Relationship between the photocatalytic activity and crystallographic orientation of rutile TiO$_2$ single crystals

Yasuro IKUMA,† Seiya OGOE, Yousuke WATANABE, Koichi NIWA, Hiroo TAJIRI* and Osami SAKATA*

Kanagawa Inst. of Tech., Atsugi, Kanagawa 243-0292, Japan
*JASRI, Sayo, Hyogo 679-5198, Japan

Although photocatalytic activity of TiO$_2$ is mainly discussed in terms of the band gap energy, the importance of surface oxygen for the decomposition of chemicals on the photocatalyst is emphasized in several reports. The availability and stability of the surface oxygen atoms on TiO$_2$ crystals depend on the surface orientation of the crystals. In this study, rutile TiO$_2$ single crystals with different orientations are used and we evaluate the progress of photocatalytic decomposition reactions by the weight loss of the salad oil and linoleic acid due to formation of gaseous species. If the surface of rutile TiO$_2$ single crystals is not reconstructed and surface oxygen is involved, the orientation of the surface affects the photocatalytic activity of TiO$_2$; the photocatalytic activity increases in the order of (114) < (100) < (101) < (001).

©2013 The Ceramic Society of Japan. All rights reserved.

Key-words : Photocatalyst, Surface orientation, Rutile TiO$_2$, Single crystal

When titanium dioxide (TiO$_2$) crystal is exposed to UV light, it exhibits photocatalytic activity$^1$ and hydrophilic behavior$^2$ at the crystal surface. The available literature explains the photocatalytic activity of TiO$_2$ is mainly discussed in terms of the band gap energy,$^3$5,6) because a light with a certain energy is required to promote electrons from the valence band to the conduction band. The electron–hole pairs created are used to reduce and oxidize chemicals that are near the photocatalyst.

There are, however, other factors that are also important for the photocatalytic activity of TiO$_2$. The importance of surface oxygen for the decomposition of chemicals on the photocatalyst is emphasized in some reports.$^3,5,6$ Wilson and Idriss$^5,6$ have shown that the oxygen of TiO$_2$ is involved in the decomposition reaction of acetic acid at the surface. An electron at the surface reacts with an oxygen molecule in the gas phase to produce O$_2$ minus radical (O$_2$$^-$) which then reacts with chemicals on the surface to form other intermediates. The final reaction products are CH$_3$/C$_2$H$_4$ and CO$_2$. The main reactions are as follows:$^7$

\[
\begin{align*}
\text{CH}_3\text{COOH} \text{ (Ads.)} & \rightarrow \text{CO}_2\text{(g)} + \text{CH}_4\text{(g)} \quad (1) \\
2\text{CH}_3\text{COOH} \text{ (Ads.)} + \text{O}_2 & \rightarrow 2\text{CO}_2\text{(g)} + \text{CH}_4\text{CH}_2\text{(g)} + \text{H}_2\text{O(g)} + \text{V}_0 \quad (2) \\
\text{V}_0 + 1/2\text{O}_2 \text{ (Ads.)} & \rightarrow \text{O}_4 \quad (3)
\end{align*}
\]

Reaction (2) suggests that surface oxygen atoms (O$_4$) on TiO$_2$ crystals play an important role in the decomposition (or oxidation) of acetic acid.

Although surface atoms or ions, which are energetically unstable, are surrounded by fewer atoms or ions compared to bulk atoms or ions, the availability and stability conditions of the surface oxygen atoms on TiO$_2$ crystals depend on the surface orientation of the crystals. Loweckamp et al.$^8$ have reported the orientation dependence of photocatalytic reactions on TiO$_2$ film surfaces and the anisotropic photocatalytic reaction on polycrystalline TiO$_2$.$^9$ In the two papers, they studied the following reaction:

\[
\text{Ag}^{+} + \text{e}^- \rightarrow \text{Ag} \quad (4)
\]

Their findings showed that TiO$_2$ grains with the (100) and (110) rutile TiO$_2$ surfaces have lower photoreduction rates than those with the (101), (111) and (001) surfaces, and that the most reactive surfaces lie near the {101} group surfaces.

Since reaction (4) does not involve oxygen at the surface of TiO$_2$, we are very interested in determining how the condition of surface oxygen affects the rate of reaction such as that of reaction (2). There are significant evidences in the literature$^5,8,10$ on the reconstruction of rutile TiO$_2$ single crystal surfaces after annealing at high temperatures. Therefore, in this study, the effect of surface orientation on the reactivity of TiO$_2$ is studied by the decomposition (or oxidation) of salad oil and other organic compounds on TiO$_2$. Salad oil was chosen for this study based on the fact that photocatalytic reactivity was characterized by the decomposition (or oxidation) of salad oil previously.$^{11}$

We evaluate the progress of photocatalytic reactions such as reactions (1) and (2) by the weight loss of the salad oil due to formation of gaseous species.

Accordingly, the crystallographic orientation effect of rutile TiO$_2$ single crystals on the photocatalytic activity of TiO$_2$ was studied by investigating the decomposition (or oxidation) of salad oil and linoleic acid. The crystals used in this study were TiO$_2$ single crystals with (001), (100), (101) and (114) surfaces (Shinkosha Co., Yokohama, Japan). These crystals were polished to obtain a flat surface with a thickness of 633 nm (the difference between the highest and lowest points) within an area of 10 mm × 10 mm. As a reference, a glass having no reactive surfaces was also used. The crystals were first submerged in 1 mol/L hydrochloric acid solution. They were placed in ethanol and subsequently in water. Finally, they were dried by exposing to UV light. These treatments ensured that the surface was not reconstructed.

For the decomposition (or oxidation) experiment, approximately $4.0 \times 10^{-3}$ g of salad oil and linoleic acid were placed on the surface of TiO$_2$ single crystals. The combined weight was
measured. The sample was placed in an UV light apparatus (Ushio, SP9-250, maximum intensity at the wavelength of 366 nm) for 60 min to expose the surface of single crystal TiO₂ to UV light, and then the combined weight was measured again. The crystal was subsequently placed in the UV light apparatus for UV irradiation. This process was repeated for different radiation durations.

Optical microscopic and Raman spectroscopic (Kaiser Co.) analyses of the salad oil and linoleic acid before and after UV irradiation on the TiO₂ crystals were conducted. For this experiment, the (100) and (001) surfaces were chosen.

The results of the salad oil weight measurement are shown in Fig. 1. For Fig. 1(a), the salad oil was placed on the glass. Since a glass surface does not have photocatalytic activity, no weight change of the salad oil on the glass surface after exposure to UV light is expected; i.e., decomposition (or oxidation) of the salad oil would not occur and the weight should be constant. This prediction is confirmed by the results shown in Fig. 1(a) that indicate no drastic weight change, but rather a gradual increase in weight. The results obtained on the different surfaces of rutile TiO₂ are shown in Fig. 1(b). The results of the (114) and (100) surfaces are almost the same as those of glass, indicating that no photocatalytic reaction occurred. A decrease in the weight of the salad oil on the (101) surface was observed. Since the main ingredient of salad oil is linoleic acid, we also performed a similar experiment on linoleic acid to confirm the results on the salad oil. The results are shown in Fig. 2. The weight of the linoleic acid on the (114) surface is almost constant. This is the same as the weight change of the salad oil on the (114) surface [Fig. 1(b)]. The weight of the linoleic acid on the (100) surface decreases slightly after 900 min of exposure. This is not the same as the weight change of the salad oil on the (100) surface. The weight of the linoleic acid on the (101) surface changes almost in the same way as the weight of the salad oil on the (101) surface. The weight of the linoleic acid on the (001) surface changes significantly, especially during the first 500 min of exposure to UV light.

The optical microscopic observations of the (100) and (001) surfaces are shown in Fig. 3. Figure 3(a) shows the edge of the salad oil before UV irradiation observed using an optical microscope. The upper region of the picture is the surface of TiO₂ and the lower region is the surface of the salad oil. The boundary of these two regions is very distinct. The edge of the salad oil on the (001) surface after UV irradiation for 3780 min is shown in Fig. 3(b). In this case, the sample weight [Fig. 1(b)] only slightly changes. We observed some slight color changes at the very edge of the salad oil. The edge of the salad oil on the (001) surface after UV irradiation for 3780 min, is given in Fig. 3(c). The curved gray region where the original salad oil exists is not due to the decomposition of salad oil. It is simply due to the point of observation. In this figure, the edge of the salad oil is not clear, and in some cases, the oil extends into the area of the TiO₂ surface. Comparing Figs. 3(b) and 3(c), we may conclude that the salad oil on the (001) surface was most probably decomposed (or oxidized).

Raman spectroscopic analysis was conducted on the salad oil. The results for the (001) surface are shown in Fig. 4. The Raman spectroscopic results of the salad oil before UV irradiation indicate the presence of cis-CH=CH-₂, -CH₂-, -CH=CH₂, and -COOH. After UV irradiation for 1240 and 2440 min, most of them disappeared. Although the result of Raman spectroscopy is qualitative rather than quantitative, we may conclude that the results are consistent with the results shown in Figs. 1, 2 and 3.

Combining the results of Figs. 1(b), 3 and 4, we may conclude that the salad oil on the rutile (001) surface changed after UV irradiation and that the change resulted in the weight decrease of the salad oil. Since the weight changes of the linoleic acid and observed.
salad oil are correlated with each other, the major weight loss in the salad oil is caused by the decomposition (or oxidation) of linoleic acid. An oxidation reaction similar to reaction (2) might have occurred. In order to write a proper chemical reaction, we need to further study the reaction from a different viewpoint.

Lowekamp et al. have reported a qualitative study on polycrystalline TiO$_2$. Their results and the current results are compared qualitatively in Table 1. Although the results of the two studies are generally in agreement with each other, there are still differences. In particular, the activity on the (114) surface for the two studies is not the same. The decomposition (or oxidation) reaction of this study involves oxygen. However, the reaction of Lowekamp et al. does not involve oxygen. Another difference between these two studies is that our TiO$_2$ was not heated after polishing, and therefore the surface was not reconstructed, while in Lowekamp et al. study, TiO$_2$ (sintered at 1600°C) was polished and then etched in air at 1200°C. Consequently, the surface of their sample was reconstructed. These differences in the photocatalytic reaction and sample condition are considered to be the cause for the different results shown in Table 1.

While studying the decomposition (or oxidation) reaction of acetic acid, Wilson and Idriss showed that the (011)-facetted (001) surface is photocatalytically active and the (114)-facetted (001) surface is not. In Figs. 1 and 2, another trend was also observed: the (101) [or (011)] surface is more active than the (114) surface.
We may conclude that if the surface of rutile TiO$_2$ single crystals was not reconstructed and O$_2$ is involved, the orientation of the surface affects the photocatalytic activity of TiO$_2$; the photocatalytic activity increases in the order of (114) < (100) < (011) < (001).

What is so special about the rutile TiO$_2$ (001) surface? According to Fujishima, the (001) crystal in Ref. 1 was not intentionally chosen. At the time, only this crystal was available. Some of the current authors have studied the structure of the reconstructed (001) surface by surface X-ray diffraction at the SPring-8 facility. The results revealed that experimentally determined crystal truncation rod (CTR) of the (001) surface at the primitive $1 	imes 1$ structure does not fit the surface created simply by cutting the bulk crystal at the (001) plane (This is close to the polished surface). When the (011) facet was introduced to the (001) surface while still maintaining the $1 	imes 1$ structure, the fit between the experimental CTR of the (001) surface with the $1 	imes 1$ structure and the calculated CTR of the surface became much better. The results indicate that the (001) surface, when reconstructed, is composed of (011) facets. However, the results in Figs. 1 and 2 indicate that the (101) [or (011)] surface is not better than the (001) surface. Since the polished rutile TiO$_2$ (001) surface is not a stable surface among the low indexed rutile surfaces, unstableness of the polished (001) surface could be an important factor for the photocatalyst.

Effect of surface orientation on the properties of both rutile and anatase TiO$_2$ has been discussed in the literature. Kavan et al. prepared rutile and anatase TiO$_2$ single crystals and studied the electrochemical and photoelectrochemical properties of these crystals. They claimed that anatase (101) and rutile (001) electrodes differ mainly in the position of the conduction band edge. Similar difference in conduction band edge could in part be responsible for the results presented in Figs. 1 and 2. To confirm this, we need further investigation. Wang et al. studied the surface wettability conversion of rutile TiO$_2$ single crystal surfaces. Using (110), (100) and (001) surfaces, they concluded that bridging site oxygen played an important role in the surface wettability conversions. The lack of bridging site oxygen on (001) surface was thought to be the reason for the slow conversion of the surface wettability in (001) surface compared with (110) and (100) surfaces. As they discussed, the defect sites on the (001) surface are more unstable when compared with the (110) and (100) surfaces. Since the unstableness of the surface would provide more oxygen which can serve as surface oxygen shown in Eq. (2), the decomposition (or oxidation) of salat oil on the (001) surface must be promoted. This is consistent with the results of this study. Ohno et al. investigated reduction of H$_2$PtCl$_6$ to Pt and oxidation of Pb$^{2+}$ ions into PbO$_2$ on rutile particles with (110) and (011) surfaces. They concluded that the oxidation site on the rutile particles is (011) surface and the reduction site is (110) surface. Since both (110) and (011) surfaces were exposed to their reactants, oxidation reaction (or reduction reaction) would take place on the surface where it is easier to occur. However, in our case the reactant was placed only on one face. Consequently both reduction and oxidation reactions must take place only on one surface and it is not straightforward to compare our results with the results of Ohno et al. Nevertheless photocatalytic activity (oxidation) on (101) [or (011)] obtained in this study is relatively high, possibly due to the contribution from the oxidation of (101) [or (011)] surface. The fact that (001) surface has higher activity for oxidation is due to the unstableness of the surface. Some of surface oxygen atoms are easily removed and used for the oxidation reaction.

Acknowledgement This work was supported in part by a Grant-in-Aid for Scientific Research (C) No. 23560807 from the Japan Society for the Promotion of Science.

References

13) A. Fujishima, private communication.

<table>
<thead>
<tr>
<th>Surface of crystal</th>
<th>(114)</th>
<th>(100) or (010)</th>
<th>(101) or (011)</th>
<th>(001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lowellamp et al.</td>
<td>M or H</td>
<td>L</td>
<td>H</td>
<td>M or H</td>
</tr>
<tr>
<td>Salad Oil (current study)</td>
<td>L</td>
<td>L</td>
<td>M</td>
<td>H</td>
</tr>
<tr>
<td>Linoleic acid (current study)</td>
<td>L</td>
<td>M</td>
<td>M</td>
<td>H</td>
</tr>
</tbody>
</table>