Kinetics of Photoinduced Hydrophilic Conversion Processes of TiO$_2$ Surfaces

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We present a theoretical method to analyze photoinduced hydrophilic conversion processes of TiO$_2$ surfaces, and apply it to recent experimental results of Sakai et al. (*J. Phys. Chem. B* **2003**, *107*, 1028). According to Young's theory, the cosine of the contact angle is a function of the interfacial energy between the solid and the liquid, which in turn changes with the surface fraction of hydrophilic regions. As the photoreaction proceeds, the surface fraction of hydrophilic regions increases, which lowers the interfacial energy between the solid and the liquid, resulting in the lowering of the contact angle. Therefore, the cosine of the contact angle is more appropriate to extract both the rates of hydrophilic conversion processes and the rates of back-processes, compared with the reciprocal of the contact angle proposed empirically by Sakai et al. Our method provides a quantitative way to analyze the kinetics of both photoinduced hydrophilic conversion processes and the back-processes to the hydrophobic states during long-term storage in the dark.

I. Introduction

Recently, photoinduced hydrophilic conversion of titanium dioxide (TiO$_2$) has been discovered and TiO$_2$ coating is shown to have antifogging and self-cleaning properties.[1−7] The TiO$_2$ surface becomes highly hydrophilic upon irradiation with UV light whose energy exceeds the band gap of TiO$_2$.[5,6] The contact angle of a water droplet on the TiO$_2$ surface decreases almost up to 0° under the irradiation with UV light for both rutile TiO$_2$ single crystal and polycrystalline TiO$_2$ (anatase), independent of their photocatalytic activities.[2,3] The hydrophilic surface gradually turns hydrophobic again in the dark. The contact angle increases up to more than 50° for both the TiO$_2$ substrates after long-term storage in the dark.[2,3] Extensive studies have been performed to understand the reaction mechanism that causes such drastic changes of surfaces.[4−6,8] It was found that the hydrophilic conversion processes depend strongly on the wavelength of irradiated lights. The wavelength of irradiated lights should be smaller than 382 nm to induce hydrophilic conversion, which indicates that the photoinduced hydrophilic conversion requires the band gap excitation of holes and electrons inside TiO$_2$.[5,6] If hole scavengers are added, competition between the hydrophilic conversion processes and the hole scavenging reactions occurs and the smallest contact angle accessible increases.[5,6] The photoinduced hydrophilic conversion of TiO$_2$ in aqueous electrolyte under potential-controlled conditions indicates that photogenerated holes trigger subsequent reactions.[5] The photogenerated electrons do not play an important role in the process.[5] Further experiments suggest that the hydrophilicity is mainly due to the increase of the surface hydroxyl groups formed by the photogenerated holes.[6] However, the issue is still controversial.[9]

Although the reaction mechanism has been extensively studied, no reasonable method to analyze the kinetics of hydrophilic conversion processes has yet been established. Sakai et al. empirically found a linear relation between the reciprocal of the contact angle and the light irradiation time.[6] However, this relation has no theoretical basis. In addition, the reciprocal of the contact angle is not a linear function of time for the reverse process in the dark. In this paper we present a theoretical method to analyze photoinduced hydrophilic conversion processes of TiO$_2$ surfaces. In this method the cosine of the contact angle is used to describe the kinetics of hydrophilic conversion process and the reverse process. According to Young's theory the cosine of the contact angle is a function of the interfacial energy between the solid and the liquid, which in turn changes with the surface fraction of hydrophilic regions.[10] As the photoreaction proceeds, the surface fraction of hydrophilic regions increases, which lowers the interfacial energy between the solid and the liquid, resulting in the lowering of the contact angle. Therefore, the cosine of the contact angle is more appropriate to extract both the rates of hydrophilic conversion processes and the rates of back-processes, compared with the reciprocal of the contact angle proposed empirically by Sakai et al.[6] We reanalyze the experimental results of Sakai et al. to extract the rates of photoinduced hydrophilic conversion processes and the reverse processes to the hydrophobic states during long-term storage in the dark.[6] Our method provides a quantitative way to analyze both processes and is applicable to search the factors controlling the processes, such as competition between the forward reactions and the back-reactions and surface heterogeneity, and to elucidate the detailed reaction mechanism.

II. Theoretical Method

The contact angle of a liquid droplet on a solid surface is a result of a force balance among three interfacial tensions,[10−12]

$$\gamma \cos \theta = \gamma_{SG} - \gamma_{SL} \qquad (2.1)$$

where γ is the surface tension of liquid (interfacial energy between the liquid and the gas), γ_{SG} is the interfacial energy between the solid and the gas, and γ_{SL} is the interfacial energy between the solid and the liquid. When the surface is irradiated with UV light, hydrophobic regions are converted into hydrophilic ones, which reduces the interfacial energy between the solid and the liquid.

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The simplest possible relation between the interfacial energy, $\gamma_{SG} - \gamma_{SL}$, and the surface fraction of hydrophilic regions, c, is a linear relation,

$$\gamma_{SG} - \gamma_{SL} = \gamma_1 c + \gamma_2 \qquad (2.2)$$

Then, Young's equation, eq 2.1, can be rewritten as

$$f \equiv \cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma} = f_1 c + f_2 \qquad (2.3)$$

where $f_1 \equiv \gamma_1/\gamma$ and $f_2 \equiv \gamma_2/\gamma$. When $c = 0$, $\cos\theta$ has the value of f_2, whereas at $c = 1$ it has a value of $f_1 + f_2$. The hydrophilic regions turn back to hydrophobic in the dark. When both the hydrophilic conversion and its back-reaction are characterized by single rate constants, the kinetics of the change of the surface fraction of hydrophilic regions is given by

$$\frac{\partial}{\partial t}c(t) = k_f(1 - c) - k_b c \qquad (2.4)$$

where k_f is the forward reaction rate constant and k_b denotes the backward reaction rate constant. By substituting the solution of eq 2.4 into eq 2.3 the time evolution of the value of $\cos\theta$ under the irradiation with UV light is obtained as

$$f(t) = f_1\left[\frac{k_f}{k_f + k_b} - \left(\frac{k_f}{k_f + k_b} - c(0)\right)\exp\{-(k_f + k_b)t\}\right] + f_2 \qquad (2.5)$$

The value of $\cos\theta$ increases from the initial value,

$$f(t=0) = f_1 c(0) + f_2 \qquad (2.6)$$

to the final value corresponding to the saturated hydrophilicity,

$$f(t \rightarrow \infty) = \frac{f_1 k_f}{k_f + k_b} + f_2 \qquad (2.7)$$

On the other hand, in the dark the value of $\cos\theta$ decays according to

$$f_b(t) = f_1 c_b(0)\exp(-k_b t) + f_2 \qquad (2.8)$$

where we indicate the decay function in the dark by $f_b(t)$ and $c_b(0)$ is the initial surface fraction of hydrophilic regions. By analyzing the experimental data in the dark, we can extract the rate of the back-reaction k_b and the interfacial energy of the hydrophobic surface (normalized by γ), f_2, from the long time limit of $\cos\theta$. Other parameters are obtained by comparison to the experimental data of hydrophilic conversion processes. This is the simplest model to analyze hydrophilic conversion processes and the reverse processes. On analyzing the experimental data, we may need to extend the present model to include more reaction species or states in the actual surface processes. In this case the reaction kinetics becomes more complicated but $\cos\theta$ is still an appropriate quantity to extract both the rates of hydrophilic conversion processes and the rates of back-processes. We conclude that the kinetics of hydrophilic conversion processes can be described more reasonably and consistently in terms of $\cos\theta$ rather than the reciprocal of the contact angle.[6]

III. Analysis of Experimental Data

We reanalyze the experimental results of Sakai et al. on the basis of the method described in the previous section.[6] We also extend the method to get better agreement with the experimental results.
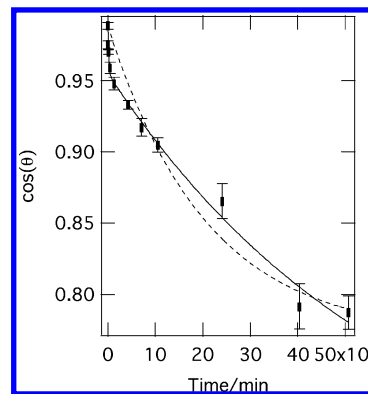

Figure 1. Plot of cosine of the contact angle against time kept in the dark after the highly hydrophilic surface is generated. Dots with error bars are the experimental results of Sakai et al.[6] The dashed line is the exponential fit, and the solid line is the double exponential fit to the experimental data.
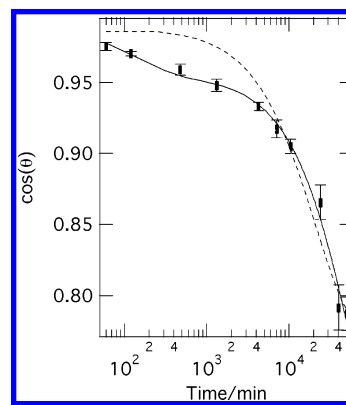

Figure 2. Same as Figure 1 but plotted with the horizontal axis on a logarithmic scale.

First, we analyze the back-processes in the dark. As we can see from Figure 1, a sharp decrease of $\cos\theta$ is followed by a single-exponential decay over a long period of time. The dashed line is the single-exponential fit to the experimental data given by eq 2.8 with $k_b = 4.82 \times 10^{-5}$ min^{-1} and $f_2 = 0.77$. The experimental results deviate from the theoretical line at short times. The reason may be that the surface is not chemically homogeneous. Therefore, the rate constant for the back-reactions has a distribution.

By assuming the bimodal distribution of rate constants the decay of $f_b \equiv \cos\theta$ in the dark is generalized from eq 2.8 to

$$f_b(t) = \sum_{i=1}^{2} f_1 g_i c_b(0)\exp(-k_{b,i}t) + f_2 \qquad (3.1)$$

where $\sum_{i=1}^{2} g_i = 1$ and g_i, $k_{b,i}$ represent the portion and the back-reaction rate constant corresponding to each component, respectively. Excellent agreement is found between eq 3.1 and the experimental data, as shown in Figures 1 and 2. The major decay component ($g_1 = 0.902$) has the rate constant $k_{b,1} = 1.66 \times 10^{-5}$ min^{-1} (the lifetime of 41.8 days) and the rate constant of $k_{b,2} = 0.0063$ min^{-1} (the lifetime of 2.6 h) is found for the minor component. The fraction of the fast decay component is only 10%. The smallest value of $\cos\theta$, f_2, is estimated to be 0.65, which corresponds to the largest contact angle, 50.3°.

The experimental results can be understood, if we consider them in the following way. Chemical species such as surface hydroxyl groups that are responsible for hydrophilicity are produced by photoreactions. However, because of the heterogeneity of the TiO$_2$ surface the stability of chemical species
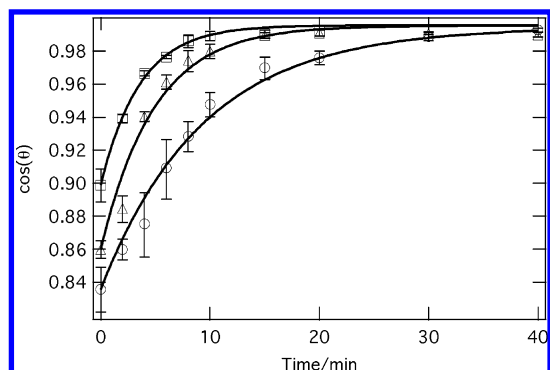
Figure 3. Plot of cosine of the contact angle against the irradiation time for the light intensities of 0.2, 0.7, and 1.0 mW/cm² (bottom to top). Symbols with error bars are experimental results of Sakai et al.[6] The solid line is the fit by the theoretical curve given by eq 3.2. The hydrophilic conversion rates are 0.11, 0.20, and 0.279 min⁻¹ from bottom to top.

produced depends on where they are produced. In other words, some hydrophilic regions have a long lifetime whereas others have a short lifetime. To describe the distribution of lifetimes of hydrophilic regions by bimodal distribution is only an approximation. The real distribution is considered to be more complex. Further experimental studies are badly needed to clarify these points.

Because the back-reaction has two components, the time evolution of $\cos\theta$ during irradiation with UV light is also modified from eq 2.5 to

$$f(t) = \sum_{i=1}^{2} f_i g_i \left[\frac{k_f}{k_f + k_{b,i}} - \left(\frac{k_f}{k_f + k_{b,i}} - c(0) \right) \exp\{-(k_f + k_{b,i})t\} \right] + f_2 \quad (3.2)$$

The initial value is still given by eq 2.6, whereas the final value corresponding to the saturated hydrophilicity is given by

$$f(t \to \infty) = \sum_{i=1}^{2} f_i g_i \frac{k_f}{k_f + k_{b,i}} + f_2 \quad (3.3)$$

The rate of hydrophilic conversion depends on the UV irradiation intensity. The rate increases by increasing the intensity of light. The most reliable value of the contact angle at the saturated hydrophilicity is obtained from the experimental data for high intensities of light, at which the forward photoreaction rate is much faster than the reverse reaction. When $k_f \gg k_{b,1}, k_{b,2}$, we have the largest value of $\cos\theta$ described by $\cos\theta = f_1 + f_2$. In the experiment of Sakai et al. the highest irradiation intensity is 80 mW/cm² and the average value of θ after the saturation is 4.9°, which corresponds to $\cos\theta = 0.996$. The value of f_1 is obtained by subtracting the value of $f_2 = 0.65$ from the largest value of $\cos\theta$, 0.996.

The kinetic data on hydrophilic conversion processes at various irradiation intensities is compared with the theoretical decay curve given by eq 3.2 with the value of k_f adjusted at each irradiation intensity. The typical results are shown in Figure 3. We found that the experimental data are fitted reasonably well by eq 3.2. The value of k_f thus obtained is shown in Figure 4 as a function of the light intensity. At weak irradiation intensities the forward rate is proportional to the irradiation intensity and it has a weaker intensity dependence at high irradiation intensities. Once we know the forward rate of
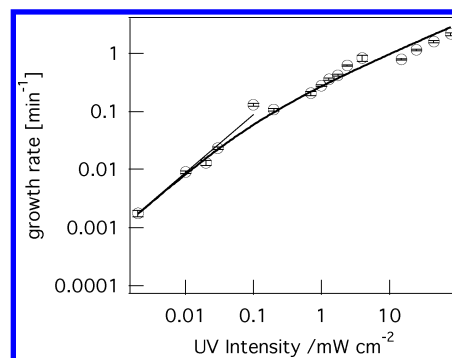

Figure 4. log−log plot of hydrophilic conversion rate against the light intensity. Symbols with error bars are obtained by analyzing the experimental results of Sakai et al. on the basis of eq 3.2.[6] The straight line is the fit by eq 3.4 together with eq 3.7. The curved solid line is the fit by eq 3.4 together with eq 3.6.
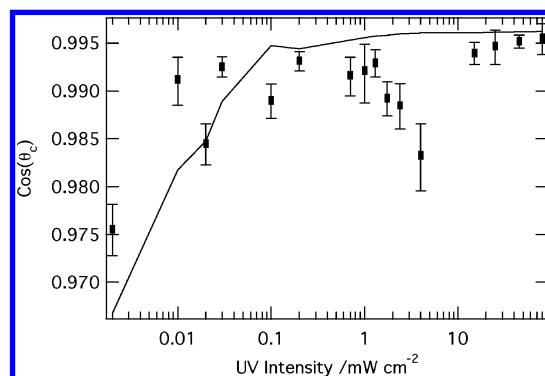

Figure 5. Plot of saturated smallest contact angle against the incident UV light intensity. Dots with error bars are the experimental results of Sakai et al.[6] The solid line is the theoretical line given by eq 3.3.

hydrophilic conversion processes, k_f, the saturated values of the contact angle at each irradiation intensity are obtained from eq 3.3. They are compared in Figure 5 with the observed values.

Agreement between theory and experiment is satisfactory, considering the complexity of the system. The saturated contact angle increases with decreasing light intensity at weak irradiation intensities and it is almost constant at high intensities.

The saturated contact angle increases by decreasing the irradiation light intensity because the forward hydrophilic conversion rate decreases with decreasing light intensity and the forward rate competes with the rates of back-processes at weak light intensities.

We consider the dependence of k_f on the light intensity. The forward rate is proportional to the concentration of reaction intermediates that trigger the hydrophilic conversion processes,

$$k_f = \kappa[M] \quad (3.4)$$

where $[M]$ is the surface concentration of reaction intermediates. The concentration of reaction intermediates is proportional to the irradiation intensity when the intensity is weak. At high irradiation intensities the concentration of reaction intermediates becomes high and recombination reaction becomes important, which suppresses the growth of intermediates by the irradiation with UV light. A candidate for such intermediates is holes created by the band gap excitation of electron−hole pairs. It is experimentally observed that the wavelength of irradiated light should be shorter than 382 nm to observe the change in the contact angle.[5,6] This indicates that the band gap excitation of electron−hole pairs triggers the subsequent hydrophilic conversion processes. The effect of hole scavengers and other evidence

support that holes rather than electrons are involved in hydrophilic conversions processes.[5,6] The holes can either decay or recombine with electrons,

$$\frac{\partial}{\partial t}[M] = \alpha I - k_h[M] - k_{e-h}[M][M_e]$$

$$\frac{\partial}{\partial t}[M_e] = \alpha I - k_e[M_e] - k_{e-h}[M][M_e] \quad (3.5)$$

where [M] and [M_e] are the concentrations of holes and electrons, respectively, α is the rate of generating the electron–hole pairs by the irradiation with UV light, k_h and k_e are the first-order reaction rates of holes and electrons, respectively, and k_{e-h} is the second-order recombination rate. We assume that the major part of the first-order decay rate of holes are not due to their participation in the generation of hydrophilic regions but due to other mechanisms such as trapping by defects or reactions with organic compounds. Then, k_h is constant, being almost independent of the surface fraction of hydrophobic regions, $1 - c$. In the steady state we have $k_h[M] = k_e[M_e]$ and the solution of eq 3.5 is obtained as

$$[M] = \frac{k_e}{2k_{e-h}}\left[\left(1 + \frac{4k_{e-h}\alpha I}{k_e k_h}\right)^{1/2} - 1\right] \quad (3.6)$$

The experimental data are in accordance with the theoretical curve given by eq 3.4 together with eq 3.6, as we can see from Figure 4. At weak irradiation intensities the concentration of holes is proportional to the light intensity,

$$[M] \sim \frac{\alpha I}{k_h} \qquad 4k_{e-h}\alpha I \ll k_e k_h \quad (3.7)$$

and at high irradiation intensity the concentration of holes obeys

$$[M] \sim \sqrt{\frac{k_e}{k_h}\frac{\alpha I}{k_{e-h}}} \qquad 4k_{e-h}\alpha I \gg k_e k_h \quad (3.8)$$

We obtain $k_h/(\alpha\kappa) \sim 1.1$ (mW min)/cm² from the fit by eqs 3.4 and 3.7 in the region below 0.1 mW/cm² and then find $k_{e-h}/(\kappa k_e) \sim 8.4$ min by fitting the entire curve by eqs 3.4 and 3.6. The analysis presented here is based on the previously proposed mechanism of the photogenerated hole triggered hydrophilic conversion processes.[5,6] We have demonstrated in this paper that both the hydrophilic conversion rate and the back-reaction rates are theoretically defined in terms of the time variation of $\cos\theta$. This is in sharp contrast with the empirical definition of the rates in terms of the reciprocal of the contact angle.[6]

IV. Spreading Dynamics

Although only contact angles are measured in the experiments of Sakai et al.[6] the base radius of a liquid droplet on the surface is also a measurable quantity.[13–16] When the volume of a droplet is conserved, the change in the contact angle is associated with that in the droplet base radius, R. The condition of constant volume is fulfilled either by observing the same liquid droplet on a substrate or by preparing liquid droplets of the same volume each time of contact angle measurements. When the shape of a droplet is sustained by the pressure difference between inside and outside the droplet, ΔP, the droplet forms a portion of a sphere with radius R_3 governed by Laplace's formula, $2\gamma/R_3 = \Delta P$.[11] Under the gravitational field Laplace's formula is valid for small droplets whose base radii are smaller than the capillary length, $R \le \sqrt{\gamma/(\rho g)}$, with g as the gravitational constant. We
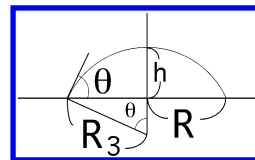

Figure 6. Schematic illustration of a liquid droplet on a solid surface. A liquid droplet forms a portion of a sphere with radius R_3. The droplet base radius is R. h is the height of the droplet.

assume that this condition is satisfied. Typical capillary lengths of liquids are from millimeter to centimeter. From the geometry illustrated in Figure 6 we obtain $R_3 \cos\theta = R_3 - h$ and the volume of the droplet, vol $= \pi h^2(R_3 - h/3)$. Therefore, the volume is written as

$$\text{vol} = \frac{\pi}{3}R^3\frac{(1 - \cos\theta)^2(2 + \cos\theta)}{\sin^3\theta} \quad (4.1)$$

When the volume is conserved, $\partial\,\text{vol}/\partial t = 0$, we obtain

$$\frac{1}{R}\frac{\partial R}{\partial t} = \frac{1}{(1 - \cos^2\theta)(2 + \cos\theta)}\frac{\partial\cos\theta}{\partial t} \quad (4.2)$$

and

$$\frac{R(t)}{R(0)} = \frac{(1 + f(t))^{1/2}}{(1 - f(t))^{1/6}(2 + f(t))^{1/3}}\frac{(1 - f(0))^{1/6}(2 + f(0))^{1/3}}{(1 + f(0))^{1/2}} \quad (4.3)$$

where $f(t) = \cos\theta$ as defined previously. When $\theta \le 1$ rad (57.3°), eqs 4.2 and 4.3 are simplified as

$$\frac{1}{R}\frac{\partial R}{\partial t} \sim \frac{1}{3}\frac{1}{1 - \cos^2\theta}\frac{\partial\cos\theta}{\partial t} \quad (4.4)$$

and

$$\frac{R(t)}{R(0)} \sim \left(\frac{1 - f(0)}{1 - f(t)}\right)^{1/6} \quad (4.5)$$

We see that the droplet base radius is sensitive to θ when θ is close to zero. On the other hand, $\cos\theta$ becomes insensitive to θ when θ is close to zero. Therefore the measurements of droplet base radius are useful to obtain reliable information on wetting around θ close to zero. Because such measurements are not performed so far for the hydrophilic conversion of TiO₂ surfaces, we calculated $R(t)/R(0)$ from the data on $f(t)$ under UV intensity of 0.2 mW/cm² by use of eq 4.3 or eq 4.5 and plotted the results in Figure 7. In the same figure we also show the results obtained from $f(t)$ given by eq 3.2. The difference between the results based on eq 4.3 and eq 4.5 is small. Therefore, simplified eqs 4.4 and 4.5 are sufficient for the study of spreading dynamics in the system whose contact angles are relatively small. It should be noted that eq 4.3 is a general relation between the droplet base radius and the contact angle when the volume of the droplet is conserved. Excellent agreement is found when we analyze experimental data on wetting in quite different systems of reactive metal/ceramic interfaces.[14,17]

So far we have assumed that the contact angle satisfies Young's equation, eq 2.1. The assumption is satisfied for the low viscous liquids considered in this paper. The characteristic spreading velocity of the fluid is the ratio of the surface tension to the viscosity of the liquid, η. For water droplets at room temperature the characteristic velocity is given by $\gamma/\eta \sim 70$ m/s. The relevant time scale for the relaxation of the contact angle by the viscous flow is roughly given by $R\eta/\gamma$.[13,15,16] The
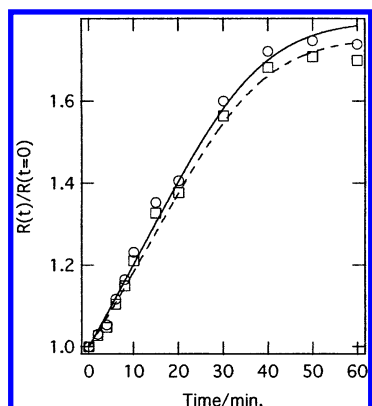
Figure 7. Plot of the droplet base radius against the irradiation time for the light intensity of 0.2 mW/cm^2. Circles and squares show results obtained from contact angles measured by Sakai et al. by use of eqs 4.3 and 4.5, respectively.[6] The solid line and dashed line show the results obtained from the contact angle given by eq 3.2 again by use of eqs 4.3 and 4.5, respectively.

relaxation time for droplets of millimeter size, e.g., $R \sim 5$ mm by the viscous flow is at most $\sim$0.01 s much shorter than the time scale of measuring contact angles. In other words, the contact angle is quickly relaxed to the value given by Young's equation. Therefore, the kinetics of the contact angle is not controlled by the viscous resistance but the change in the interfacial energy due to photoreaction on the surface.

V. Conclusion

We have presented a method to extract the hydrophilic conversion rates and the reverse rates from the time variation of the contact angle of a liquid droplet on the solid surface. According to Young's theory, $\cos \theta$ is a linear function of the interfacial energy between the solid and the liquid that in turn changes with the surface fraction of hydrophilic regions. As the photoreaction proceeds, the surface fraction of hydrophilic regions increases, which lowers the interfacial energy between the solid and the liquid, resulting in the growth of $\cos \theta$. Therefore, the cosine of the contact angle is an appropriate quantity to extract both the rates of hydrophilic conversion processes and the rates of back-processes. We have noticed that a similar relation is recently proposed for conversion to the less wettable surface by reaction.[18] For the hydrophilic conversion by UV light Sakai et al. empirically found a linear relation between the reciprocal of the contact angle and the UV irradiation time.[6] However, this relation has no theoretical basis. In addition, the reciprocal of the contact angle is not a linear function of time for the reverse process in the dark.[6] Recent experimental results on the kinetics of the back-processes as well as hydrophilic conversion processes are reproduced by our model. In this paper we have assumed that when the surface is irradiated with UV light, hydrophobic regions are converted into hydrophilic regions, which changes the interfacial energy between the solid and the liquid. We have further assumed that the interfacial energy as measured by cosine of the contact angle is proportional to the surface fraction of hydrophilic regions. If the size of each hydrophilic region is much smaller than the size of liquid droplets on the solid surface, the surface can be considered as homogeneous as far as the interfacial energy measured by the cosine of the contact angle is concerned. In the other limit the interfacial energy measured by cosine of the contact angle changes from region to region on the surface. In this case the interfacial energy in eq 2.3 stands for the average over the regions. Experimental results on the back-reaction in the dark are analyzed by using two exponentially decaying

functions, which suggest heterogeneous surfaces with different rate constants for the back-processes. We propose to perform further experimental investigation for the identification of surface species especially at different times in the dark. A single rate constant is obtained for the forward hydrophilic conversion processes within the accuracy of experimental errors. The results that two rate constants are required to describe the back-process whereas the forward process is described by a single rate constant can be understood in the following way. Chemical species such as surface hydroxyl groups, which are responsible for hydrophilicity, are produced by photoreactions. However, because of the heterogeneity of the TiO$_2$ surface, the stability of chemical species produced depends on where they are produced. In other words, some hydrophilic regions have a long lifetime, whereas others have a short lifetime. The rate of hydrophilic conversion obtained in our method exhibits the irradiation intensity dependence typical of the second-order recombination reactions of intermediate species at high intensities. The saturated smallest contact angle increases when the incident UV intensity is lowered, which is explained in our model by the competition between the forward and the backward processes of hydrophilic conversion. Our procedure to extract the rates from the contact angle measurements is simple and provides useful insight into the surface reaction by combining it with chemical analysis. So far, most of investigations have been performed on the forward hydrophilic conversion processes and less attention has been paid to the reverse processes.[4−6] As we have shown, the complete kinetic analysis of the forward hydrophilic conversion processes is possible only after the back-reaction rates and the saturated largest contact angle are measured in the dark, although it takes months to perform such experiments.

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