co., Ltd, ELSZ-2). A solid sample was suspended in distilled water, ethanol (99.5%, Kanto Chemical Co., Inc.), and acetone (99.0%, Kanto Chemical Co., Inc.). The pH of the suspension was adjusted using a 1M NaOH or HCl solution. The dispersion stability of samples in various solvents was determined by a sedimentation experiment. A typical procedure was used to prepare the suspension; first, 15 mg of TiO$_2$ was mixed with 15 mL solvents and sonicated for 1 h.

2.4 Photocatalytic activity measurements

The UV–Vis absorption spectra of samples were recorded on a Hitachi U-3900H spectrophotometer with an integrating sphere assembly. The photocatalytic activity of samples was evaluated using the photocatalytic decomposition of methylene blue (MB, C$_{16}$H$_{18}$C1N$_3$S) [23]. Samples (5 mg) were dispersed in a methylene blue (1 × 10$^{-5}$ mol/L)
aqueous solution (50 mL). Three milliliters of test liquid was taken from this solution and fed into a quartz cell. The test solution was irradiated at 365 nm by an ultraviolet lamp (Spectroline Spectronics, 4W), and the absorbance at 665 nm, which is the maximum absorption wavelength of methylene blue, was measured using a UV–Vis spectrometer (U-3900H). The decomposition rate of methylene blue containing samples was evaluated from the absorbance obtained with irradiation times.

3. RESULTS and DISCUSSION

3.1 Characterization of samples

Sample names, reaction conditions, total surface area (BET), and fluorine contents (x) in TiO$_{2-x}$F$_{2x}$ are summarized in Table 1, in which, fluorinated TiO$_2$ (F-TiO$_2$) samples prepared at various reaction conditions with F$_2$ gas were named as the F1-TiO$_2$, F2-TiO$_2$, F3-TiO$_2$, and F4-TiO$_2$, respectively. The fluorine contents in surface region of F-TiO$_2$ particles were evaluated from the XPS data. Fluorination temperature and F$_2$ pressure were increased to enhance the fluorine contents (x) in TiO$_{2-x}$F$_{2x}$. At a temperature higher than 200°C, x became 1.10, which suggests the formation of TiOF$_2$. The relative surface area of the samples was determined by the BET method. The BET surface areas of fluorinated TiO$_2$ samples were in the range of 56.4–61.3 m$^2$/g, which are obviously higher than that of untreated TiO$_2$ (54.6 m$^2$/g).

Table 1. Reaction conditions of TiO$_2$ particles treated with F$_2$ gas and the fluorine contents (x) in TiO$_{2-x}$F$_{2x}$.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Temperature (°C)</th>
<th>F$_2$ pressure (kPa)</th>
<th>Time (h)</th>
<th>Total surface area (BET, m$^2$/g)</th>
<th>x in TiO$<em>{2-x}$F$</em>{2x}$ $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>54.6</td>
<td>0.00</td>
</tr>
<tr>
<td>F1-TiO$_2$</td>
<td>25</td>
<td>1.3</td>
<td>1</td>
<td>56.4</td>
<td>0.13</td>
</tr>
<tr>
<td>F2-TiO$_2$</td>
<td>25</td>
<td>6.7</td>
<td>1</td>
<td>61.3</td>
<td>0.18</td>
</tr>
<tr>
<td>F3-TiO$_2$</td>
<td>25</td>
<td>50.5</td>
<td>1</td>
<td>57.2</td>
<td>0.44</td>
</tr>
<tr>
<td>F4-TiO$_2$</td>
<td>200</td>
<td>50.5</td>
<td>1</td>
<td>55.9</td>
<td>1.10</td>
</tr>
</tbody>
</table>

$^a$ Fluorine contents (x) in TiO$_{2-x}$F$_{2x}$ were evaluated from XPS results shown in Fig. 3.

The effects of reaction temperature and F$_2$ pressure on the TiO$_2$ crystal structure are shown in Fig. 1 (A). Only a single phase of anatase TiO$_2$ was observed when fluorination was performed at room temperature (25°C). Fluorination did not cause any shift in the peak position of the TiO$_2$ phase. This is easily understood because the ionic radius of the fluorine atom (0.133 nm) is nearly the same as that of the replaced oxygen atom (0.132 nm) [16]. However, as shown in Fig. 1 (B), the peak intensity ratio of (101)/(200) shown in Fig. 1 (A) decreased when fluorine pressure increased to 5.5 kPa. This indicates that the crystallinity of TiO$_2$ gradually decreased by the fluorine substitution. After the fluorination temperature was increased from 25°C to 200°C, some
peaks (●) assigned to TiOF\textsubscript{2} appeared for F4-TiO\textsubscript{2} (TiO\textsubscript{2-x}F\textsubscript{2x}, x = 1.10). SEM images of untreated and fluorinated TiO\textsubscript{2} samples are presented in Fig. 2. As seen from Fig. 2 (A) and (C), obvious agglomerates composed of TiO\textsubscript{2} particles with an approximate size of 20 nm were found in all samples. The fluorination effect on the surface morphology of TiO\textsubscript{2} particles could not be detected in the SEM images. However, XPS data confirm the existence of fluorinated surface layer of TiO\textsubscript{2} particles as shown in Fig. 3.

Fig. 3 shows F 1s (A and B), Ti 2p (C), and O 1s (D) spectra of untreated and fluorinated TiO\textsubscript{2} samples. All binding energies were calibrated to the C 1s peak at 284.8 eV of carbon. An F 1s peak located at the binding energy (BE) of 684.3 eV was observed in all F-TiO\textsubscript{2} samples, as shown in Fig. 3 (A). However, the peak at 684.3 eV disappeared after Ar\textsuperscript{+} ions etching, as shown in Fig. 3 (B). Because the fluorine at 684.3 eV is assigned to fluorine atoms chemically adsorbed on TiO\textsubscript{2} surface, they can be easily eliminated by low-energy argon etching (300 V, 5 s). Moreover, an asymmetrical F 1s peak was observed for F3-TiO\textsubscript{2} and F4-TiO\textsubscript{2} samples, where a tailing peak could be found. This means that various chemical forms of F atoms might exist in the samples. Therefore, the F 1s peaks of F3-TiO\textsubscript{2} and F4-TiO\textsubscript{2} samples were deconvoluted into two separated peaks with Gaussian distributions, as shown in Fig. 3 (A). The peak located at 685.2 eV was attributed to the F atom in TiOF\textsubscript{2} [17]. This is easily understood in case of F4-TiO\textsubscript{2} because an obvious TiOF\textsubscript{2} phase appeared in the XRD patterns, as shown in Fig. 1. The peak located at 687.2 eV may be attributed to substituted fluorine atoms in TiO\textsubscript{2-x}F\textsubscript{2x} [24]. In the case of Ti 2p (C), the Ti (IV) 2p\textsubscript{1/2} and Ti (IV) 2p\textsubscript{3/2} spin-orbital splitting
photoelectrons of the original TiO$_2$ were located at binding energies of 464.9 eV and 458.9 eV, respectively. However, in the XPS spectrum after fluorination at 25 °C, the peak of Ti 2p$_{3/2}$ shifted to an energy lower than that of original TiO$_2$. This result showed that the valence state of Ti$^{4+}$ (458.9 eV) gradually changed to Ti$^{3+}$ (457.0 eV) with increasing F$_2$ pressure. In the case of F3-TiO$_2$, a Ti 2p$_{3/2}$ peak due to Ti$^{2+}$ (455.2 eV) is especially evident in Fig. 3 (C). Furthermore, when the reaction temperature was increased from 25 °C to 200 °C, the Ti 2p$_{3/2}$ peak of F4-TiO$_2$ shifted to high energy with the creation of Ti–F bond (461.2 eV) of TiOF$_2$. Fig. 3 (D) shows the peaks of various samples found at 530.6 eV. The peak intensity decreased with increasing of F$_2$ pressure. In case of F4-TiO$_2$, similar in the F 1s and Ti 2p peaks, the O 1s peak shifted to higher energy. This result seems to be related to the formation of TiOF$_2$, as indicated in Fig. 1.

3.2 Dispersion stability of samples

Fig. 4 shows the suspension of samples dispersed in water (A), and ethanol (B) as polar protic solvents and acetone (C) as a polar aprotic solvent over retention times. In the untreated TiO$_2$ suspension (a), TiO$_2$ particles reformed into large agglomerates within 4 h in all solvents. Especially in ethanol (24.3) and acetone (20.7), which have a lower dielectric constant than water (78.3) [10], decreased turbidity in the untreated TiO$_2$ suspension (a) was observed within 1 h. The dielectric constant of a substance is closely related to the dipole moment. Also, the polarity of a substance with a high dielectric constant is considered to be large. The dispersion stability of
fluorinated TiO\textsubscript{2} could be sustained in all solvents for 24 h. The stability of colloidal suspensions is primarily governed by interparticle (or surface) forces, especially by the repulsive electrostatic interaction of these charges. Because fluorine at TiO\textsubscript{2} surface has high electronegativity and high acidity, it changes the OH at TiO\textsubscript{2} surface to O\textsuperscript{−} by releasing H\textsuperscript{+} and/or the fluorine (F) changes into the fluoride ion (F\textsuperscript{−}) by taking the electron (e\textsuperscript{−}) from the O\textsuperscript{−}. That is, the surface of F-TiO\textsubscript{2} particles becomes negatively charged and enhances the repulsive interaction between F-TiO\textsubscript{2} particles, as shown later in Fig. 6. Consequently, surface fluorination can alter the particle-particle interactions. However, the formation of TiOF\textsubscript{2} (e) in TiO\textsubscript{2} particles could adversely affect the dispersion stability in all solvents, as shown in Fig. 4.

Fig. 5 depicts the effects of surface fluorination on the particle size (A) and zeta potential (B) of TiO\textsubscript{2} particles in water (■), ethanol (◆), and acetone (▲) at a constant pH of 6.5. The average size and zeta potentials of TiO\textsubscript{2} particles fluorinated at 25°C in all solvents were approximately 11 times smaller and 1.5 times larger, respectively, than those (2.5×10\textsuperscript{3} nm and −19 mV) of untreated TiO\textsubscript{2} particles. Therefore, it can be said that the fluorinated particles can be stabilized against agglomeration by electrostatic forces because the charges increased by surface fluorination are able to create electrostatic repulsion between the particles. However, the dispersion stability of TiO\textsubscript{2} samples (e) fluorinated at 200°C decreased owing to the formation of TiOF\textsubscript{2} film at the particle surface. To improve the dispersion stability of TiO\textsubscript{2} particles, it is important to control the surface fluorination to maintain the state of fluorine adsorbed or partly bonded on the TiO\textsubscript{2} surface without TiOF\textsubscript{2} formation because the high electronegativity and high acidity of fluorine increase the repulsive interactions between TiO\textsubscript{2} particles that is related to dispersion stability in solvents.

3.3 Photocatalytic activity of samples

Surface fluorination obviously affects the UV-Vis absorption characteristics of TiO\textsubscript{2}, as shown in Fig. 6. The absorption spectra of the fluorinated TiO\textsubscript{2} samples showed a stronger absorption in the UV-Vis range and a red shift in the band gap transition than untreated TiO\textsubscript{2}. This is probably because surface fluorination can expand the wavelength response range of TiO\textsubscript{2} to the visible region. For example, the wavelength range of F3-TiO\textsubscript{2} samples containing Ti\textsuperscript{3+} and Ti\textsuperscript{2+} valences, as shown in Fig. 3 (C), could expand to approximately the 500 nm range owing to a downshift of the conduction band edge. However, in the case of F4-TiO\textsubscript{2} samples, the wavelength range became narrower than that of F3-TiO\textsubscript{2}, as indicated in Fig. 6. Also the decrease of surface area
caused by the TiOF$_2$ formation may seriously affect the wavelength response range. To compare the photocatalytic activity of untreated and fluorinated TiO$_2$, the MB degradation reaction was performed and the results are shown in Fig. 7. The MB degradation ratio (73%) with fluorinated TiO$_2$ was much higher than that (18%) with untreated TiO$_2$ (○) at 4 h. As suggested by Yang [25], a large number of holes created in fluorinated TiO$_2$ (F-TiO$_2$) yields many hydroxyl radicals:

$$\text{hv}^+ + \text{H}_2\text{O}_{\text{ad}} \rightarrow \text{H}_2\text{O}^+ \text{(on F-TiO}_2\text{)} \quad (1)$$
$$\text{H}_2\text{O}^+ \rightarrow \text{H}^+ + \text{OH}_{\text{free}}^- \text{(on F-TiO}_2\text{)} \quad (2)$$
$$\text{hv}^+ + \text{Ti-OH}_{\text{surf}} \rightarrow \text{Ti-OH}_{\text{surf}}^- \text{(on untreated TiO}_2\text{)} \quad (3)$$

The preferential formation of free OH radicals on F-TiO$_2$ should subsequently oxidize the MB molecules and the adsorbed amount of MB near the surface will increase simultaneously. Consequently, the photocatalytic activity is enhanced by surface fluorination. In particular, the photocatalytic activity of the F3-TiO$_2$ sample (●) was superior to other samples because the Ti$^{3+}$ and Ti$^{2+}$ conduction band edges in F3-TiO$_2$ can trap the photogenerated electrons and lead to the reduction of the recombination rate between excited electrons and holes.

4. CONCLUSIONS

We have reported the effects of surface fluorination on the dispersion stability and photocatalytic activity of TiO$_2$ particles. Fluorinated TiO$_2$ (F-TiO$_2$) was successfully prepared by direct fluorination using F$_2$ gas. The fluorine contents (x) in TiO$_2$-$x$F$_{2x}$ were primarily dependent on the reaction temperature and fluorine pressure. At room temperature (25°C) and fluorine pressure lower than 6.7 kPa, the fluorine contents (x) were controlled below 0.18, and the fluorine was chemically adsorbed on the TiO$_2$.
surface. At 200 °C, the fluorine content (x) in TiO$_{2-x}$F$_{2x}$ increased to 1.10 and the existence of TiOF$_2$ was confirmed. The chemically adsorbed fluorine on the TiO$_2$ surface might play a positive role both toward the dispersion stability and photocatalysis. Especially for the photocatalytic activity of TiO$_2$, F$_3$-TiO$_2$ with Ti$^{3+}$ and Ti$^{2+}$ valences could expand to approximately 500 nm of the UV−Vis range, and the photocatalytic activity of F$_3$-TiO$_2$ was also 4 times higher than the MB degradation ratio (18%) of untreated TiO$_2$. However, the dispersion stability and photocatalysis of F$_4$-TiO$_2$ prepared at 200 °C was negatively affected by the formation of TiOF$_2$. Therefore, considering the dispersion stability and photocatalytic activity of TiO$_2$, it is essential to control the fluorine contents (x), 0 < x < 0.5 in TiO$_{2-x}$F$_{2x}$ to optimize the beneficial effects of surface fluorination.

REFERENCES


